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An Alternative Description of the Structure of Cu_4Cd_3

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Abstract

The Cu_4Cd_3 structure, cubic with $a = 25{\cdot}87$ Å and 1124 atoms in the unit cell, has been analyzed and described in terms of octahedra and tetrahedra. The structure is described as an intergrowth of blocks of the pyrochlore structure, of the Cu metal structure and also of the $MgZn_2$ and $MgCu_2$ structures. Parameters of this ideal arrangement agree well with those of the observed structure.

Introduction

We have found that the unit-cell dimensions for a number of cubic structures follow the simple formula $a = nd\sqrt{2/3}$, where d is the polyhedral edge and n is an integer; $n = 4$ for SiF_4, $n = 8$ and 10 for the two interpenetrating structures in pyrochlore or W_3Fe_3C, $n = 11$ for $Mg_3Cr_2Al_{12}$, and $n = 14$ for Rh_7Mg_{44} (Andersson, 1980). One of the most complex alloy structures ever solved is that of Cu_4Cd_3 and Samson (1967) describes it in terms of two kinds of infinite, three-dimensional frameworks that interpenetrate. One is built up of Friauf polyhedra in a polytypic mixture of the $MgZn_2$ and $MgCu_2$ structures and the other consists of two different kinds of building blocks. One building block is made up of sixteen icosahedra and eighteen pentagonal prisms; the other is a complex of fourteen icosahedra and 42 pentagonal prisms. According to Samson, the unit cell contains 568 centered icosahedra, 288 centered pentagonal prisms, 144 μ-phase polyhedra and finally 124 Friauf polyhedra. In our alternative description we shall retain Samson's 124 Friauf polyhedra but instead of the other 1000 complex polyhedra we use octahedra and tetrahedra, and arrive at some simple structural relationships with the other cubic structures mentioned above.

Derivation of description

The structure of Cu_4Cd_3 was plotted on a cubic axis with half the volume in the form of a bounded projection, Fig. 1. The Friauf framework structure as recognized by Samson is shown in part in Fig. 1 and also as a model in Fig. 2. The calculated unit-cell dimension is $a = 22d\sqrt{2/3}$, or $n = 22$ in the formula given above. Coordinates for all the atoms, given by simple trigonometry and derived from the framework structure, are contained in the equation: $x,y,z = m/4n$; m odd (3, 5,..., 21) gives the coordinates for all Cu atoms belonging to Friauf polyhedra, while m even (6, 10, 12 and 16) gives the coordinates for the Cd atoms at the centers of Friauf polyhedra (Table 1). The average deviation between observed and calculated coordinates for the Cu atoms is 0·0007 and for Cd atoms it is 0·0003 (0·019 and 0·007 Å). This agreement is extraordinarily good, and almost within the e.s.d.'s of Samson's structure determination.

Table 1. *Atom coordinates* $(x,y,z) = m/4n$: *m odd for* Cu *atoms, m even for central* Cd *atoms in Friauf polyhedra*

Example (Samson's values in parentheses):

$x_1 = \frac{9}{88} = 0{\cdot}1022\ (0{\cdot}1018)$, $x_{19} = \frac{12}{88} = 0{\cdot}1362\ (0{\cdot}1365)$,

$y_1 = \frac{15}{88} = 0{\cdot}1705\ (0{\cdot}1714)$, $z_1 = \frac{3}{88} = 0{\cdot}0341\ (0{\cdot}0338)$.

Atom identification number

					m													
6	19	23	24	25	Cd	Cu	1	3	4	5	7	8	9	10	26	15	27	29
					2													
						3	z				x			z	x	x		
					4													
						5				x			z					
				x	6													
						7		z	z									
					8													
						9	x							x				
x					10													
						11											x	
	x		x		12													
						13			x			z						
					14													
						15	y			z								x
		x			16													
						17							x			z		
					18													
						19		x				x						
					20													
						21					z							
z					22													

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The other framework consists mainly of Cd atoms which form two building blocks. One of the blocks is a big pyrochlore unit of 21 octahedra, shown in the upper center of Fig. 1 and as the red unit in Fig. 3; the other is a smaller pyrochlore unit of five octahedra, capped by six double octahedra to form a building block which has also been found in Rh_7Mg_{44} and is shown in Fig. 3 as a blue unit. Fig. 4 shows the entire framework. The blue unit has a central octahedron of Cu(21) atoms (red balls) which are also visible in Fig. 3. This Cu octahedron is perfectly regular and has an edge = $(\sqrt{2}/\sqrt{3}).d$, where d is a normal Cd octahedral edge in this framework. This blue unit forms parts of 14 icosahedra and one of them is shown in Fig. 3, between this unit and the red pyrochlore unit, and is centered by Cu(28) (Samson's original atom identification numbers are used here). This atom, with three other equivalent Cu atoms and the inner Cu octahedron, ten Cu atoms in all, forms a perfect block of cubic close packing (Fig. 1). The ideal inner octahedron of Cu atoms has $x = 0{\cdot}1793$ in 24(g). If this value is used to calculate the parameter for Cu(28), it becomes 0·8207 (observed 0·8203). The ten-atom Cu block has perfectly regular cubic close packing and this block is also completely surrounded by Cd atoms.

There is about 1% misfit in joining the red and blue units in Fig. 3. However, in deriving the unit-cell dimension, red blocks are assumed to be separated by one octahedral edge and we obtain: $a = n\sqrt{2}/3$, with $n = 19$. The formulae for deriving the atomic coordinates are given in Table 2. The mean deviation from the observed parameters is ~0·16 Å, which is about ten times greater than for the Friauf framework. Cu(22) and Cu(15) in icosahedra are part of a pyrochlore unit and are equivalent to the Fe atoms in W_3Fe_3C, a pyrochlore with two interpenetrating frameworks (Nyman, Andersson, Hyde & O'Keeffe, 1978). The W atoms form the octahedral network (red in Cu_4Cd_3)

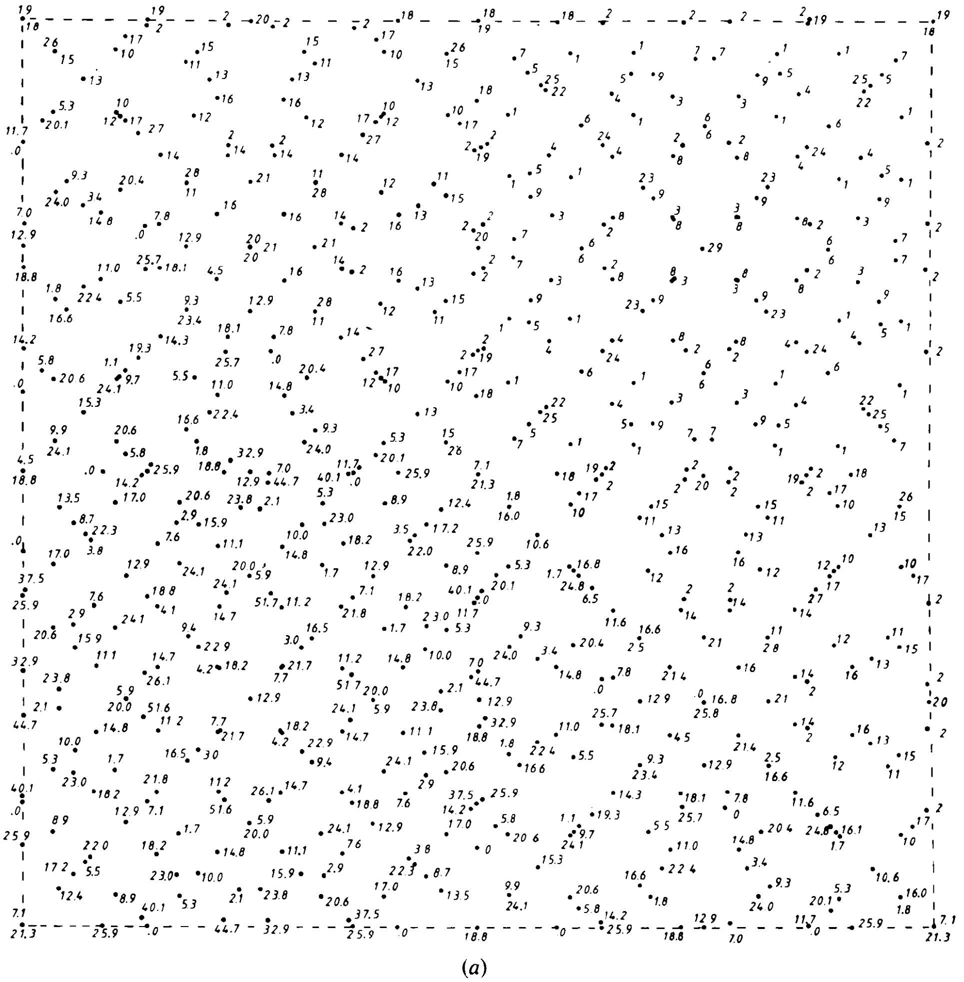

(a)

Fig. 1. (a) The cubic unit cell of Cu_4Cd_3, indicated by dotted lines. On the lower left side of a mirror plane the atom heights are given, on the upper half are only the atom identification numbers. All atom heights must be divided by two to obtain the heights in ångströms.

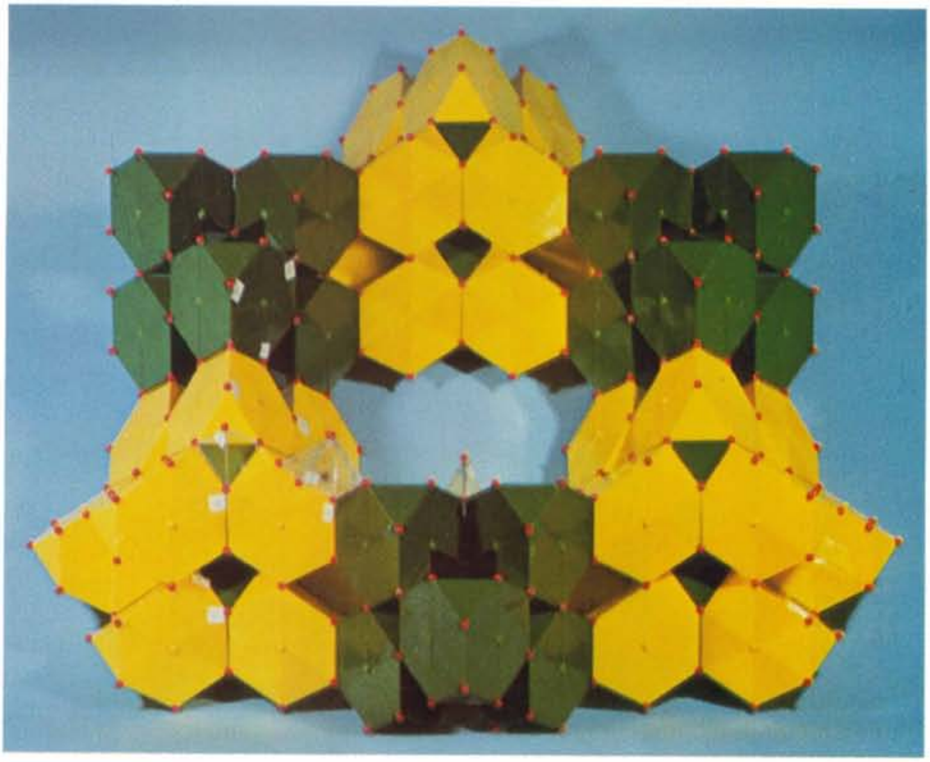


Fig. 2. The Friauf framework. Red balls are Cu atoms.

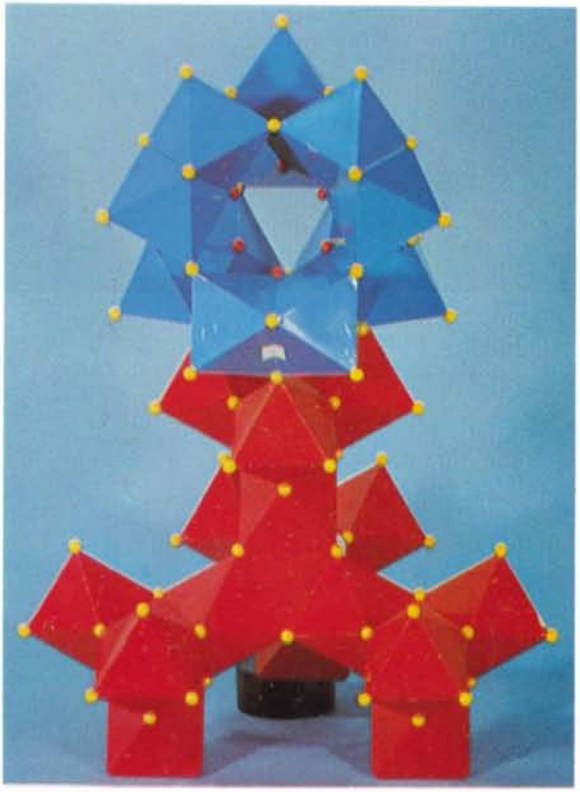


Fig. 3. A red pyrochlore intergrowing with a Rh_7Mg_{44} unit, creating an icosahedron. Red balls show the central Cu octahedron, yellow balls are Cd.

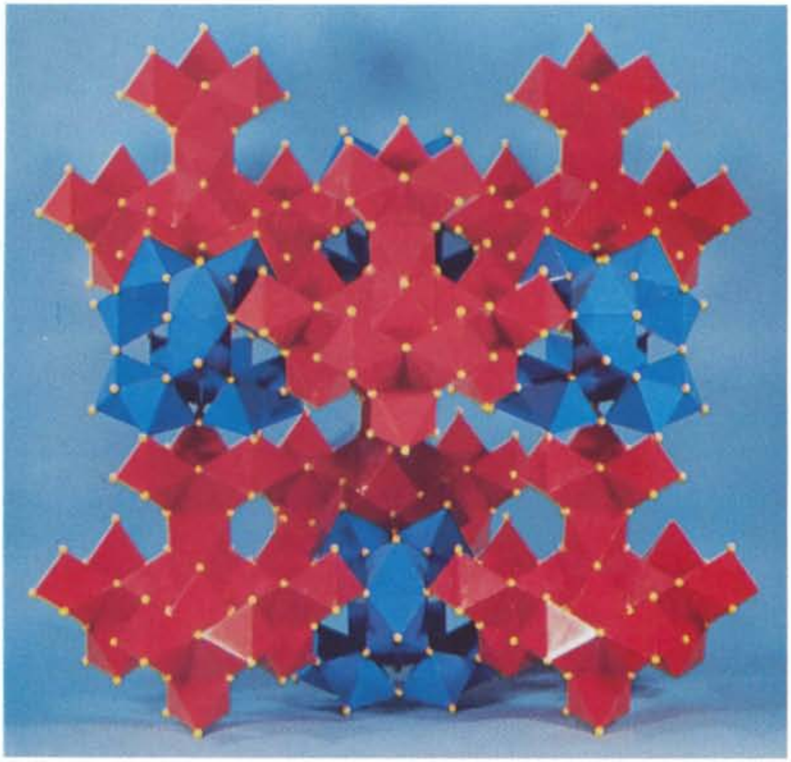


Fig. 4. The entire Cd-pyrochlore framework.

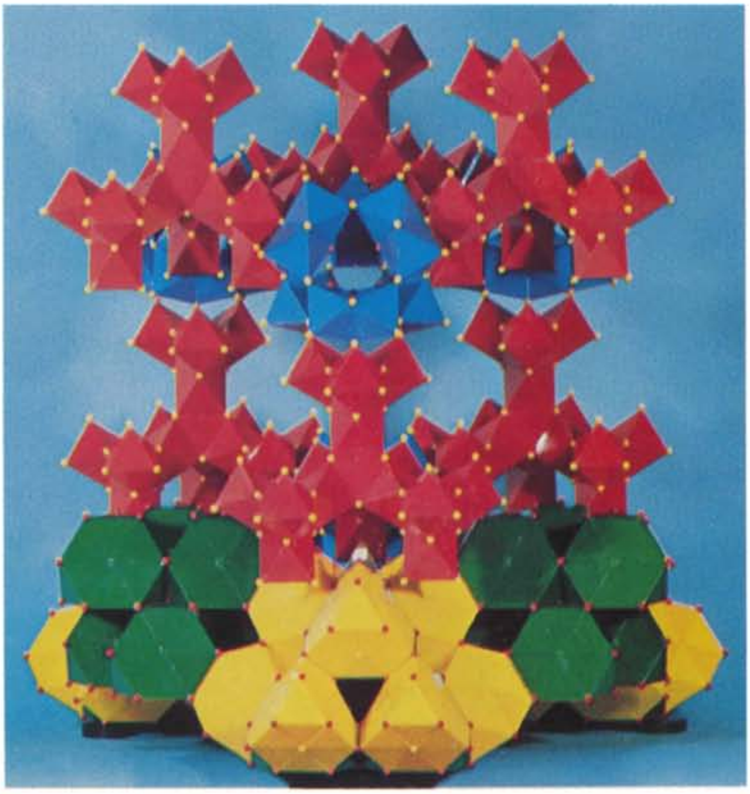
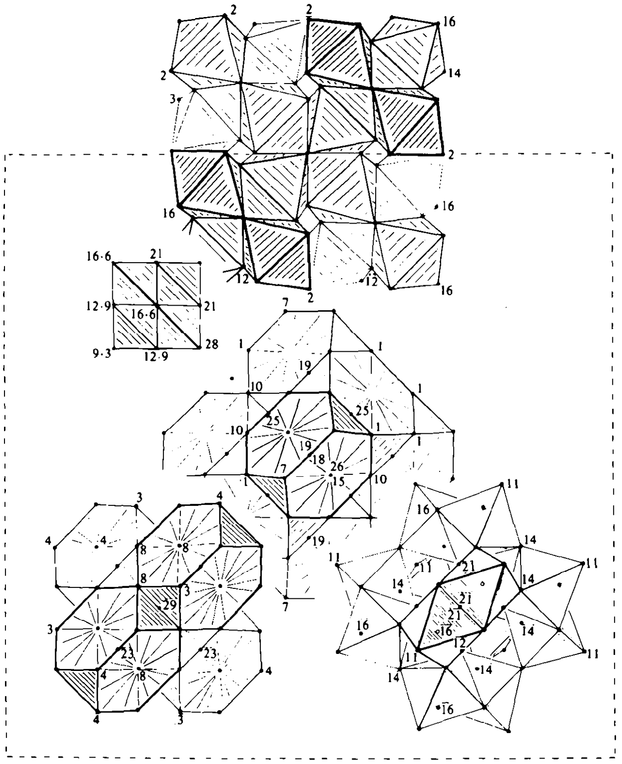


Fig. 5. The entire structure of Cu_4Cd_3. Note that there is a size ratio between the two interpenetrating structures of $\frac{22}{19} = 1{\cdot}158$, which explains why the Friauf framework seems to be too big in the model. Red balls are Cu, yellow balls Cd.



(b)

Fig. 1 (*cont.*) (*b*) Same unit as in Fig. 1(*a*), but all heights and most of the identification numbers are omitted to show the structural blocks. In the upper center is the big pyrochlore unit of 21 octahedra, shown as red in Figs. 3, 4 and 5. The two different building blocks of the Cu_2Mg structure (yellow and green in Figs. 2 and 5) are in the center and lower left part. The ten-atom Cu metal block (a large tetrahedron) is in the upper left part, while the octahedrally capped pyrochlore unit (blue in Figs. 3, 4 and 5) is in the lower right.

Table 2. *Formulae for atom coordinates*

(*a*) Atom numbers 2, 12, 16, 17 and 18: $(x,y,z) = m/2n$, $n = 19$

Atom identification number

m	2	12	16	17	18
0	x				
1				z	
3			z		x
4		x		x	
5	y				
7		z			
8	z		x		

(*b*) Atom numbers 11, 14, 21, 28: $(x,z) = \frac{1}{4} - m\sqrt{6}/4n$, $n = 19$

Atom identification number

m	11	14	21	28
1		z		
2	x		x	x
3		x		
6	z			

while the Fe atoms form the *stella quadrangula* network. In order to calculate the coordinates for these two Cu atoms, we assume a perfect intergrowth between the Friauf network and this tetrahedral pyrochlore network. Cu(27) and Cu(30) are at the centers of the icosahedra created by the blue unit and the Friauf network, and the coordinate for Cu(27) has been calculated by assuming that it is tetrahedrally packed in the Friauf network. Coordinates for Cd(13) have not been calculated because it is the atom capping the Friauf polyhedron with Cd(19) as the central atom. Fig. 5 shows how the two frameworks interpenetrate to form the entire structure; yellow balls are Cd, red balls are Cu.

Discussion

The network of Friauf polyhedra is extremely regular in the sense that the atomic coordinates calculated from an exact geometrical model agree almost within the e.s.d.'s of the observed parameters taken from Samson's crystal structure determination. The exact geometrical model is best described as the cubic intergrowth of two different building blocks of the Cu_2Mg structure over a $MgZn_2$-structure arrangement of Friauf polyhedra.

This Friauf-polyhedra network (Cd_5Cu_{19}) forms large cavities which are centered by a ten Cu-atom section of perfect cubic close packing. Between the Cd_5Cu_{19} network and the c.c.p. block of Cu, a somewhat distorted Cd-pyrochlore structure is intergrown. The Cu metal tetrahedron of ten atoms is inscribed in a small pyrochlore unit of 18 Cd atoms (blue) which is orientated towards the larger red pyrochlore unit to create an icosahedron, as in $Mg_3Cr_2Al_{18}$ (Nyman, Andersson, Hyde & O'Keeffe, 1978, Fig. 10). This smaller pyrochlore unit is octahedrally capped as in Rh_7Mg_{44} (blue unit in Fig. 3) and is joined to the larger pyrochlore unit (red in Fig. 3) to form the whole network. Some Cu or Cu and Cd atoms complete the structure by forming the second interpenetrating structure of pyrochlore, the so-called *stella quadrangula* part. The larger octahedral pyrochlore unit is approximately ten times less regular than the Friauf framework together with the c.c.p. and *stella quadrangula* parts. It is obvious that Nature in its efforts to make certain structural arrangements perfectly regular sacrifices some regularity in others.

There are several remarkable features of the structure of Cu_4Cd_3. One is the complete separation of the Cd_5Cu_{19} and Cu structures. and the absence of Cu—Cu contacts between the structures. Cu(28) is in an icosahedron and also belongs to the *stella quadrangula* interpenetrating the red octahedral pyrochlore unit, and the inner octahedron in the blue unit of Cd atoms is

Cu(21). In Rh_7Mg_{44} this octahedron consists entirely of Mg atoms. It is difficult to understand why these Cu atoms (21 and 28) do not interact with the Cd-pyrochlore part of the structure.

The most obvious and remarkable feature of the Cu_4Cd_3 structure is its size and complexity. Would it not be simpler to have instead two coexisting phases such as a Laves phase and a Ni_2Ti phase (pyrochlore)? A Laves phase exists in the Cu–Cd system in Cu_2Cd, and also in Cu_5Cd_8, of γ-brass structure type, which is structurally related to pyrochlore (Nyman & Andersson, 1979).

In order to try to answer these questions we make the following observation: *Complex structures are built from units of simpler structures.* When doing so, Nature aspires to attain maximum symmetry and this means that each unit is as regular as possible and its original symmetry is kept topologically intact. The experimental background for this observation has been discussed recently by Andersson (1978*a*,*b*). Small units of simple structures are put together at the atomic level in ways which can be described by (*a*) the three symmetry transformations translation, rotation and reflection, and (*b*) intergrowth. With high-resolution electron microscopy, several alloy phases have been studied and the structures of the defects found give strong support for this description of structures and crystal formation. This has been reported in a number of papers on the μ phase (Stenberg & Andersson, 1979), the Mo_3CoSi phase (Stenberg, 1979), the *M* phase and several others (Stenberg & Andersson, 1980).

We also observe that the calculated unit-cell volumes (using metal–metal distances from the individual metals) are higher than the observed volumes (this is also true for the other alloys in this group, *viz* W_3Fe_3C, $Mg_3Cr_2Al_{10}$ and Rh_7Mg_{44}). The densities for Cu as well as for Cd are both lower than the density of Cu_4Cd_3. In the complex structure the invariant intergrowth of blocks of simpler structure occurs with very efficient packing – the complex structures are better packed than the metals.

A consequence of this observation of maximum symmetry (which often seems to be combined with maximum density) is that complex structures are preferred to coexisting phases. Many examples exist and we mention here only the higher titanium oxides, the tantalum oxide fluorides, aluminum carbide nitrides and also the vernier structures. [For relevant literature see the review articles by Wadsley & Andersson (1970), Andersson (1967), Bursill & Hyde (1972), and Hyde, Bagshaw, Anderson & O'Keeffe (1974).]

Indeed, many more compounds with new and complex structures should exist for alloys and these will undoubtedly be found at elevated pressures.

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