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An Error Parameter Analysis of Tetrahedral Configurations in γ Brass Structures

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It is shown that it is reasonable to describe some structures such as γ brass and α- and β-Mn completely in terms of tetrahedral configurations of the atoms, even though constraints of the structural geometry do not uniquely prescribe the selected tetrahedra as they do for example in the Laves phases and the β-W structure. Such descriptions use a freedom of choice of tetrahedra in addition to the accepted distortion of tetrahedra in approximating to the non-attainable ideal of filling space with regular tetrahedra. An error parameter is developed which allows comparison of the average distortions of all of the tetrahedra for structures described in terms of tetrahedral configurations of the atoms. Comparison of the error parameters for the γ brasses Cu_5Cd_8 and Fe_3Zn_{10} and for other structures such as α- and β-Mn where there is freedom of choice in the selection of tetrahedral configurations, with error parameters for other structures such as Cu_2Mg and β-W where the tetrahedra are uniquely prescribed by the structural geometry, indicates that the first group of structures can reasonably be regarded as tetrahedral configurations of atoms, although slightly less effectively so than the Cu_2Mg and β-W structures. Other γ brasses such as Cu_5Zn_8 and Cu_9Al_4 are found to be poorer examples of structures possessing overall tetrahedral configurations.

Introduction

The γ brass structure can be described as being built from an arrangement of clusters each containing 26 atoms (Bradley & Jones, 1933). The construction of individual clusters is as follows: (1) an inner tetrahedron (IT) of four atoms in contact with each other; (2) an outer tetrahedron (OT) of four atoms each in contact with three IT atoms, (3) an octahedron (OH) of six atoms each in contact with two IT and two OT, and (4) a cubo-octahedron (CO) of 12 atoms each in contact with two OH, one OT and one IT atoms. This building principle clearly suggests an attempt to fill space with tetrahedral configurations of atoms. That the clusters which pack together in the body-centred cubic arrangement do not extend beyond 26 atoms each by the addition of a further shell, confirms this interpenetration since effective tetrahedral packing would cease with a further addition. Instead, the clusters pack together as best they can with somewhat more distorted tetrahedral (or other) configurations in the intercluster region. These facts, together with the observation that (110) layers of γ brass possess features common to other tetrahedrally configurated structures (Brandon, Brizard, Chieh, McMillan & Pearson, 1974), suggest that quantitative measurement of the deviations from ideal tetrahedral configurations in γ brass is worthwhile.

In this paper we consider some extension to previous considerations of tetrahedral configurations of atoms in alloy crystal structures, and we establish a parameter to describe quantitatively the deviations from ideal tetrahedral configurations. This error parameter is then calculated for several known γ-brass-type structures to show how well γ brass approaches the unattainable ideal tetrahedral packing, and the values are compared with those for a sample of other structure types which have previously been regarded as tetrahedrally configurated.

Tetrahedral configurations of atoms

Although the filling of space with *ideal* tetrahedral configurations of atoms is impossible, many tetrahedrally close-packed structures have been described (*e.g.* Frank & Kasper, 1958, 1959; Shoemaker & Shoemaker, 1967, 1968, 1971, 1972; Pearson & Shoemaker, 1969; Manor, Shoemaker & Shoemaker, 1972) in which space is filled with distorted tetrahedral configurations of atoms. Such structures (*e.g.* Friauf–Laves phases, μ and σ phases, the β-W structure) are built from 'completely interpenetrating' icosahedra and CN14, 15 or 16 polyhedra with triangulated surfaces (Frank & Kasper, 1958). The coordination polyhedra in a structure are said to be 'completely interpenetrating' when they all obey the condition that the atom A at the centre of a polyhedron also lies on the surface of polyhedra severally surrounding atoms $B, C, D, \cdots$ which form the polyhedron about A, and furthermore that neighbouring atoms E, F on the surface of any polyhedron are each on the surface of the polyhedron surrounding the other. In such structures the distorted tetrahedral configurations of the atoms are uniquely prescribed by the geometry of the structures, and recognition of a particular tetrahedral configuration of atoms in the structure means that it has to be recognized in the surroundings of *each* of the four atoms at its corners. The distortion of the tetrahedra is the only degree of freedom that can be used in approximating to the unattainable ideal of filling space with regular tetrahedra of atoms. If, however, the coordination polyhedra surrounding the atoms in a structure are *not completely interpenetrating*, then recognition of a particular tetrahedral configuration in the surroundings of a certain atom does not mean that it must also be recognized as part of the configurations surrounding each of the other three atoms at the corners of the tetrahedron. Thus, for example, if the structural arrangement requires the adoption of one very distorted tetrahedral configuration in the surroundings of a particular atom, the same tetrahedral configuration does not necessarily have to be used in the surroundings of the other three atoms at its apices; it may be possible to describe their surroundings with less distorted tetrahedral configurations.

Allowing a choice of whether or not a particular tetrahedral configuration of atoms is to be recognized in the surroundings of one of the atoms at its corners does not invalidate the description of a structure as a tetrahedral configuration of atoms if it satisfies the sufficient condition that *each atom in the structure can be described as being surrounded by a convex coordination polyhedron of appropriate size which has a triangulated surface*, so that all of the space around *each* atom in the structure is filled by distorted tetrahedra of atoms. Neither does it matter if some of the configurations chosen to show distorted tetrahedra are, for example, more obviously octahedral; it is sufficient that a description in terms of distorted tetrahedral configurations can be given.

At this point it should be emphasized that the actual arrangement of the atoms in the structure is the only fact of importance, and whatever description we wish to apply to this arrangement is purely an artifact. However, it is legitimate to examine what building principle may be the basis of structural stability, and in considering γ brass structures, this has led us to broaden previous criteria for recognizing tetrahedral packing.

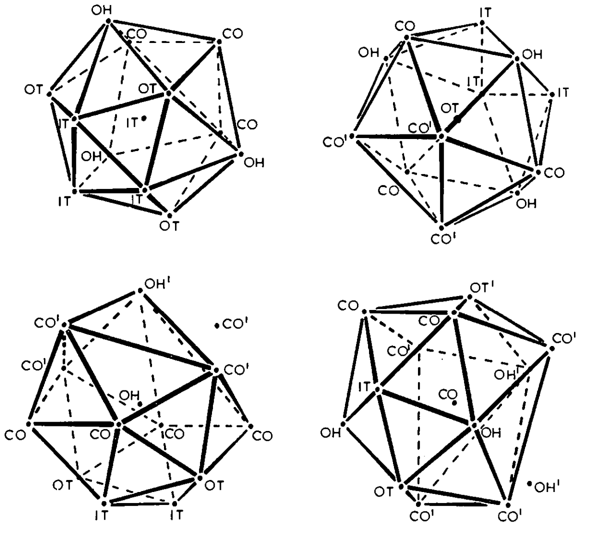

Fig. 1. Convex CN12 polyhedra with triangulated surfaces chosen around each of the IT (x,x,x), OT $(\bar{x},\bar{x},\bar{x})$, OH $(0,0,z)$ and CO (x,x,z) sites in the γ brass structure of Cu_5Cd_8. All polyhedra are drawn as viewed along [010]. Primed site labels indicate an atom in a different cluster. For OH and CO, the position of an extra site is shown which could be used to make a CN13 polyhedron. The CN12 polyhedra outlined refer to case *C* in Table 2.

The central atom in the completely interpenetrating CN12, 14, 15 or 16 polyhedra found in the tetrahedrally packed structures referred to above, is the common apex to 20, 24, 26 or 28 distorted tetrahedra respectively. Hypothetical tetrahedral packing using regular tetrahedra would require each atom to be the common apex to some 21·5 tetrahedra.* Thus it would appear that the closest approximation to hypothetical ideal tetrahedral packing might be achieved in a structure built of completely interpenetrating icosahedra where 20 rather than 21·5 tetrahedra would meet at a point, with the possibility that a mixture of icosahedra with some large-CN polyhedra might give an overall average closer to 21·5. Frank & Kasper (1958) have noted that a structure using only completely interpenetrating icosahedra is impossible if the icosahedra are regular, and as far as they could ascertain, there were no known structures built with completely interpenetrating distorted icosahedra. Nevertheless Pearson, Brandon, McMillan & Brizard (1972) showed that the γ brass structure could be described in terms of distorted icosahedra that were not completely interpenetrating. Although the generally accepted coordination about the four independent atoms (IT, OT, OH and CO) in the γ brass structure is 12, 12, 13, and 13 (or 15) atoms in convex polyhedral arrangement with triangulated surfaces, it is also possible to choose about each of the atoms CN12 polyhedra (Fig. 1) that have all of the properties of distorted icosahedra. They are convex with no internal atoms except the central one, and they have triangulated surfaces on which all atoms have surface coordination number 5, so that each atom is the common vertex to 20 distorted tetrahedra surrounding it.

Both the description based on distorted icosahedra and that based on CN12, 12, 13 and 13 polyhedra allow γ brasses to be considered as structures with tetrahedral configurations, but in neither description are the polyhedra completely interpenetrating as defined above. It will be shown that the arbitrariness in the choice of possible tetrahedral configurations of the atoms in the γ brass structure (two different CN12 or CN13 polyhedra about the OH site, and CN12 or 13 polyhedra about the CO site) is a triviality which only

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* This number is derived by considering how many regular tetrahedra with edge length unity would fill the same volume as 20 distorted tetrahedra such as those found in an icosahedron with centre-to-vertex distance unity. An alternative estimate using the fraction of the total solid angle subtended internally at the vertex of a regular tetrahedron $(0{\cdot}551/4\pi)$ suggests that each atom would be the common apex of 22·8 tetrahedra. This latter value overestimates the number since steric hindrances are not taken into account as in the estimate based on the volume of an ideal icosahedron.

affects the analysis of the overall effectiveness of the description based on tetrahedral packing to a small degree.

An error parameter to measure distortions from hypothetical tetrahedral configurations

In order to make a quantitative assessment of the effectiveness of γ brass in achieving tetrahedral configurations and to compare quantitatively its success with that of other structures previously accepted as being tetrahedrally packed, a parameter is needed which will measure the average deviations from a non-attainable hypothetical structure built with regular tetrahedra of atoms. Such a parameter must sum the average distortion from ideal for every tetrahedron which surrounds every atom in the unit cell according to the structural description adopted, and it must avoid metrical effects arising from the different sizes of atoms and therefore of tetrahedra in the structure. The error parameter will then allow us to evaluate whether structures such as γ brass (and α- and β-Mn, for example), where the chosen coordination polyhedra are not completely interpenetrating when they are described in terms of distorted tetrahedral configurations of the atoms, are as good an approximation to hypothetical regular tetrahedral packing as for example the Laves, β-W, σ and μ phases, where the tetrahedral configurations are uniquely prescribed by the complete interpenetration of the coordination polyhedra.

Since a regular tetrahedron has six equal edges, one can measure the distortion of a *single* irregular tetrahedron through the root-mean-square deviation of the lengths of its six edges from the average length of the six,

$$i.e.\ \{\tfrac{1}{6}\sum_{i=1}^{6}(\chi_{ij}-\langle\chi_j\rangle)^2\}^{1/2}$$

where χ_{ij} is the length of the ith edge of the jth tetrahedron and $\langle\chi_j\rangle=\frac{1}{6}\sum_{i=1}^{6}\chi_{ij}$. Dividing this by the average length of the six edges, $\langle\chi_j\rangle$, yields a normalized root-mean-square deviation which is independent of the size of the particular tetrahedron.

One can now define E, an average root-mean-square error parameter per tetrahedron *for the structure*, by summing the normalized root-mean-square deviations over all M_k tetrahedra selected as having a common apex at the kth atom, summing these for all N atoms in the unit cell, and dividing the result by the total number T of tetrahedra in the two summations

$$i.e.\ E=\frac{100\%}{T}\sum_{k=1}^{N}\sum_{j=1}^{M_k}\left[\frac{1}{\langle\chi_j\rangle}\{\tfrac{1}{6}\sum_{i=1}^{6}(\chi_{ij}-\langle\chi_j\rangle)^2\}^{1/2}\right]$$

where

$$T=\sum_{k=1}^{N}M_k\,.$$

In general, E will be expected to be larger for structures containing a high proportion of large coordination polyhedra such as the Friauf CN16 polyhedron which surrounds each atom with 28 tetrahedra instead of the ideal 21·5. E will also be expected to be larger for structures which contain regions of misfit causing large distortion of some of the selected tetrahedra, whereas structures containing a high proportion of icosahedra surrounding each atom with 20 tetrahedra should have low values of the error parameter. For instance the r.m.s. error parameter for each single ideal Friauf CN16 polyhedron* is 6·40% whereas it is only 2·51% for the tetrahedra in an ideal icosahedron (Table 1).

Comparison of E for γ brasses and other structures containing tetrahedral configurations

Table 1 gives the percentage r.m.s. error parameters per tetrahedron E, as defined above for a selection of isolated polyhedra and for several phases with the γ-brass-type structure. In order to examine whether E for γ brasses is at all similar to E for other structure types previously described as tetrahedral configura-

Table 1. *Percentage r.m.s. error parameters per tetrahedron for a selection of isolated ideal polyhedra and actual crystal structures*

Polyhedron or crystal structure	Error parameter (%)	Reference*	Polyhedron or crystal structure	Error parameter (%)	Reference*
Tetrahedron	0		Cu_5Zn_8	7·70	3
Octahedron	14·44		Cu_5Cd_8	6·50	3
Icosahedron (CN12)	2·51		Fe_3Zn_{10}	6·74	3
Friauf polyhedron (CN16)	6·40		Cu_9Al_4	7·81	4
Face-centred Cubic	8·66		α–Mn	6·99	5
Cu_2Mg	6·21	1	β–Mn	6·76	6
β–W (Nb_3Sn)	6·31	2			

* References for structural parameters used: 1. Friauf (1927). 2. Geller, Matthias & Goldstein (1955); Geller (1956). 3. Brandon, Brizard, Chieh, McMillan & Pearson (1974). 4. Heidenstam, Johansson & Westman (1968). 5. Gazzara, Middleton, Weiss & Hall (1967). 6. Preston (1928); Kasper & Roberts (1956).

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* The ideal Friauf CN16 polyhedron used for the E calculation is one for which all edges not involving the sixfold vertices are of the same length. A variety of Friauf polyhedra still possessing T_d symmetry can exist with two different lengths among such edges.

tions, the error parameters have also been calculated for Cu_2Mg and β-W structures as examples of structures with completely interpenetrating coordination polyhedra, and for α and β-Mn as examples in which the chosen coordination polyhedra are not completely interpenetrating.

The value of 2·51 % for the ideal icosahedron sets the unobtainable lower limit if regular icosahedra could pack together in a completely interpenetrating fashion. Among structures previously regarded as approximations to tetrahedral packing, the r.m.s. errors of 6·21 and 6·31 % for Cu_2Mg and β-W respectively suggest typical values expected for structures built with completely interpenetrating polyhedra. The Cu_2Mg structure contains larger polyhedra (CN16) than the β-W structure (CN14) but they comprise a smaller proportion (33 %) of the total number of polyhedra than do the CN14 polyhedra in β-W (75 %). An r.m.s. error parameter of 14·44 % is found for an ideal octahedron, regarded as four distorted tetrahedra sharing a common edge. This value provides an upper limit of the error parameter when the configurations are octahedral and should not be described as distorted tetrahedra. The r.m.s. error parameter for the face-centred cubic (cubic closest packing) crystal structure described entirely in terms of tetrahedral configurations of the atoms is 8·66 %. Since this structure fills space with regular tetrahedra ($E=0$) and octahedra in the ratio 2:1, the value of 8·66 % should be typical of structures where the packing ought to be described as a mixture of tetrahedral and octahedral configurations. This value is relevant for comparison with the r.m.s. error parameters found for some phases with the γ brass structure where, for example, some inter-cluster groupings involving CO atoms may be more appropriately described by distorted octahedral rather than tetrahedral configurations.

R.m.s. error parameters of 7·70 and 7·81 % respectively for the Cu_5Zn_8 and Cu_9Al_4 γ brass structures indicate that they are not good overall approximations to tetrahedral packing, but values of 6·50 and 6·74 % for the Cu_5Cd_8 and Fe_3Zn_{10} structures respectively suggest that an overall description in terms of tetrahedral configurations of the atoms is reasonable. Indeed if 6·77 % of the tetrahedra are neglected in the summations for the Cu_5Cd_8 and Fe_3Zn_{10} structures the r.m.s. error parameters for the remainder are only 5·62 and 5·88 % respectively, *i.e.* significantly better than those of the Cu_2Mg and β-W structures, indicating that much of the structure is a rather good approximation to tetrahedral packing. It is in the regions where the 26-atom clusters join, and some of the configurations may better be described as distorted octahedral rather than distorted tetrahedral, that this description is least satisfactory. Nevertheless we believe that the description of the γ brass structure based on 26-atom clusters (Bradey & Jones, 1933), the layer description (Brandon, Brizard, Chieh, McMillan & Pearson, 1974), and the present data all indicate that the building principle of the structure is an approximation to tetrahedral packing.

Why the r.m.s. error parameter is so much larger in some phases with the γ brass structure than in others, and indeed why Cu_9Al_4 has the *P* rather than the *I* structure is not entirely clear. These facts do not correlate with the relative sizes of the component atoms alone; they also involve the relative numbers of larger and smaller atoms in the structure.

The α- and β-Mn structures with r.m.s. error parameters of 6·99 and 6·76 % respectively can also reasonably be considered as overall examples of approximate tetrahedral packing, although significantly less so than Cu_2Mg and β-W which are built with completely interpenetrating polyhedra.

One final point concerns the arbitrariness in descriptions of the γ brass structures in terms of tetrahedral configurations of the atoms. That this is but a relative triviality is apparent from Table 2 which gives values of the r.m.s. error parameters obtained for six different structural descriptions of Cu_5Cd_8 in terms of tetrahedral configurations of the atoms. The values for these six cases show a spread of only 0·22 % which is not very significant, emphasizing that it is the atomic arrangement and not the assumed description that is important.

Table 2. *Percentage r.m.s. error parameters per tetrahedron for six different structural descriptions of* Cu_5Cd_8 *in terms of tetrahedral configurations*

	Structural description details	Error parameter (%)
A	CN12 polyhedra about IT and OT, CN13 about OH and CO.	6·60
B	CN12 polyhedra about IT, OT and CO, CN13 about OH.	6·50
C	CN12 polyhedra about all sites, taking one possible CN12 choice about OH.	6·62
D	CN12 polyhedra about all sites, taking an alternate CN12 choice about OH.	6·54
E	CN12 polyhedra about IT, OT and OH, CN13 about CO, taking one possible CN12 choice about OH.	6·72
F	CN12 polyhedra about IT, OT and OH, CN13 about CO, taking an alternate CN12 choice about OH.	6·64

Conclusions

By developing a quantitative error parameter that measures the total average deviation from ideal tetrahedra of the edges of all of the tetrahedra in a structure completely described in terms of tetrahedral configurations of the atoms, it has been shown that γ brasses such as Cu_5Cd_8 and Fe_3Zn_{10} are quite good approximations to tetrahedral packing, although for Cu_5Zn_8 and Cu_9Al_4 a description in terms of tetrahedral configurations of the atoms is less satisfactory. Indeed, in Cu_5Cd_8 and Fe_3Zn_{10} the description in terms of tetrahedral configurations of the atoms is exceedingly good apart from some 6·8% of the tetrahedra in the regions where the individual 26-atom clusters pack together.

These results (together with those for α- and β-Mn, also considered as examples) indicate that the coordination polyhedra need not be completely interpenetrating (as in structures such as the Friauf–Laves phases, σ, β-W *etc.*) in order for a structure to achieve an approximation to hypothetical packing of regular tetrahedra to fill space.

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Theory of X-ray Diffraction from Stacking Faults and Antiphase Domain Boundaries in the DO_{19}-Type Ordered H.c.p. Structures

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The mathematical theory of X-ray diffraction from stacking faults and antiphase domain boundaries on the basal plane in the DO_{19}-type ordered hexagonal close-packed structures, exhibited notably by Mg_3Cd and Ti_3Al, has been worked out. In all, seven cases have been considered. There are generally two kinds of diffraction effect obtained, namely the changes in the integrated intensities and the broadening of the reflexions.

Introduction

The first mathematical formulation of the theory of X-ray diffraction from antiphase domain boundaries (APDB's) was carried out by Wilson (1943) (see also Wilson & Zsoldos, 1965) in the ordered face-centred cubic (f.c.c.) structure of the type $L1_2$, a notable example of which is Cu_3Au. Further extensive X-ray work on Cu_3Au has been done by Cohen and his coworkers (see Mikkola & Cohen, 1965, 1966). Rothman, Merion & Cohen (1969) worked out the theory of X-ray diffraction from stacking faults (SF's) and APDB's in the B_2-type body-centred cubic (b.c.c.) structure. In the following is given the theory of SF's and APDB's in another important structure, the hexagonal close-packed (h.c.p.) structure of the type DO_{19}, exhibited notably by Mg_3Cd and Ti_3Al (Fig. 1). After Lele (1969) and Prasad & Lele (1971) the method has been considerably simplified. In general, these 'faults' affect the reflexions in two ways: by changing the integrated intensities and by broadening the reflexions. Reflexions with $H-K=3N$ and $L=2N\pm1$