

Statistical studies of intermetallics stressing the validity of three principles

John R. Rodgers and Pierre Villars*

National Research Council Canada, Ottawa K1A 0S2 (Canada)

Abstract

The design of new materials and the prediction of their properties are becoming an essential component of materials science. Combinations of phase diagram information, structural information and a variety of physical property information are necessary components of such predictive systems. In this paper we analyse structural and chemical data of intermetallic compounds and show how they comply with the following principles: (1) symmetry principles, (2) simplicity principles, (3) chemistry principles.

The results of many of the statistics shown in this paper can be used to develop additional information for a knowledge base in a predictive system. With the aid of statistical plots we will demonstrate some practical applications, such as exploring certain research trends and querying the database to narrow down the number of compounds of specific interest.

1. Introduction

CRYSTMET [1] is a numerical (crystallographic) and factual (chemical, physical) database of evaluated crystallographic data for intermetallic compounds. The version we discuss here, which covers the world literature for the period 1913–1989, contains 48189 entries (including multiple entries). This database is updated annually. At the outset it is interesting to look at the distribution of intermetallic phases by elemental composition (Fig. 1). In calculating the number of compounds, starting with 89 elements and assuming two compounds per system would result in 198 unaries, 7823 binaries, 227 128 ternaries and 4.8×10^6 quaternaries. Figure 1 shows the distribution of compounds which have been studied by diffraction techniques and which fall into the above categories: 551 (1.4%) unaries, 18 586 (45.6%) binaries, 19 597 (48.1%) ternaries and 1928 (4.7%) quaternaries. These numbers, relative to the estimated maximum number of compounds for each group, show that binaries are more fully investigated, whilst only 8% of the ternaries have been studied and research in the quaternary field has only just started. These numbers demonstrate that future research will be undertaken in the ternary and multinary systems, since the binary system has already been extensively investigated. However, moving from binaries to ternaries forces us, because of the enormously high number of

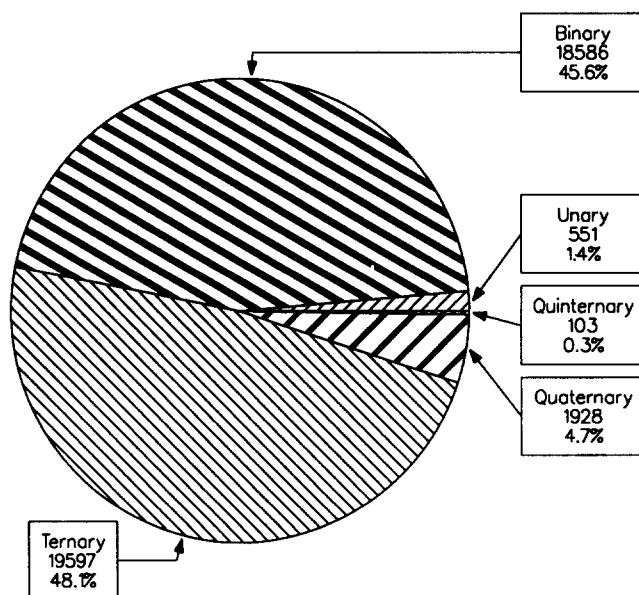


Fig. 1. Distribution of intermetallic compounds by elemental composition.

potential systems, to use databases to be efficient in the search for novel materials.

Under intermetallic compounds we define all compounds (unary, binary, ternary, quaternary, etc.), but exclude ternary and higher oxides and compounds containing halides and noble gases. Analyses of this database using a variety of database tools and clustering algorithms reveal many interesting patterns which can be used

*Permanent address: Intermetallic Phases Databank, Postfach 15, CH-6354 Vitznau, Switzerland.

(1) to check the consistency of new entries with previously studied materials (data evaluation and registration),

(2) to predict the structure of new compounds,

(3) to locate intermetallic fields which are actively studied at the moment (statistical studies)

(4) to investigate regularities in intermetallics,

(5) to locate *gaps* in intermetallic systems (regions where there has been no elemental combination),

(6) to show relationships between structures (mathematical, structural, property and chemistry).

In this paper we analyse the following crystallographic and chemical data elements:

(1) unit cell dimensions and space group,

(2) coordinate and point set,

(3) chemical formula.

The results of these analyses are presented with a range of statistical plots which are grouped under the following principles:

(1) symmetry principles,

(2) simplicity principles,

(3) chemistry principles.

The concepts for each principle are demonstrated with plots.

2. Symmetry principle

This principle is present in the majority of intermetallic compounds. Figure 2 shows the distribution of intermetallics by symmetry class: 70% of all intermetallics belong to the seven crystal classes 5, 8, 15, 20, 27, 31 and 32; all other compounds are distributed between the remaining 25 crystal classes, each having a 1% frequency. A closer look at these seven classes shows that they all belong to the highest symmetry

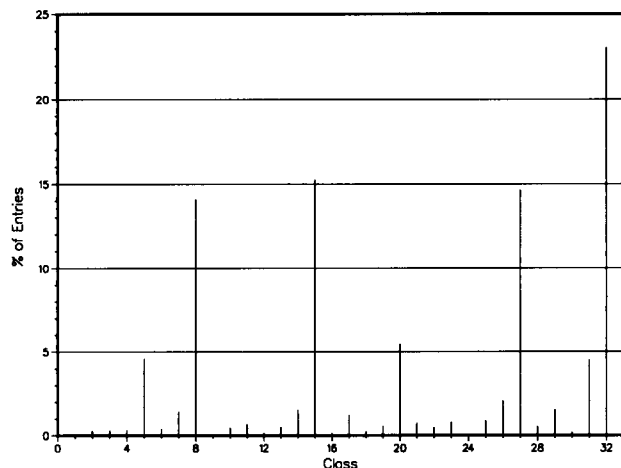
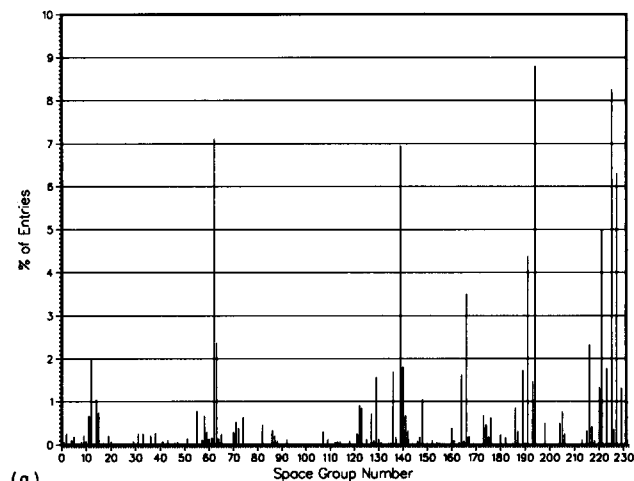


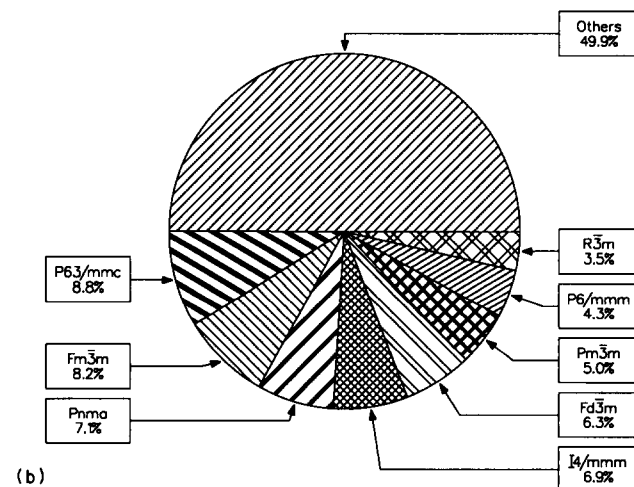
Fig. 2. Distribution of intermetallics by symmetry class. The seven most populous classes 5, 8, 15, 20, 27, 31 and 32 belong to the highest symmetry class for each crystal system.

class of the crystal system*. Even more notable is the distribution of intermetallics by space group (Fig. 3(a)). From Fig. 3(b) it is observed that over 50% of all intermetallic compounds crystallize in the following eight space groups: 62 (*Pnma*), 139 (*I4/mmm*), 166 (*R $\bar{3}m$*), 191 (*P6/mmm*), 194 (*P6₃/mmc*), 221 (*Pm $\bar{3}m$*), 225 (*Fm $\bar{3}m$*), 227 (*Fd $\bar{3}m$*).

These space groups represent 3.5% of all space groups (230). Each of the remaining space groups (222) has less than 2%, most of them having a frequency of less than 1%. The only lower symmetry space group which is preferred is space group *Pnma* (Fig. 3(b)). In reviewing the statistics for the crystal systems (Fig. 4), it is observed



(a)



(b)

Fig. 3. (a) Distribution of all intermetallic space groups. (b) Distribution of intermetallics by space group showing the eight most popular space groups 62 (*Pnma*), 139 (*I4/mmm*), 166 (*R $\bar{3}m$*), 191 (*P6/mmm*), 194 (*P6₃/mmc*), 221 (*Pm $\bar{3}m$*), 225 (*Fm $\bar{3}m$*), and 227 (*Fd $\bar{3}m$*).

*The highest symmetry classes for each crystal system are: 5, *2/m* monoclinic; 8, *mmm* orthorhombic; 15, *4/mmm* tetragonal; 20, *3m* rhombohedral; 27, *6/mmm* hexagonal; 31, *43m* cubic; 32, *m3m* cubic.

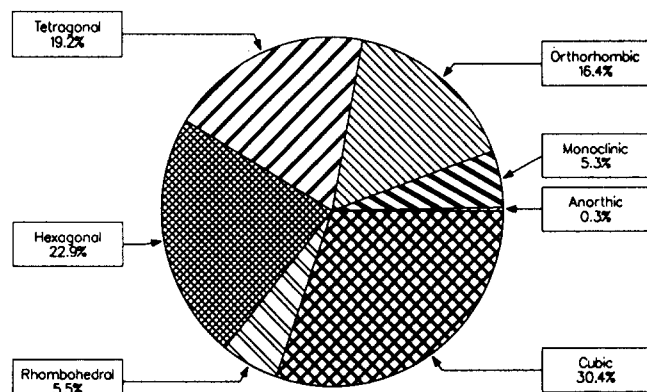


Fig. 4. Distribution of intermetallics by crystal system.

that the cubic space groups are preferred to the hexagonal and the hexagonal to the tetragonal. It is remarkable that about 95% of all intermetallics crystallize in a crystal structure with 90° or 120° interaxial angles of the unit cell. This is in complete contrast to organics and inorganics [2, 3]. The remaining 5% are mainly compounds containing the elements S, Se or Te. These compounds represent the "boundary" compounds between intermetallics and inorganics (oxide, halides).

The distribution of unaries (chemical elements) by their crystal systems is shown in Fig. 5(a). Similar distributions of crystal systems are seen for binary, ternary and quaternary compounds (Figs. 5(b)–5(d)).

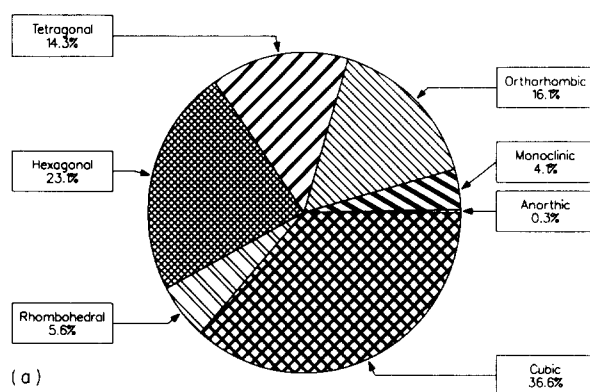
In a first approximation, alloying additional different elements to unaries, *i.e.* moving them to binaries, ternaries, etc., does not significantly change the symmetry distribution. This observation indicates that the bonding situation is not substantially different between unaries, binaries and ternaries (multinaries).

3. Simplicity principle

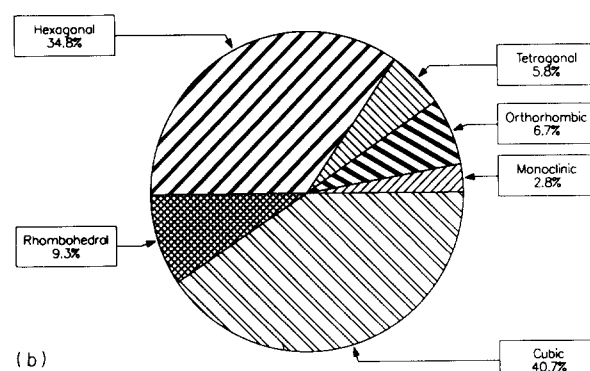
This principle is partly a consequence of the symmetry principle. It states that intermetallic compounds strongly prefer crystal structures that are simple.

3.1. Minimal point sets per compound

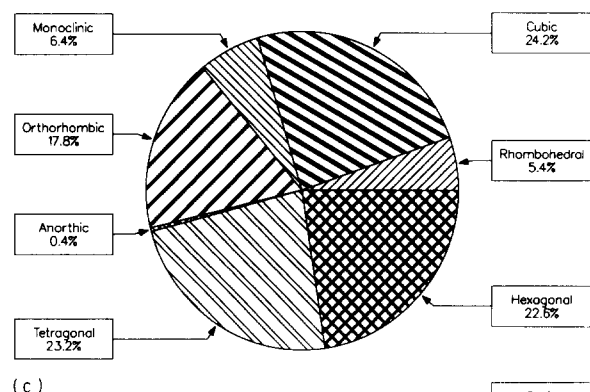
A first measure of simplicity is the number of point sets within a crystal structure. Figure 6 shows the number of structure types *vs.* the number of point sets per structure. From this figure one can observe that structure types with less than 12 point sets are highly preferred. Multiplying the structure type by its representative gives the total number of compounds. A plot of this number *vs.* the number of point sets within a compound is shown in Fig. 7. This distribution shows that for intermetallics there are more restrictions indicating that intermetallics prefer structure types with less than five different point sets. Daams *et al.* [4] reported that of



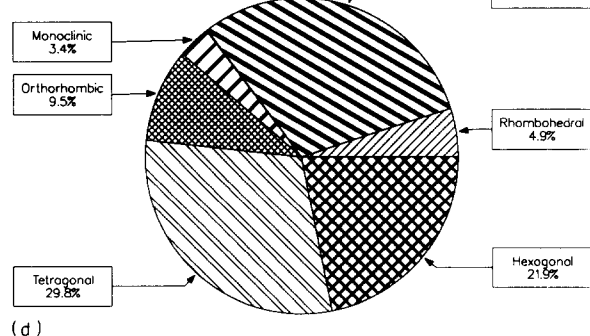
(a)



(b)



(c)



(d)

Fig. 5. Distribution of number of intermetallic compounds by crystal system for (a) unaries, (b) binaries, (c) ternaries and (d) quaternaries.

the 5521 compounds crystallizing in one of the 128 cubic structure types, 46% belong to single-environment groups (structures in which all atoms have the same

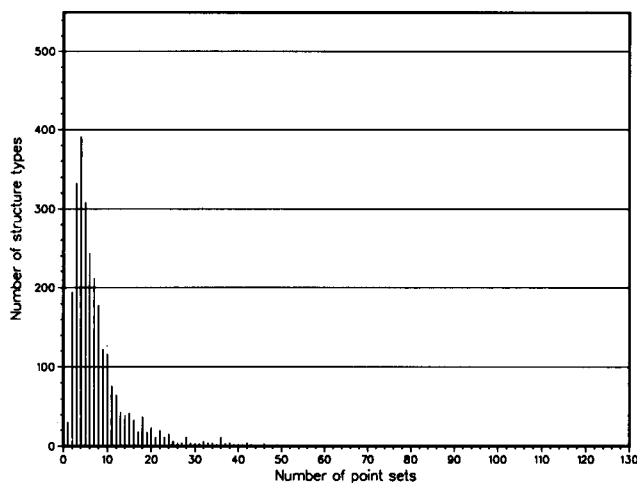


Fig. 6. Distribution of number of structure types vs. number of point sets.

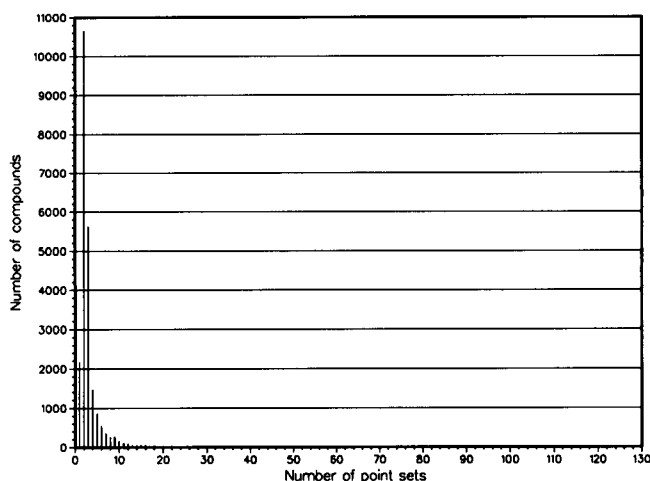


Fig. 7. Distribution of number of compounds vs. number of point sets.

atomic environment type), 37% contain two different atomic environment types, 9% have three different environment types and the remaining 8% have four or more atomic environment types (Fig. 8). A closer look at the atomic environments (AEs, coordination polyhedra) [5] of each point set* of all cubic structure types by Daams *et al.* [4] showed that 12 790 (92%) out of 13 917 AEs studied belong to 13 different atomic environment types (AETs) (Fig. 9). These results show that nature prefers the formation of geometrically simple structures containing one or two AETs. For example, a structure type which has three point sets may only have one type of atomic environment, *e.g.* *tP4* AuCu type has a cubo-octahedron as atomic environment for all atoms (point sets) in the structure. This means that

*The number of point sets in a given structure type is the upper limit for the possible different atomic environments in the structure.

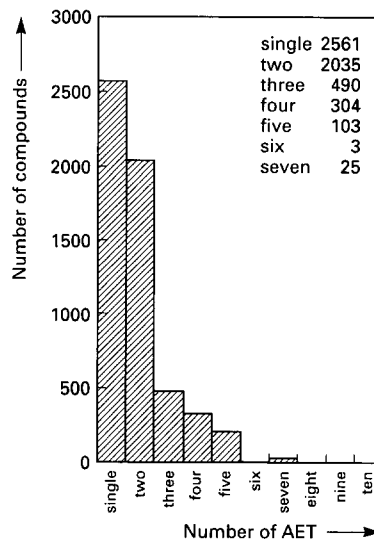


Fig. 8. Number of compounds vs. number of AETs per structure type for 5521 cubic compounds [4].

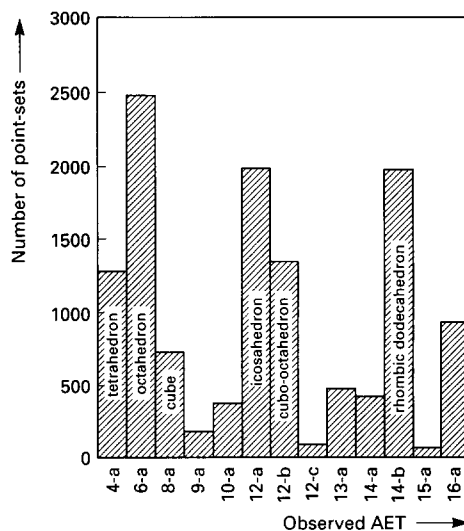


Fig. 9. Frequency plot of the 13 most frequently occurring AETs [4]. The AET labels are built up by a number followed by a character. The number is the coordination number; the character ensures a unique key.

short-range order is preferred to long-range order of the atoms. As a consequence the number of different atomic environments must be limited.

Figure 8 shows the number of compounds vs. the number of different atomic environment types per compound for all cubic compounds. In the cubic case [4] it is clear that more than 90% of all compounds have three or less different atomic environment types within the structure. Looking at the coordination polyhedra, the following are highly preferred: tetrahedron, octahedron, icosahedron, cubo-octahedron and rhombic dodecahedron (see Fig. 9). Preliminary investigations have shown that a similar situation exists in the hexagonal and rhombohedral structures [6].

3.2. Minimal number of atoms per unit cell

A second measure of simplicity is the number of atoms per unit cell. Figures 10(a) and 10(b) show the number of compounds *vs.* the number of atoms per unit cell within the Bravais types *tP* and *tI*. Again, nature prefers for intermetallics that there should be a few atoms per unit cell for all Bravais types. The number of atoms per unit cell varies in the *tP* Bravais-type compounds from one to 280, but 90% of all *tP* Bravais-type compounds have less than 40 atoms per unit cell (an exception is *tP*68 BFe₁₄Nd₂; see Fig. 10(a)). For the *tI* Bravais-type compounds the majority have less than 32 atoms per unit cell (Fig. 10(b)) in a structure.

3.3. Simple stoichiometric ratio plots

A third measure of simplicity is the stoichiometric ratio of the chemical elements within a compound. The plots of Figs. 11 and 12 show the distribution of compounds *vs.* the stoichiometry within binaries and ternaries respectively. These plots show how the con-

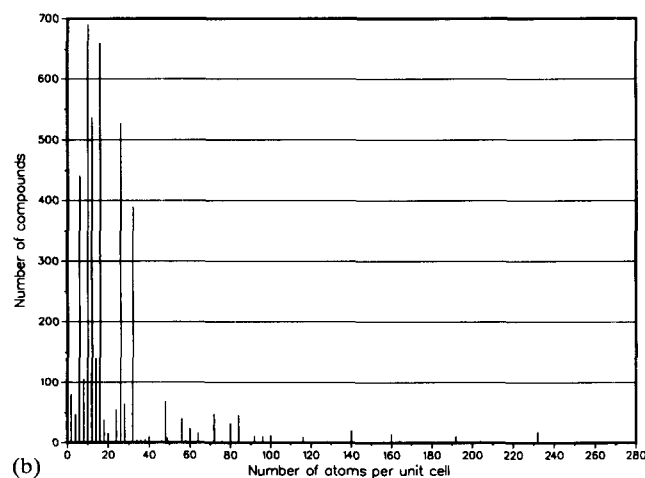
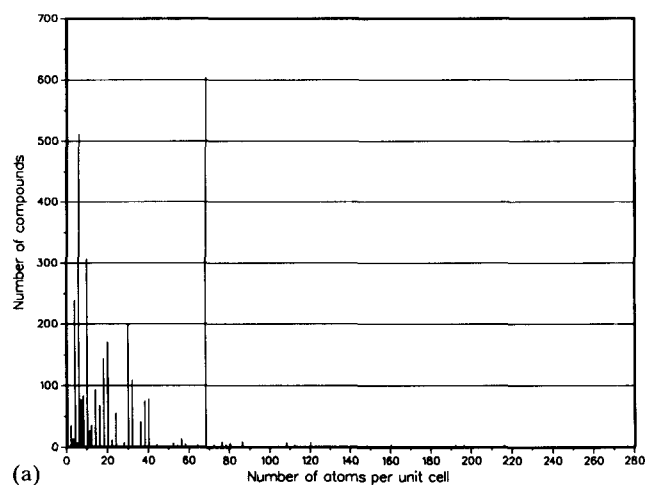


Fig. 10. Number of compounds *vs.* number of atoms per unit cell for (a) *tP* and (b) *tI* Bravais types.

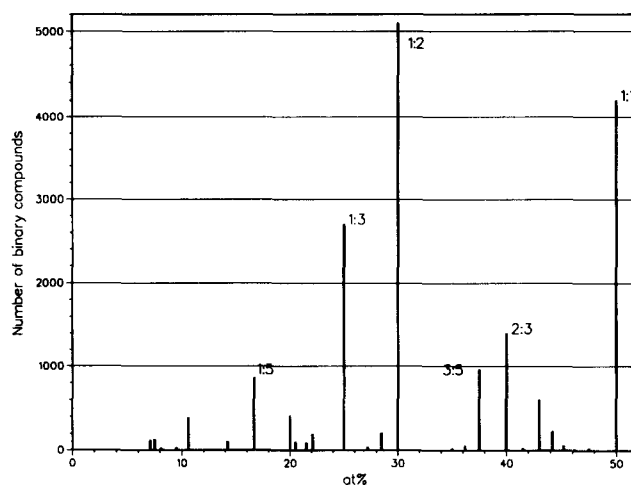


Fig. 11. Distribution of number of compounds *vs.* stoichiometry for binaries.

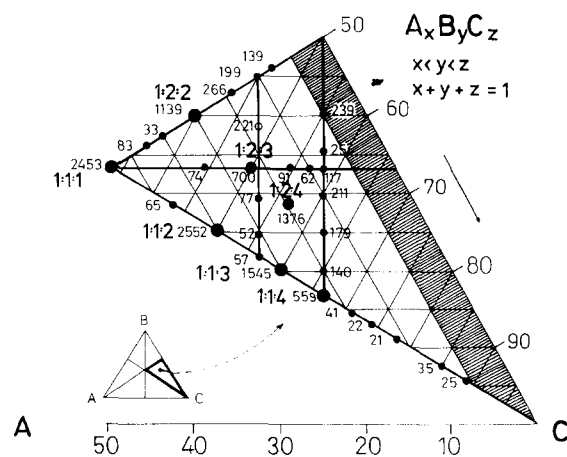


Fig. 12. Distribution of number of compounds *vs.* stoichiometry for ternaries.

centrations are restricted to a limited number of different stoichiometric ratios instead of being statistically distributed over the whole available concentration range. The highly preferred ratios for binaries are 1:1, 1:2, 1:3, 2:3 and 3:5. Figure 11 shows all the stoichiometric proportions which have been found for binaries, with more than 20 compounds per stoichiometric ratio. For ternaries 1:1:1, 1:1:2, 1:1:3, 1:1:4, 1:2:2, 1:2:3 and 1:2:4 are by far the most prevalent (Fig. 12). These seven stoichiometric ratios represent over 80% of all ternary compounds. Almost all are located along three different concentration directions in the concentration plane: one along the direction 1:1:*x*, *x* > 1, another along the direction 1:*x*:*x*, *x* > 1, and the third along the direction with one concentration fixed at 33.3 at.%.

This distribution is far away from statistical scatter and limits the number of potential probable compounds per system drastically. For ternaries the following experimental observation is very helpful: at least 10% of the lowest concentration third element is needed to

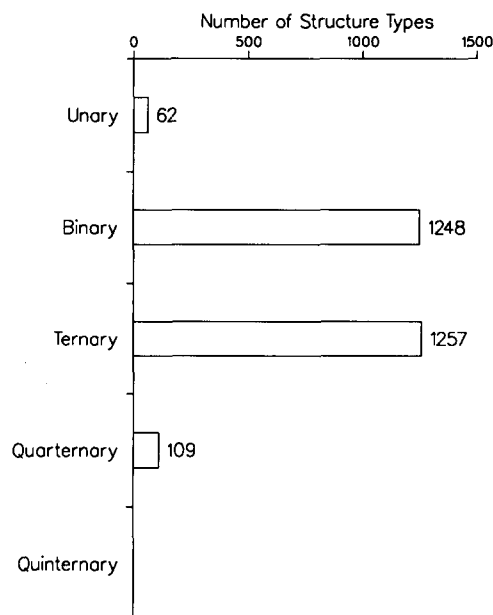


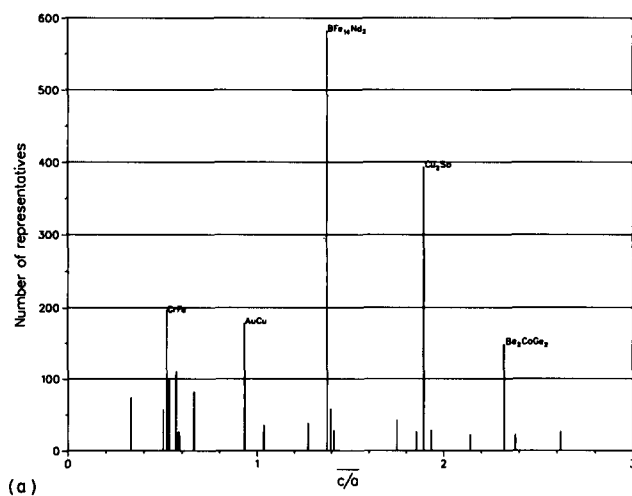
Fig. 13. Distribution of 2700+ structure types named according to the first found binary, ternary and quaternary compounds, giving always the lowest number of chemical element preference.

Binary 1:1 Sulphides									
Sc cF8 ClNa	Ti hP4 AsNi hP2 CW hR6 ST1 hP20 S5Ti4	V hP4 AsNi oP8 MnP	Cr hP4 AsNi mC8 CrS	Mn cF8 ClNa cF8 SZn hP4 SZn	Fe hP4 AsNi oP8 MnP hP6 FeS tP4 OPb	Co hP4 AsNi	Ni hP4 AsNi hP4 NiS hR6 NiS	Cu hP12 CuS oC24 CuS	Zn cF8 SZn hP4 SZn
Y cF8 ClNa	Zr cF8 ClNa tP4 CuTi	Nb hP4 AsNi oP8 MnP hP2 CW hP16 NbS	Mo	Tc	Ru	Rh	Pd tP16 PdS	Ag	Cd cF8 SZn hP4 SZn cF8 ClNa
	Hf	Ta hP2 CW	W	Re	Os	Ir	Pt tP4 PtS	Au	Hg cF8 SZn cF8 ClNa hP6 HgS
La-Lr cF8 ClNa									

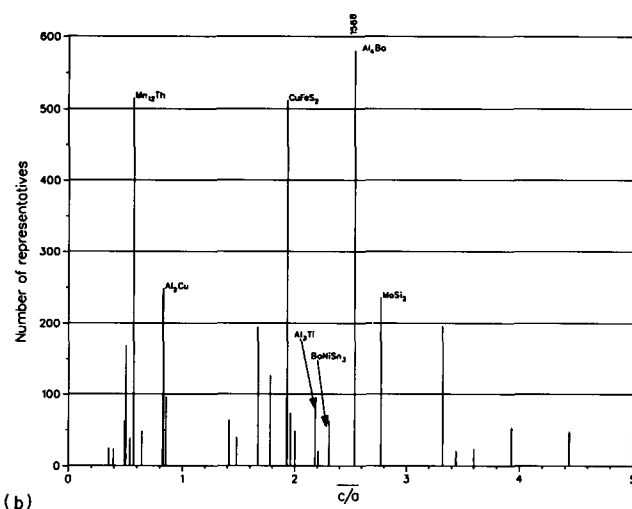
Fig. 14. Experimentally found structure types for binary 1:1 sulphides.

create new ternaries; in a few cases at least 5% is needed (Fig. 12, hatched area). This means that in practice to produce a new ternary intermetallic $A_xB_yC_z$ (where $x > y > z$ and $x + y + z = 1$) which is different from its "neighbouring" binary boundary compound requires a minimum change of $z = 0.1$ in the C element. Otherwise the bonding conditions are not sufficiently changed to create a new atomic arrangement as compared with the starting binary situation.

At present about 2700+ structure types (prototype structures) are known. Figure 13 shows the distribution of unary, binary, ternary and quaternary structure types. The prototype has been defined such that each different set of point set(s) in a certain space group has been named according to its first binary representative or, if not found, its first representative; the same definition applies to higher systems. The majority of structure types (93%) are binaries and ternaries; there are only



(a)



(b)

Fig. 15. Ratio \bar{c}/a vs. number of compounds for (a) tP and (b) tI Bravais-type structures.

a few quaternary prototypes. The simplicity principle indicates strongly that with the presently known 2700 prototypes we have a robust database of different atomic arrangements. This implies that by further exploring ternaries, quaternaries, etc., it would be unlikely to find completely different atomic arrangements and therefore different atomic environments (coordination polyhedra). The low number of quaternary structure types supports this argument. We are convinced that sooner or later in all 109 (4%) of the presently known experimental quaternary prototypes one will find a ternary of binary representative. This has often happened in the past — except for those which move by total ordering of all atoms to a lower space group but still have the same atomic arrangement as the *starting* ternary structure type. Such structure types are a consequence of the definition of prototypes based on the space group theory but are not new atomic arrangements.

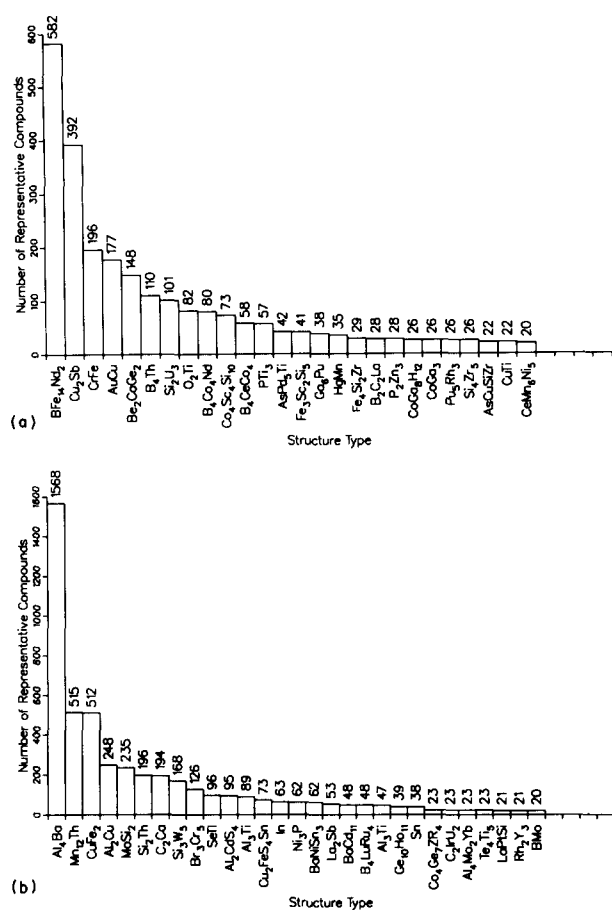


Fig. 16. Number of representative compounds for (a) *tP* and (b) *tI* Bravais types.

It can be argued that the simplicity principle is the result of experimentalists investigating simple structures first. There also seems to be some connection between the complexity of compounds studied and the evolution of both structure solution techniques and computer software and hardware. Nevertheless, we have made some observations which indicate that this is a rule, rather than arbitrarily choosing simple structures first.

(1) Figure 4 shows that 0.3% of all intermetallics crystallize in the anorthic system. It is not accidental that over 80% of these compounds contain S, Se or Te, which represent the “boundary” compounds between intermetallics and inorganics (see Section 2).

(2) Investigations of the AETs of cubic and rhombohedral crystal structures with many atoms per unit cell (*e.g.* greater than 50) show that they have the same AETs as the ones found in simple structures (*e.g.* less than 50).

(3) In the last decades the techniques for determining crystal structures have improved significantly; therefore one could argue that the ratio of experimentally determined complex structures to simple structures (*e.g.* number of atoms per unit cell greater than 50 to those less than 50) should also have increased, but this has

not happened. (However, this situation has occurred for organic and inorganic compounds [2, 3].)

4. Chemistry principle

In this section we classify all dependences which represent in some way the periodicity of the periodic table. In many cases these dependences can be used to predict the structure type or a choice of probable structure types of presently unknown compounds by extrapolating from experimentally known data. The problem here is to find ways which will allow us to cluster (*sort, group*) the variety of physical, chemical and structural information on experimentally known compounds in such a way that interpolation will be trivial.

4.1. Periodic table representation

One very efficient way to show this observation is to plot, for a constant stoichiometry in the binary case, the periodic table and fill in the type of all known compounds with a fixed element, *e.g.* all sulphides in the ternary case with two elements fixed. This approach works well only if sufficient data are already experimentally known. Figure 14 shows the distribution for binary sulphides (1:1). Highly preferred structure types in this distribution are *cF8* ClNa, *hP4* AsNi and *cF8* (*hP4*) SZn types. All structures are grouped to a certain degree, *e.g.* for the lanthanides all sulphides of type AB are *cF8* ClNa.

4.2. Average *c/a* ratio representation

The dimensionless ratios for unit cells are useful parameters for structural predictions. For example, in tetragonal systems the *c/a* ratios for most structure types and their representatives are grouped within a certain range. In Figs. 15(a) and 15(b) we show the average *c/a* vs. the number of compounds for the 26 most popular *tP* Bravais-type structures and the 29 most popular *tI* Bravais-type structures respectively. For these plots we include as an arbitrary limit all structure types with more than 20 representatives. There exist 207 *tP* Bravais-type and 190 *tI* Bravais-type compounds. To use these plots as predictive tools, one has only to determine a unit cell, the corresponding Bravais type and go with the *c/a* value in a plot similar to Figs. 15(a) and 15(b) (such plots can be produced for each Bravais type) together with the estimated number of atoms per unit cell or values of the unit cell dimensions *a* and *c* and one has already a strong indication of its structure type. The limitation of this approach is that it works only for compounds which crystallize in a structure type with many representatives. Figures 16(a) and 16(b) show for the *tP* and *tI* Bravais-type compounds

p-elements: literature years 1969–1979

B	C	N	O	F
974	590	435	281	
Al	Si	P	S	Cl
1107	1336	647	2656	
Ga	Ge	As	Se	Br
806	921	753	1344	
In	Sn	Sb	Te	I
843	689	630	749	
Tl	Pb	Bi	Po	At
317	348	320	3	

s-elements: for literature years

1969-79		1980-89	
H		H	
233		662	
Li	Be	Li	Be
291	120	286	76
Na	Mg	Na	Mg
160	173	228	214
K	Ca	K	Ca
142	247	190	287
Rb	Sr	Rb	Sr
65	194	96	188
Cs	Ba	Cs	Ba
49	254	139	197
Fr	Ra	Fr	Ra
	2		

d-elements: literature years 1969–1979

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
221	499	573	814	1005	1302	1451	1336	1182	478
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
548	547	692	230	24	227	435	515	486	468
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	335	286	195	201	102	209	500	335	89

p-elements: literature years 1980–1989

B	C	N	O	F
1770	620	226	343	
Al	Si	P	S	Cl
1319	1786	983	2143	
Ga	Ge	As	Se	Br
1551	1457	653	1402	
In	Sn	Sb	Te	I
983	1114	593	781	
Tl	Pb	Bi	Po	At
431	298	243		

d-elements literature years 1980–1989

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
365	585	432	751	1357	2326	1892	2172	1498	443
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
875	648	444	681	18	610	805	720	484	373
	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	302	262	137	164	266	445	509	247	144

(a)

(b)

(c)

f-elements: literature years 1969–1979

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
644	610	499	480	4	422	266	595	383	449	355	458	236	348	209
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	301	9	470	86	130	45	40	6	9	1				

f-elements: literature years 1980–1989

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
797	1022	618	764		655	381	789	796	664	619	682	369	388	366
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
	321	7	639	51	47	16	18	15	8					

(d)

Fig. 18. Number of compounds studied during the periods 1969–1979 and 1980–1989 for compounds containing (a) p-elements, (b) s-elements, (c) d-elements and (d) f-elements.

metry principle formulated by Laves [8] and the chemistry principle for isostoichiometric element *vs.* element plots by Villars *et al.* [9] and Pettifor [10] have been verified. Others such as the simplicity principle and additional examples of the chemistry principle have been illustrated. The uses of this database to develop additional patterns in structural chemistry are plentiful as are the applications to material characterization.

Another important application is the use of this database to study “research trends” (*e.g.* materials such as magnetic, hydrogen storage, thin films) in the structural intermetallic field and show how these trends vary over time. We illustrate this by plots. Figures 18(a)–18(d) show the numbers of compounds studied during the

periods 1969–1979 and 1980–1989 presented in a periodic table form *vs.* the number of compounds. From these figures it is seen that Fe, Co, Ni and Cu are the most often investigated d-elements (Fig. 18(c)) and B, Si, S and Se the most often studied p-elements (Fig. 18(a)).

In the last 10 years extremely high research activity has been observed on H-, B- and Ga-containing compounds compared with the previous decade. Figures 19(a) and 19(b) show the numbers of compounds crystallizing in the *hP6* CaCu₅ and *tP68* BFe₁₄Nd₂ types since their discovery; both are very important in the permanent magnet field. It can be seen that after the discovery of *tP68* BFe₁₄Nd₂-type permanent magnets

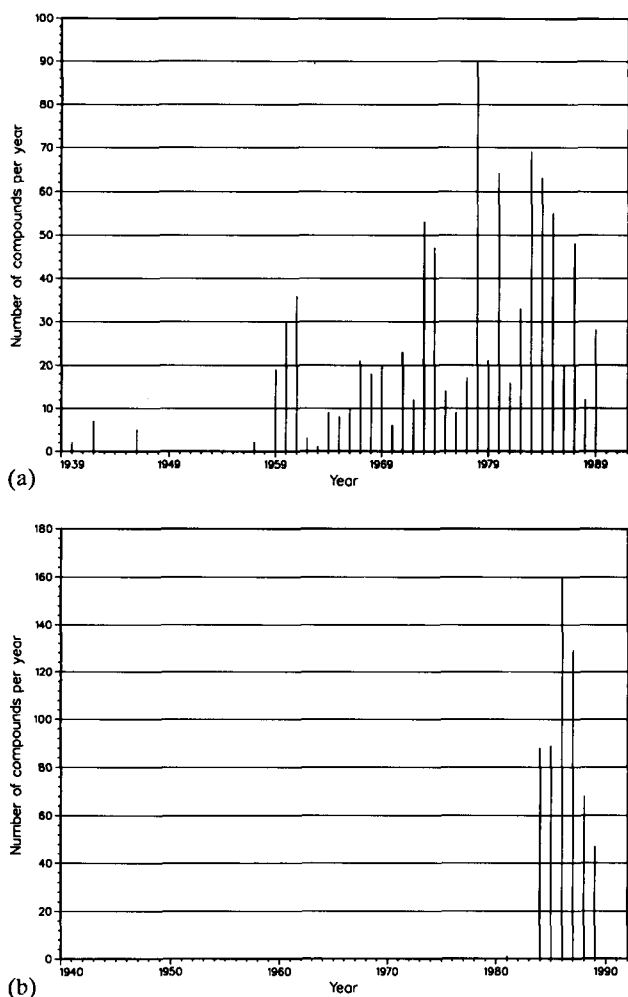


Fig. 19. Number of compounds crystallizing in (a) *hP6* CaCu₅ and (b) *tP68* BFe₁₄Nd₂ types *vs.* year of publication.

work on these novel compounds increased significantly and research on the *hP6* CaCu₅-type compounds decreased.

This database (CRYSTMET) is one major component of the necessary scientific knowledge to aid in the discovery and prediction of new materials. The clustering and classification of a variety of data elements in this database – structural, chemical and physical properties – have led to the empirical discovery of new intermetallics [11, 12]. The applications of clustering and classification techniques to crystallographic data are uncovering new and interesting relationships between many of the data entities [13].

References

- 1 J. R. Rodgers and P. Villars, *Computer Evaluation of Crystallographic Data, 11th Int. CODATA Conf., Karlsruhe, 1988, CODATA Bulletin*, 68 (1988) 22.
- 2 A. D. Mighell and J. R. Rodgers, *Acta Crystallogr. A*, 36 (1980) 321.
- 3 W. H. Baur and D. Kassner, *Acta Crystallogr. B*, 48 (1992) 356.
- 4 J. L. C. Daams, J. H. N. van Vucht and P. Villars, *J. Alloys Comp.*, 182 (1992) 1.
- 5 G. O. Brunner and D. Schwarzenbach, *Z. Kristallogr.*, 133 (1971) 127.
- 6 J. L. C. Daams and P. Villars, *J. Alloys Comp.*, 197 (1993) 243.
- 7 P. Villars and K. Girgis, *Z. Metallk.*, 73 (1982) 455.
- 8 F. Laves, in P. S. Rudman, J. Stringer and R. I. Jaffee (eds.), *Phase Stability in Metals and Alloys*, McGraw-Hill, New York, 1967, pp. 85–99.
- 9 P. Villars, K. Mathis and F. Hulliger, in F. R. de Boer and D. G. Pettifor (eds.), *The Structure of Binary Compounds*, Vol. 2. North-Holland, Amsterdam, 1989, pp. 1–102.
- 10 D. G. Pettifor, *Mater. Sci. Technol.*, 4 (1988) 675.
- 11 P. Villars, J. C. Phillips, K. M. Rabe and I. D. Brown, *Ferroelectrics*, 130 (1992) 129.
- 12 K. M. Rabe, A. R. Kortan, J. C. Phillips and P. Villars, *Phys. Rev. B*, 43 (1991) 6280.
- 13 K. M. Rabe, J. C. Phillips, P. Villars and I. D. Brown, *Phys. Rev. B*, 45 (1992) 7650.