ouxite into rauenthalite can be classified as a reaction of the type in which two-dimensional elements (layers) are conserved.

The activation energy for all these 'layer-conserving' dehydration processes is surely very small owing to the small number of bonds broken and reconstructed during the reactions. This should be particularly true for mechanisms involving loss of lattice H_2O molecules, where only low-energy hydrogen bonds are broken, as in the present case and in other examples, *e.g.* the dehydration of $MoO_3.2H_2O$ (Günter, 1972). On these grounds the oriented intergrowth of phaunouxite and rauenthalite observed in natural crystals at room temperature can be easily understood. A slightly different mechanism is observed for the dehydration of $Ca_5H_2(AsO_4)_4.9H_2O$ (Catti & Ivaldi, 1981), where interlayer H_2O—Ca bonds are also broken, in addition to hydrogen bonds, so that a higher activation energy should be necessary for that reaction.

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A Description of the Leucophoenicite Family of Structures and its Relation to the Humite Family

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Abstract

Two distinct though closely related structural families are described. One, which we call the leucophoenicite family, consists of mimetically twinned, cubic-close-packed (c.c.p.) arrays of A cations with B cations in A_6 trigonal prisms in the composition planes and anions in (usually) BA_3 tetrahedra. A general 'twin formula' may be written as $(1,2^x)$, the twin individuals being one and two cations wide. (The superscript x indicates the number of consecutive twin lamellae of thickness 2.) The other is the humite family which has twin individuals two or three cations wide and twin formula $(2^x,3)$. In addition to the type structures such as leucophoenicite and the humite minerals which are all silicates there are also borates, germanates, *etc.* whose cation arrays place them in these families, especially the former.

Introduction

It has frequently been noted that the structures of leucophoenicite and some related compounds and those of forsterite (olivine) and of the humite minerals (norbergite, chondrodite, humite and clinohumite) have common geometrical features. Moore (1970) determined the structure of leucophoenicite, and used a module of five edge-sharing MO_6 octahedra, 'the generalized olivine type', to construct a leucophoen-

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Table 1. *Summary of compounds belonging to the leucophoenicite family and the humite family*

Structural family	Twin layer repeat	Structure type	'Stuffed' alloy type	Examples
↑ Leucophoenicite family	(1)		CrB	$BaGeO_3$ (Hilmer, 1962), $CsBeF_3$ (Steinfink & Brunton, 1968), high $KClO_3$ (Ramachandran & Lonappan, 1975), low $KClO_3$ (Bats, 1978)
	(1,2)	Kotoite	W_2CoB_2	Kotoite $Mg_3(BO_3)_2$ (Berger, 1949), $Ni_3(BO_3)_2$ (Pardo, Martínez-Ripoll & García-Blanco, 1974), jimboite $Mn_3(BO_3)_2$ (Watanabe, Kato, Matsumoto & Ito, 1963), $Cd_3GeO_4(OH)_2$ (Belokoneva, Simonov & Belov, 1974)
	$(1,2^2)$			$Mg_5(BO_3)_3F$ (Brovkin & Nikishova, 1975)
	$(1,2^3)$	Leucophoenicite		Leucophoenicite $Mn_7[SiO_4]_2[(SiO_4)(OH)_2]$ (Moore, 1970)
	$(1,2^x)(x > 3)$			Microscopic quantities observed (White & Hyde, 1982*c*)
●	(2)	Olivine*	Ni_2In	Forsterite Mg_2SiO_4 (Hazen, 1976), $FeNiBO_4$ (Capponi, Chenavas & Joubert, 1973), tephroite Mn_2SiO_4 (Francis & Ribbe, 1980)
Humite family ↓	$(2^x,3)(x > 3)$ $(2^3,3)^x(3,2^5)$ $(2^2,3,2^3,3)$			Identified by electron diffraction and high-resolution electron microscopy (White & Hyde, 1982*a*,*b*)
	$(2^3,3)$	Clinohumite		Clinohumite $4Mg_2SiO_4 . Mg(OH,F)_2$ (Fujino & Takéuchi, 1978), sonolite $4Mn_2SiO_4 . Mn(OH,F)_2$ (Yoshinga, 1963)
	$(2^2,3)$	Humite		Humite $3Mg_2SiO_4 . Mg(OH,F)_2$ (Ribbe & Gibbs, 1971), $3(Mg,Mn)_2SiO_4 . (Mg,Mn)(OH,F)_2$ (Francis & Ribbe, 1978)
	(2,3)	Chondrodite		Chondrodite $2Mg_2SiO_4 . Mg(OH,F)_2$ (Fujino & Takéuchi, 1978), Ca-chondrodite $2Ca_2SiO_4 . Ca(OH)_2$ (Kuznetsova, Novskii, Ilyukhin & Belov, 1980), alleghanyite $2Mn_2SiO_4 . Mn(OH)_2$ (Rentzeperis, 1970), $Al_4Co(BO_4)O_2$ (Capponi & Marezio, 1975), Cd-chondrodite $2Cd_2SiO_4 . Cd(OH)_2$ (Egorov-Tismenko, Duneko, Simonov & Belov, 1972)
	(3)	Norbergite	Re_3B	Norbergite $Mg_2SiO_4 . Mg(OH,F)_2$ (Gibbs & Ribbe, 1969), Fe_3BO_6 (White, Miller & Nielson, 1965), Mn-norbergite $Mn_2SiO_4 . Mn(OH,F)_2$ (Francis & Ribbe, 1978)

* For a more complete list of compounds with the olivine structure see Hanke (1965) and Muller & Roy (1974).

icite family of structures (Fig. 1), as did Belokoneva, Simonov & Belov (1973) and Brovkin & Nikishova (1975). But this module cannot generate the structure of any member of the humite family (except the olivine type); norbergite structure elements do not contain it, *cf.* Belokoneva *et al.* (1973). Hence, a well founded relation between the two groups of structures has remained elusive. A summary of compounds belonging to the leucophoenicite family and the humite family is presented in Table 1.

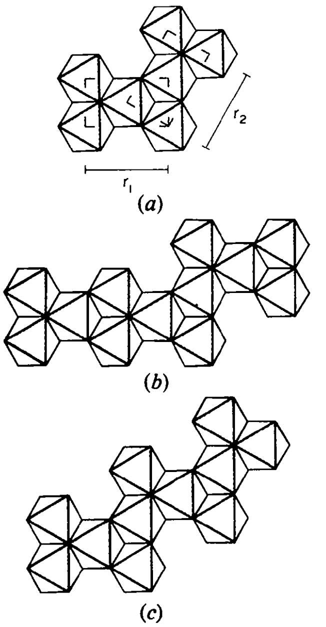


Fig. 1. (*a*) Two of the five-octahedral units used by Moore (1970) to construct members of a leucophoenicite family. They are designated r_1 or r_2 according to their direction. (*b*) The octahedral arrangement in leucophoenicite; it consists of two r_1 clusters followed by an r_2 cluster. In Moore's notation leucophoenicite is represented by $\ldots r_1, r_1, r_2, r_1, r_1, r_2 \ldots$. (*c*) The octahedral arrangement in olivine which is represented by $\ldots r_1, r_2, r_1, r_2 \ldots$.

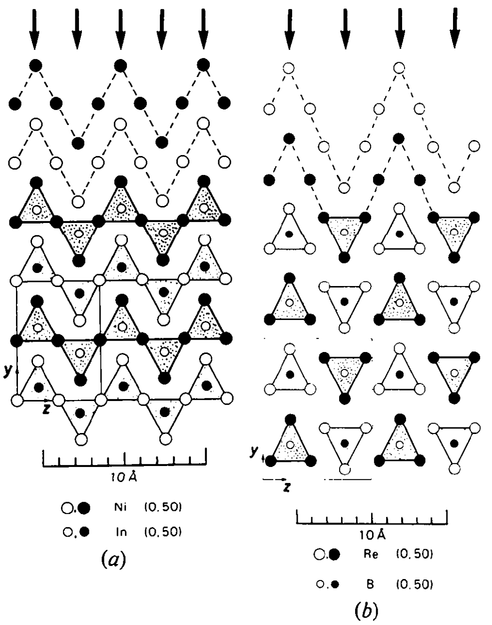
The humite family

Elsewhere we have given a new, simple and systematic description of the structures of the humite-series members (O'Keeffe & Hyde, 1982; see also White & Hyde, 1982*a*) which we need to outline briefly here. It is based on two straightforward observations. The first is that many structures, otherwise difficult to describe, are readily visualized as anion-stuffed cation arrays rather than the conventional inverse, *viz.* cation-stuffed anion arrays. The cation arrays are well known alloy structures, in the case of the humites those of Ni_2In and Re_3B and their intergrowths (Fig. 2). The second is that these alloy structure types are conveniently described in terms of unit-cell twinning (Andersson & Hyde, 1974; Hyde, Bagshaw, Andersson & O'Keeffe, 1974; Hyde, Andersson, Bakker, Plug & O'Keeffe, 1979). Both are twinned cubic-close-packed (c.c.p.) arrays of the majority atom (A = Ni, Re), with the minority atoms (B = In, B) occupying trigonal prisms (BA_6 = $InNi_6$, BRe_6) in the composition planes between the twin lamellae. The former has twin bands two atoms wide, the latter three atoms wide. They are therefore described as twinned c.c.p. ...2,(2,2)2... = $(2)^2$ and ...3,(3,3),3... = $(3)^2$ respectively, where the parentheses in the sequences denote the unit-cell repeat. Forsterite, Mg_2SiO_4, is then twinned c.c.p. $Mg(2)^2$ and norbergite, ideally $Mg_2SiO_4.Mg(OH,F)_2$, is twinned $Mg(3)^2$ with, in both cases, Si atoms in Mg_6 trigonal prisms. Divalent anions (O^{2-}) occupy $SiMg_3$ tetrahedra and monovalent anions $(OH^-,F^-)Mg_3$ triangles.

In an analogous way chondrodite, $2Mg_2SiO_4.Mg(OH,F)_2$, is twinned c.c.p. Mg ...3,(2,3)2... = (2,3); humite, $3Mg_2SiO_4.Mg(OH,F)_2$, is twinned c.c.p. Mg ...3,(2,2,3,2,2,3),2... = $(2^2,3)^2$; and clinohumite, $4Mg_2SiO_4.Mg(OH,F)_2$, is twinned c.c.p. Mg...3,(2,2,2,3),2... = $(2^3,3)$.*

Examples of all these structures are shown in Figs. 3 to 6. In addition to silicates, borates containing $(BO_4)^{5-}$ anions are also known: Fe_3BO_6 = $Fe_2BO_4.FeO_2$ is isostructural with norbergite (White *et al.*, 1965) but differs from it by containing no monovalent anions (Fig. 3). A series of high-pressure borates with the chondrodite structure has been described by Capponi & Marezio (1975). They have the general formula $M^{3+}_{4-x}M^{2+}_{1+x}(BO_4)_2(OH)_xO_{2-x}$ (M^{3+} = Al, Ga, Fe; M^{2+} = Ni, Co, Mg, Fe) and include hydrogen-free boron chondrodite (x = 0) $Al_4Co(BO_4)_2O_2$ [= $2(Al_{1\cdot5}Co_{0\cdot5})BO_4.AlO_2$].

It is noteworthy that all the cation arrays are regular whereas every anion array is considerably distorted from the conventional description of hexagonal 'close-packing'. Fig. 4 shows the structure of $2Cd_2SiO_4.Cd(OH)_2$ (Egorov-Tismenko *et al.*, 1972), in which the distortion of the anion array is extreme but, significantly, the cation array is rather regular.* [In this example an additional distortion apparently doubles d(001).]



(*a*)

(*b*)

Fig. 2. (*a*) The structure of the Ni_2In type. The Ni ...(2,2)... twin bands are shown in the upper half, and edge-sharing Ni_6In trigonal prisms are emphasized in the lower part. (*b*) The Re_3B structure. It is close-packed Re ...(3,3)..., in which isolated trigonal prisms are occupied by B. In both cases the twinning is by mirror planes parallel to (001), indicated by arrows.

The leucophoenicite family

This may be described in similar terms, the end members being anion-stuffed twinned c.c.p. $(2)^2$ (olivine structure) and twinned c.c.p. $(1)^2$. The latter has a cation array which is the CrB (alloy) structure, Fig. 7(*a*). Intermediate structures will be anion-stuffed twinned c.c.p. (1,2), which is the W_2CoB_2 type (Fig. 7*b*), $(1,2^2)^2$, $(1,2^3)$, *etc.* Insertion of anions into analogous BA_3 tetrahedra yields structures with the following

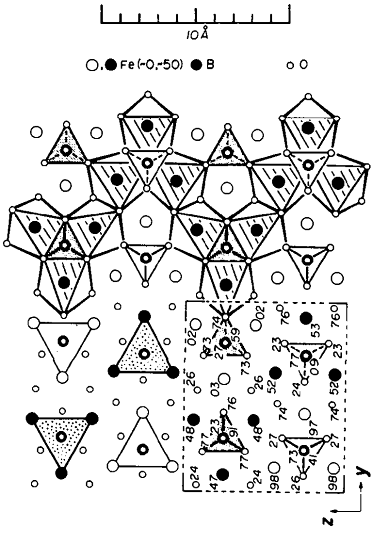


Fig. 3. The structure of Fe_3BO_6 = $Fe_2BO_4.FeO_2$. It is isostructural with norbergite and has twin formula $(3)^2$. The upper half shows the conventional description as serrated chains of edge-sharing FeO_6 octahedra. Also shown are the BFe_6 trigonal prisms (lower left).

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* That is, twinned c.c.p. Mg $(2^x,3)$ yields $nMg_2SiO_4.Mg(OH,F)_2$ with $n = x + 1$. The number of twin individuals in the unit cell must be even; hence *e.g.* $(2^2,3)^2$ instead of $(2^2,3)$, although the latter type of symbol is sufficient to identify the structure type.

* In the original paper there appears to be a misprint: the y coordinates of O(3) and O(8) need to be multiplied by −1.

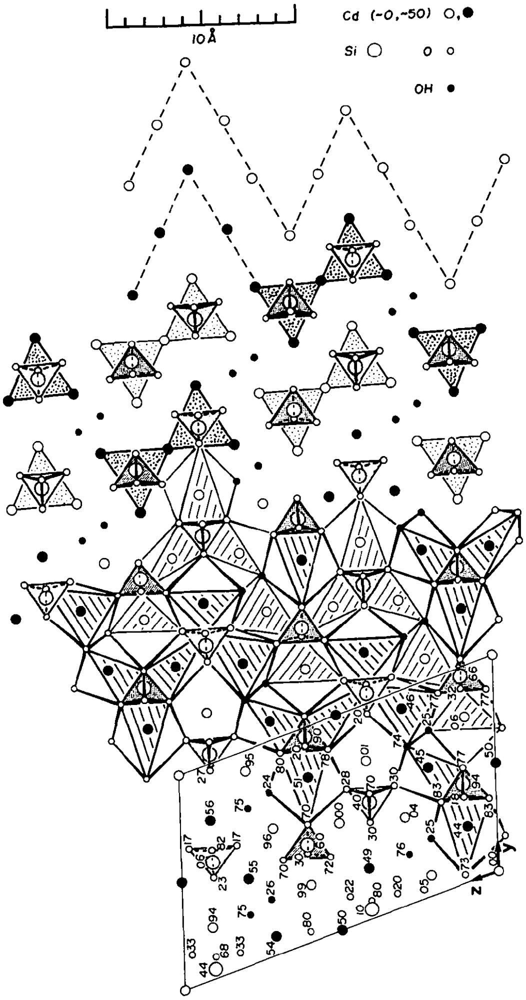

Fig. 4. Cadmium chondrodite, $2Cd_2SiO_4.Cd(OH)_2$ twin formula (2,3). Both the conventional cation-centred polyhedra of anions and the intergrowth of $Ni_2In(2)$ and $Re_3B(3)$ structures are shown.

stoichiometries: $(1)^2 = ABX_2$, $(1,2) = ABX_2.A_2BX_4$ or $A_3B_2X_6$, $(1,2^2)^2 = ABX_2.2A_2BX_4$ or $A_5B_3X_{10}$, $(1,2^3) = ABX_2.3A_2BX_4$ or $A_7B_4X_{14}$, *etc.* and olivine $= (1,2^\infty) = (2)^2 = A_2BX_4$. It is assumed that single lamellae of 1 are dispersed in a matrix of 2 in the same way as single lamellae of 3 are dispersed in a matrix of 2 in the members of the humite family. Experimental studies of the latter (White & Hyde, 1982*a*,*b*) and of the former (White & Hyde, 1982*c*) reveal no exceptions to such distributions.

$(1)^2$: *anion-stuffed* CrB *type*; ABX_2 *and related structures*

The ideal orthorhombic ABX_2 structure, produced by inserting anions into all appropriate BA_3 tetrahedra, is unlikely since each BX_4 tetrahedron then shares two adjacent edges with neighbouring tetrahedra, forming BX_2 chains, Fig. 8(*a*). It is therefore not surprising that

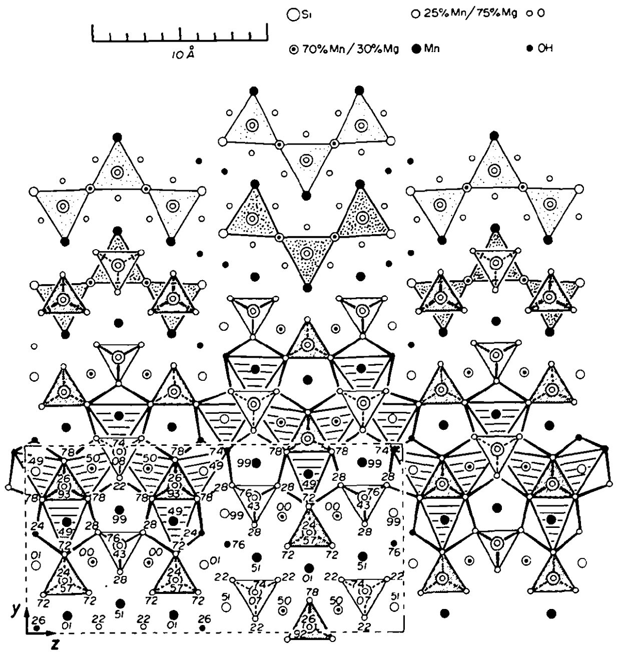

Fig. 5. The structure of magnesium manganhumite, $[(Mn_{0.68}Mg_{0.30}Fe_{0.01}Ca_{0.017})]_7(SiO_4)_3(OH)_2$ (Francis & Ribbe, 1978). In the lower half of the drawing is shown the conventional description of the structure as serrated chains of Mn/Mg octahedra while the cation array is emphasized in the upper portion.

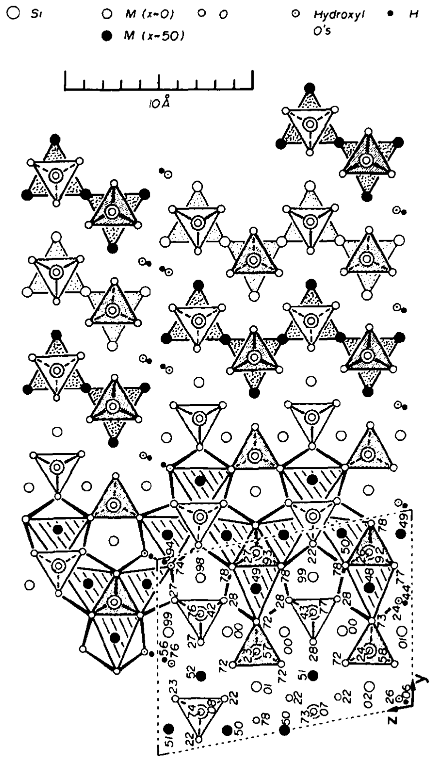

Fig. 6. The crystal structure of titanian clinohumite, $(Mg_{7.44}Fe_{1.09}Mn_{0.02}Ni_{0.02}Ti_{0.43})(SiO_4)_4OH_{1.13}O_{0.86}$ (Fujino & Takéuchi, 1978). The lower half shows the serrated chains of MO_6 octahedra, while above the SiM_6 trigonal prisms and the SiO_4 tetrahedra are emphasized.

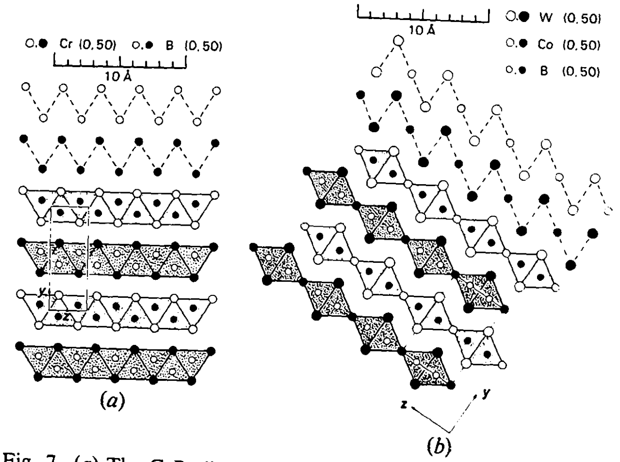

Fig. 7. (*a*) The CrB alloy type end-member of the leucophoenicite family. It is twinned Cr ...(1,1)... forming walls of face-sharing BCr_6 trigonal prisms. (*b*) The W_2CoB_2 structure. It is twinned c.c.p. W_2Co ...(1,2)... forming face- and edge-sharing, boron-centred, trigonal prisms.

no example of this structure type has been found. A more feasible structure would contain BX_3 chains of corner-connected tetrahedra, *i.e.* an ABX_3 compound. An example is $CsBeF_3$ (Steinfink & Brunton, 1968). There is an oxide which is a slightly deformed version of the same structure, but it has oblique rather than right BA_6 trigonal prisms. This is the high-temperature modification of barium metagermanate, $BaGeO_3$ (Hilmer, 1962), shown in Fig. 8(*b*).

Other ABX_3 structures with the same AB array include the high- and low-temperature forms of $KClO_3$ (Ramachandran & Lonappan, 1957; Bats, 1978). Both contain isolated ClO_3 (BX_3) pyramids (*i.e.* unconnected BX_3E tetrahedra, where E represents the stereochemically active lone pair of electrons on the Cl atom). They differ only by tilts of the ClO_3 groups.

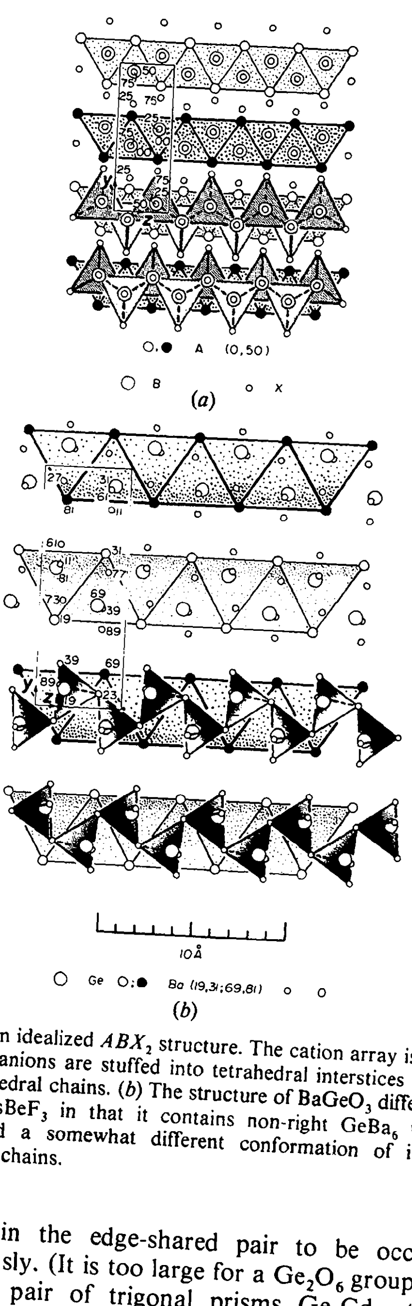

Fig. 8. (*a*) An idealized ABX_2 structure. The cation array is that of CrB. The anions are stuffed into tetrahedral interstices to form BX_2 tetrahedral chains. (*b*) The structure of $BaGeO_3$ differs from that of $CsBeF_3$ in that it contains non-right $GeBa_6$ trigonal prisms and a somewhat different conformation of its BX_3 tetrahedral chains.

(1,2): *anion-stuffed* W_2CoB_2 *type;* $A_3B_2X_6$ *structures*

We have commented that chains of edge-sharing BX_4 tetrahedra are unlikely. At ordinary pressure pairs of SiO_4 tetrahedra sharing edges (Si_2O_6 groups) are hardly more plausible. But the substitution of boron for silicon gives a stable B_2O_6 group which occurs in, for example the structure of kotoite, $Mg_3(BO_3)_2$ = $MgBO_2^+.Mg_2BO_4^-$ (Berger, 1949), an oxygen-stuffed version of a twinned c.c.p. (1,2) cation array, shown in Fig. 9(*a*). The Mg_3B_2 array is of the $(W_2Co)B_2$ type. Repulsion between the tetrahedrally coordinated boron atoms pushes them from the centres of the edge-shared tetrahedra into opposite faces, giving triangular coordination.

The majority (A) cation array in cadmium orthogermanate, $Cd_3GeO_4(OH)_2$ (Belokoneva *et al.*, 1973, 1974) is also isostructural with the (W_2Co) portion of W_2CoB_2, Fig. 9(*b*), but Ge is too large for both the O_4 tetrahedra in the edge-shared pair to be occupied simultaneously. (It is too large for a Ge_2O_6 group, or a face-shared pair of trigonal prisms Ge_2Cd_8, to be possible.) Only one of them is occupied; the other presumably accommodates the two protons. So this $A_3B_2X_6$ type is $Cd_3[Ge(H_2)]O_6$. The hydroxyl ions occupy the two anion sites remote from the GeO_4 tetrahedron.

(It is interesting that the first determination of the structure yielded a statistical distribution of one Ge atom over the two edge-shared tetrahedra, but that a subsequent analysis gave an ordered arrangement of filled and empty anion tetrahedra.)

Note that the composition of this compound corresponds to that of the norbergite type, $A_2BX_4.AX_2$ = $Cd_2GeO_4.Cd(OH)_2$.

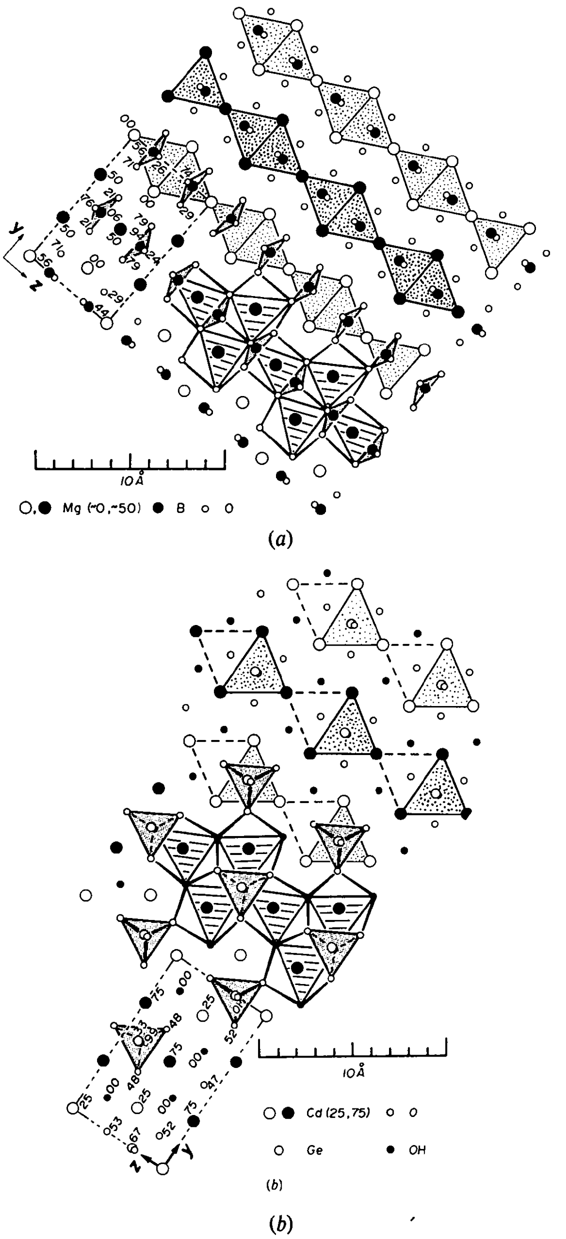

Fig. 9. (*a*) Structure of kotoite, $Mg_3(BO_3)_2$. It is an anion-stuffed version of the W_2CoB_2 alloy type with twinned c.c.p. Mg ...(1,2).... (The B atoms are displaced from the centre of the trigonal prisms.) (*b*) Structure of $Cd_3[GeO_4](OH)_2$. Only half the Cd_6 trigonal prisms are occupied by Ge; the 'empty' prisms presumably accommodate the protons of two hydroxyl groups.

$(1,2^2)^2$: *$A_5B_3X_{10}$ structures*

Although there appears to be no known alloy of the twinned c.c.p. $(1,2^2)^2$ type there is an anion-stuffed counterpart. This is the orthorhombic magnesium fluoroborate, $Mg_5(BO_3)_3F$ (Brovkin & Nikishova, 1975). The boron coordination 'polyhedra' are best described as BO_3 triangles, although in Fig. 10 they are in fact shown as tetrahedra to emphasize the relation between this structure and that of leucophoenicite (below). But the boron atoms are slightly displaced from the centres of the O_3 triangles, and in directions towards the fourth anion of the tetrahedron, by 0·06, 0·03 and 0·04 Å respectively for B(1), B(2) and B(3).

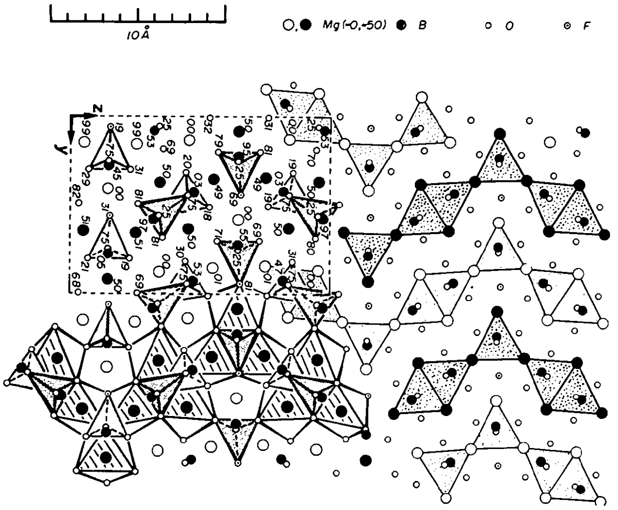

Fig. 10. The structure of $Mg_5(BO_3)_3F$. Its cation array is c.c.p. ...2,(1,2,2,1,2,2),1..., an intergrowth of CrB and $NiIn_2$. The B atoms are in triangular coordination, but are shown as BO_4 tetrahedra to emphasize the relation to leucophoenicite.

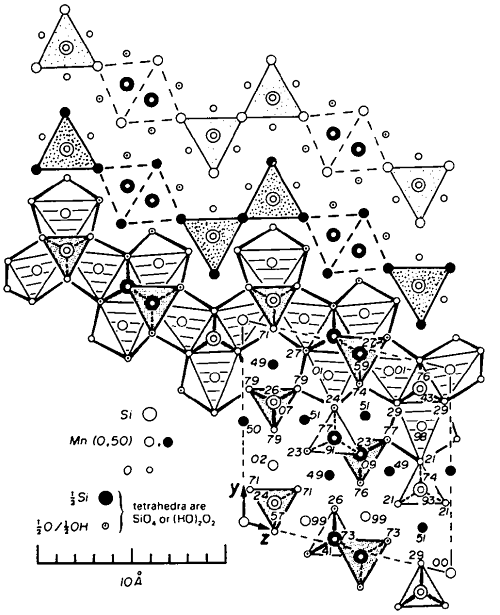

Fig. 11. The structure of leucophoenicite $Mn_7(SiO_4)_2[(SiO_4)(OH)_2]$. Half the face-sharing Mn_6 trigonal prisms are said to be occupied by Si in a statistical manner; its twin formula is $(1,2^3)$.

$(1,2^3)$: *$A_7B_4X_{14}$, the leucophoenicite structure*

So far, leucophoenicite (Fig. 11) is the only substance reported to have this structure (Moore, 1970). Its stoichiometry is $Mn_7(SiO_4)_3(OH)_2$ = $Mn_7Si_3(H_2)]O_{14}$. Written as $3Mn_2SiO_4.Mn(OH)_2$ its dimorphism with manganhumite is clear. The structure determination revealed only that the edge-shared tetrahedra were half-occupied by Si, and that the four peripheral (non-bridging) anions consist of two oxygen ions plus two hydroxyl oxygens. Presumably, as in cadmium orthogermanate, the occupied Si sites and the OH groups are strictly ordered, with Si atoms in one of each of the pair of edge-sharing anion tetrahedra (*i.e.* one of each of the Mn_6 trigonal prisms in the face-shared pairs) and two hydrogen atoms in the other. This, and any pattern of ordering between adjacent prism chains, remains to be determined.

$(1,2^x)$: $ABX_2.xA_2BX_4 = A_{2x+1}B_{x+1}X_{4x+2}$ *structures*, $x > 3$

As far as we are aware, none of these structures has been reported; a situation analogous to that in the humite series where the highest reported member is $(2^3,3)$. But, as with the humites (White & Hyde, 1982*a*,*b*), microscopic amounts of such higher members of the leucophoenicite family have been observed by electron microscopy (White & Hyde, 1982*c*).

$(2)^2$: *anion-stuffed* Ni_2In *type*; A_2BX_4, *the olivine structure*

In the unit-cell (cation) twinning description the olivine structure is the common member bridging the leucophoenicite and humite families, $(1,2^x)$ and $(2^x,3)$ with $x = \infty$. Its structure provides the matrix in which the lamellae of 1 or 3 are dispersed. Very many compounds have this structure, including borates, germanates, *etc.*, as well as silicates. Two examples are given in Fig. 12.

Conclusion

Inverting the customary approach to crystal chemistry, by describing structures as anion-stuffed derivatives of cation arrays rather than as cation-stuffed derivatives of anion arrays, plus the description of some simple alloy structure types as unit-cell twinned c.c.p. arrays of the majority atoms, yields simple and accurate descriptions of the structures of a number of minerals and other compounds in the leucophoenicite and humite families. The cation arrays are very regular in contrast to the anion arrays which are, in every case, far from regular.

This approach leads naturally to a relation between the structures of the two families: humites are regular intergrowths of 3 elements in a 2 matrix; leucophoenicites are regular intergrowths of 1 elements in a 2 matrix. The bridging structure common to both families is $(2)^2$, which is the olivine type.

All but the lowest possible member of the leucophoenicite family have stoichiometries identical with those of the humite family if, as is the case, the edge-shared pairs of anion tetrahedra (face-shared pairs of A trigonal prisms) are half-occupied by B atoms; then $xA_2BX_4.ABX_2$ becomes $xA_2BX_4.AX_2$.

Starting with norbergite, $(3)^2$, regularly repeated crystallographic shear generates successive members of the humite family, and eventually olivine, $(2)^2$. Continuing the process yields successive members of the leucophoenicite family, and eventually a hypothetical ABX_2 structure, $(1)^2$, which is close to that of $CsBeF_3$.

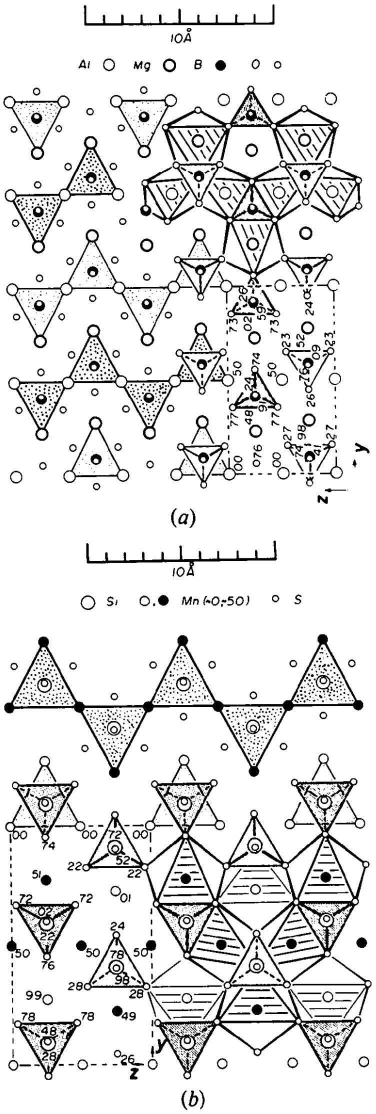

Fig. 12. Olivine-type structures: (*a*) The structure of sinhalite, $MgAlBO_4$ (Fang & Newnham, 1965). Mg and Al atoms are mimetically twinned to give the $(2)^2$ twin formula. (*b*) Structure of Mn_2SiS_4 (Hardy, Perez & Serment, 1965).

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Application of Modulated Structure Analysis to Two-Dimensional Antiphase-Domain Structure of $Au_{2+x}Cd_{1-x}$

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Abstract

The two-dimensional antiphase-domain structures of $Au_{2+x}Cd_{1-x}$, which are two-dimensionally modulated structures with a hexagonal cell [$a = 2{\cdot}919\ (4)$, $c = 4{\cdot}808\ (7)$ Å] and the wavevectors $\mathbf{k}^1 = N(\mathbf{a}^* + \mathbf{b}^*)/M$, $\mathbf{k}^2 = N(-\,\mathbf{a}^* + 2\mathbf{b}^*)/M$, were considered based on the five-dimensional description of modulated structures. The refinement of the structure with $N/M = 3/7$ (7*a* structure) of Au_2Cd was carried out by using a model with two positional, two thermal and one occupational parameters based on the five-dimensional space group $P_{p6\;1mm}^{P6_3/mmc}$ and gave R factors of 0·065, 0·049 and 0·17 for all, fundamental and satellite reflections, respectively. The displacement wave was almost longitudinal in agreement with a previous result. This method reduces the number of parameters to one eighth of that in the usual three-dimensional analysis. The 9*a* structure ($N/M = 4/9$) has the same five-dimensional space group and its five-dimensional structure is isomorphic with that of the 7*a* structure.

Introduction

There exist many binary alloys with one- and two-dimensional long-period superlattices (Cowley, Cohen, Salamon & Wuensch, 1979). These structures are regarded as modulated structures with incommensurate or commensurate wavevectors and can be analyzed on the basis of a unified theory of the modulated structure analysis (de Wolff, 1974; Janner & Janssen, 1977; Yamamoto, 1982*a*). In this theory, an n-dimensionally modulated structure is described in a $(3 + n)$-dimensional space and its symmetry is designated by a $(3 + n)$-dimensional space group. The

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