More statistics on intermetallic compounds – ternary phases

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How many different intermetallic compounds are known so far, and in how many different structure types do they crystallize? What are their chemical compositions, the most abundant ones and the rarest ones? These are some of the questions we are trying to find answers for in our statistical analysis of the structures of the 20 829 intermetallic phases included in the database *Pearson's Crystal Data*, with the goal of gaining insight into some of their ordering principles. In the present paper, we focus on the subset of 13 026 ternary intermetallics, which crystallize in 1391 different structure types; remarkably, 667 of them have just one representative. What makes these 667 structures so unique that they are not adopted by any other of the known intermetallic compounds? Notably, ternary compounds are known in only 5109 of the 85 320 theoretically possible ternary intermetallic systems so far. In order to get an overview of their chemical compositions we use structure maps with Mendeleev numbers as ordering parameters.

1. Introduction

There are still many open questions concerning the origin, formation and stability of intermetallic phases. In particular, we do not know much about the factors leading to the more than two thousand different structure types, with unit cells containing between one and more than twenty thousand atoms, let alone the aperiodic intermetallics with incommensurately modulated or host/guest structures, and quasicrystals. Of course, some of their formation and stabilization mechanisms are quite well understood, such as Fermi-surface/Brillouin-zone nesting (Hume-Rothery mechanism), for instance, favoring particular chemical compositions and unit-cell sizes. The classical example are the brass phases in the system Cu–Zn. However, it is less clear which structure types phases can adopt that are stabilized in this way, and whether they will be periodic or aperiodic. In the case where there is no such predominant electronic stabilization of an intermetallic compound, and if chemical bonding is expected to be more complex, then the prediction of its structure or even just of the number of atoms per unit cell becomes difficult or is still impossible due to the lack of computing power. Once a structure is known, however, we can understand the origin of its stability and the kind of atomic interactions by employing quantum-mechanical calculations. Consequently, there is a steadily growing number of publications reporting in-depth studies of stability and chemical bonding of selected intermetallic phases. However, while we understand a few particular intermetallics quite well now, the question remains as to why intermetallic phases crystallize in such a large variety of structure types. Since the maximization of attractive interactions and the minimization of repulsive ones under the
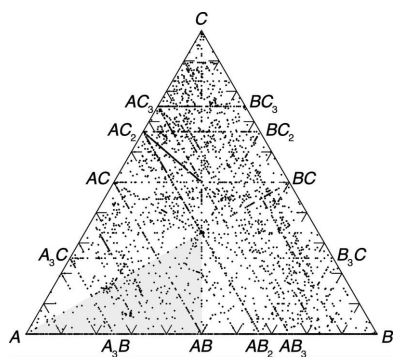
constraint of a given chemical composition requires well balanced atomic arrangements, purely structural considerations have to be taken into account as well.

The goal of the present statistical study was to draft an outline of the big picture of intermetallic phase stability by an analysis on a meta-level, based on the structural data of the intermetallic phases included in the database *Pearson's Crystal Data* (Villars & Cenzual, 2012/2013) (PCD). Apart from structural data taken at ambient conditions, the PCD also contains data for high/low-temperature/-pressure phases; however, none for aperiodic crystals. Consequently, the data for quasicrystals had to be taken directly from literature. In this follow-up to our previous paper on binary intermetallics (Dshemuchadse & Steurer, 2015), we will focus on the subset of 13 026 ternary intermetallic compounds remaining after massively filtering the database as described there. Although duplicates as well as multiple representatives from different parts of compositionally extended stability regions of single phases have been removed, there may be still a significant number of unconfirmed, metastable and even wrongly determined structures in the data set, partly based on older, outdated publications.

Also, the choice of investigated systems is, of course, biased by the experience of the scientist conducting the respective studies. Specific elements might be over-represented due to their perceived usefulness (*e.g.*, Al, Fe) or under-represented due to the experimental challenges that their handling involves (*e.g.*, toxic or radioactive elements). In other cases, certain combinations of elements might be especially problematic (*e.g.*, largely differing melting points and high vapor pressure). The process of structure determination also potentially influences which structures show up in databases and which do not: while simple structure types can be recognized from X-ray powder diffraction patterns, more complex ones have to be investigated in more detail and take more time to determine. This might lead to complex structures not being published at all and to simple structures being mis-identified due to features of the diffraction pattern being overlooked.

Structures are described by their structure types in our studies, whereas more general characterizations *via* atomic environment types and the ensuing statistical analysis have been performed by Villars *et al.* (2004) and Villars, Daams, Shikata, Chen & Iwata (2008).

For our present study, we consider elements as being metallic if they occur in groups 1 (except H) and 2–12, as well as in groups 13–18 underneath a zigzag line in the periodic table of elements with Al, Ge, Sb and Po included and B, Si, As, Te and At *etc.* not; these are 81 metallic elements in total.[1]

As ordering parameters for our structure maps, we use the Mendeleev numbers, which are based on a kind of empirical chemical scale, and which have been proven suitable for the

identification of stability fields of binary structure types by Pettifor (1984, 1988, 1995).[2] An alternative elemental parameter – the 'periodic number' PN – was introduced a few years ago (Villars, Daams, Shikata, Rajan & Iwata, 2008); it scans the periodic table of elements not in horizontal lines, as the atomic number does, but in vertical lines, and thus conforms to the common properties that atoms within one group of the periodic table usually share. Based on this parameter, a recent publication also offers statistical considerations (Villars & Iwata, 2013).

2. Chemical compositions

Among the 20 829 validated entries in the PCD, 277 refer to elements, and 6441 to binary, 13 026 to ternary and 1085 to higher multinary intermetallic compounds. It is obvious that – compared with the number of possible combinations of the 81 metallic elements – ternary systems are under-represented, and the higher multinary ones even more so. For each of the 81 elements, slightly more than three structures (allotropes) are found in the database on average. While approximately two phases are known for each of the possible $81 \times 80/2 = 3240$ binary intermetallic systems, there are $81 \times 80 \times 79/6 = 85\,320$ possible ternary systems and just one compound has been reported so far for every six to seven systems.

One reason for this low number of reported ternary compounds is surely that, compared to their sheer number, only a few ternary intermetallic systems have been studied thoroughly so far. Indeed, although the 13 026 ternary compounds come from 5109 ternary systems, phase diagrams of only 2068 of the 85 320 possible ternary systems have been studied well enough to be included in the ASM Alloy Phase Diagram Database[3] (Fleming, 2014). Furthermore, up to now only the elements have been studied systematically as a function of pressure, and only a few of them as a function of both pressure and temperature. This has also rarely been done for binary or ternary intermetallic compounds.

Despite an increasing number of constituents, the number of compounds formed by three or more metallic elements is limited by their combinations into structures with a maximum of attractive and a minimum of repulsive interactions, leading to a minimum in the Gibbs free energy. It is, for example, unlikely for an intermetallic system to form ternary compounds if a third element that does not form compounds with either of the two other elements is added to a binary system. The situation is even more unfavorable if all three binary subsystems of a ternary system do not form any binary compounds; no ternary intermetallics are known for this case.

There are 1401 different binary systems (out of the 3240 theoretically possible ones) forming at least one intermetallic phase, compared to 5109 (out of 85 320 possible) ternary ones. For 4041 of the ternary systems, binary phases have been reported for each binary subsystem. For 1053 ternary systems, one of the binary subsystems does not form any binary phase.

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[1] We are aware that this is a somewhat arbitrary border; however, there is no official definition by IUPAC or other official body of metallic elements or intermetallic phases, and we had to draw a boundary line somewhere.

[2] Again, we are aware that the Mendeleev numbers only partially consider the influence of chemical bonding; however, they are still a powerful tool for the identification of stability fields of particular structure types.

[3] Altogether, the ASM database contains 6499 systems, 4431 of which also contain non-metallic elements.

Table 1
Number N of elements out of specific M ranges that constitute the 13 026 ternary intermetallics, which come from 5109 intermetallic systems.

The numbers are also given for compounds with unique structure types for both truly ternary ones and including binary and unary ones. Mendeleev numbers $M = 7$–16 correspond to alkali and alkaline-earth metals, 17–33 to rare-earth elements, 34–48 to actinoids, 49–77 to transition metals as well as Mg and Be with $M = 73$ and 77, respectively, and 78–91 to metallic main-group elements.

	M				
N	7–16	17–33	34–48	49–77	78–91
Non-unique structure types (ternary, binary and unary)					
0	4361	2083	4819	574	1367
1	673	2755	283	2693	3326
2	73	269	7	1480	407
3	2	2	0	362	9
Unique structure types (ternary, binary and unary)					
0	432	423	646	150	67
1	192	238	21	334	471
2	42	6	0	162	128
3	1	0	0	21	1
Unique truly ternary structure types					
0	352	343	543	132	46
1	175	217	19	294	408
2	34	2	0	126	108
3	1	0	0	10	0

One example of such a ternary system is Al–Cu–Ta, where Cu and Ta are immiscible. Three complex intermetallic compounds have been discovered in this ternary system so far (Weber *et al.*, 2009; Conrad *et al.*, 2009; Dshemuchadse *et al.*, 2013). In the remaining 15 ternary systems already studied, ternary compounds have been observed, although two of the three binary subsystems do not form any intermetallic phase. These are the following systems: Al–Cs–Tl, Bi–Fe–Zn, Bi–Li–V, Ca–Co–Pb, Ca–Cr–Pb, Ca–Pb–Ru, Cr–La–Pb, Cu–Ta–V, Ge–Np–Tc, Ge–Tc–U, Hf–V–Y, K–Tc–Tl, La–Mn–Pb, Mn–Rh–Tl and Mn–Sn–W. From this finding we can conclude that the probability of the existence of ternary intermetallics in a ternary system increases with the number of its binary subsystems featuring binary intermetallic compounds. This does not necessarily mean that it would be impossible that a ternary intermetallic phase can form in a system without any binary ones; maybe they have been deemed impossible by chemical intuition and therefore not been searched for until now. This has to be the subject of future studies of both experimental and theoretical nature.

The distribution of the chemical compositions of the 13 026 ternary compounds over the 5109 ternary systems is shown in Table 1 and in M(A)–M(B)–M(C) structure maps in Fig. 1. The big gap in the distribution for $34 \leq M \leq 48$ results from the lack of ternary intermetallics with actinoids as constituents (except $M = 43$, Pu; $M = 45$, U; and $M = 47$, Th); the small gaps at $M = 13, 29, 59$ mark the locations of the not-yet-studied ternary intermetallics containing radioactive Ra, Pm and Tc, respectively. It is remarkable that there are compounds for only four systems with $7 \leq M$(A), M(B), M(C) ≤ 33. If $7 \leq M$(A), M(B) ≤ 33, it seems to be necessary to have $60 \leq M$(C) ≤ 88 to find stable ternary compounds.

Concerning the distribution of the chemical compositions of the subset of unique structure types, the main feature is that it is significantly less dense. This is not unexpected, since there are 13 026 different ternary intermetallic phases in 5109 different ternary systems crystallizing in 1391 structure types (1095 ternary prototypes), out of which just 667 types are unique and occur in 489 different systems (562 unique ternary prototypes). Although more than half of all ternary structure types are unique ($562/1095 \approx 0.51$), this is not true for the number of systems featuring ternary intermetallic compounds with unique structure types compared with the number of ternary systems featuring ternary compounds in general ($489/5109 \approx 0.10$). Furthermore, there are on average about two ternary intermetallic compounds with non-unique structure types per system ($12359/5014 \approx 2.46$) compared with, on average, approximately one intermetallic with unique structure type per system ($667/489 \approx 1.36$).

In most cases, compounds with unique structure types are found in the same ternary intermetallic systems as the non-unique ones. So, it is mainly the stoichiometry that makes them unique. From the chemical point of view, most compounds with unique structure types contain any element except actinoids for A, a few alkali and alkaline-earth metals plus a few rare-earth (RE) elements, but mainly late transition-metal (TM) elements for B, and late TM and main-group elements for C.

It is remarkable that RE elements ($17/81 = 0.210$) provide one of the three constituents in as many as 2755 of the 5109 ternary intermetallic systems ($2755/5109 = 0.539$) (see Table 1), slightly more often than the 29 TMs (including Be and Mg) ($29/81 = 0.358$) with 2693 cases ($2693/5109 = 0.527$), but both significantly less frequently than the ten main-group elements ($10/81 = 0.123$) with 3326 cases ($3326/5109 = 0.651$). That all three constituents come out of the same class of elements is rare except for TMs with 362 cases. Only 574 ternary intermetallic systems (11.2%) do not contain TM elements. The distribution for intermetallic compounds with unique structure types is similar.

3. Most-common structure types

Of the 20 829 intermetallics, 13 026 are ternary compounds crystallizing in 1391 different (296 binary and 1095 ternary) structure types, *i.e.*, 9.4 representatives per structure type. By comparison, the 6441 binary intermetallics crystallize in 943 different (41 unary and 902 binary) structure types leading to a ratio of $6441/943 = 6.8$, while this ratio amounts to $277/86 = 3.2$ for the elements. Consequently, there are not only more ternary compounds than binary ones, but also more representatives per structure type. This is also true if we only count the ternary intermetallics that crystallize in one of the 1095 truly ternary structure types. Then the ratio amounts to $8145/1095 = 7.4$, and for the 5378 binary compounds in the 902 binary structure types we get $5378/902 = 6.0$.

The distribution of unit-cell sizes of all 13 026 ternary compounds, as well as all 8145 ternary compounds crystallizing
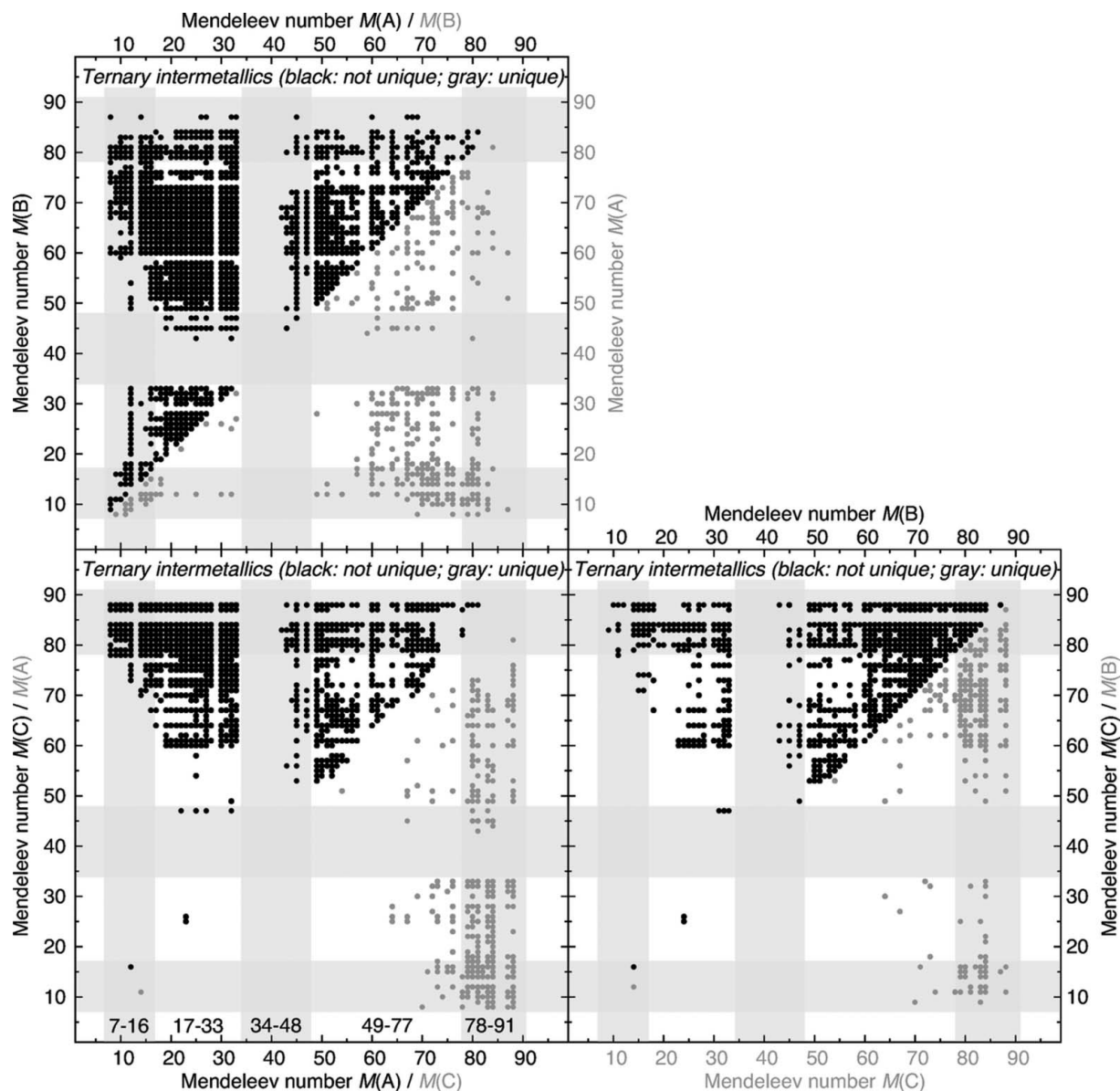
Figure 1
Chemical compositions of ternary intermetallic phases (each dot marks a ternary system with any chemical composition). Among the 13 026 ternary intermetallics crystallizing in 1391 structure types, 667 (48.0%) structure types occur only once. In the *M–M* plots, these unique structures are shown in gray, while the remaining 12 359 – not unique – structures are shown in black. The components to all compounds have been assigned to elements A, B and C according to $M(A) < M(B) < M(C)$, but for better illustration, the plots are shown with reversed axes for the unique structure types. Each two-dimensional *M–M* plot is projected along the third coordinate. Mendeleev numbers 7–16 mark alkali and alkaline-earth metals, 17–33 rare-earth elements, 34–48 actinoids, 49–77 transition metals as well as Mg and Be with $M = 73$ and 77, respectively, and 78–91 refer to metallic main-group elements.

in truly ternary structure types, and the 1095 ternary structure types themselves, are shown in Fig. 2. The histograms for all 13 026 ternary compounds and that for the only 8145 ternary compounds crystallizing in ternary structure types differ only marginally. With a few exceptions, there are hardly more than ten compounds for given unit-cell sizes larger than 100 atoms per primitive unit cell. The distribution of structure types with given unit-cell sizes peaks at around 14 atoms per primitive unit cell with a value of *ca.* 50 and falls off to less than 10 beyond ~50 atoms per primitive unit cell. Remarkably, almost all structure types become unique ones beyond ~170 atoms per primitive unit cell.

How is it possible that a well ordered ternary intermetallic compound crystallizes in a binary structure type? The current definition in the Online Dictionary of Crystallography on the IUCr website says

> Two crystals are said to be isostructural if they have the same structure, but not necessarily the same cell dimensions nor the same chemical composition, and with a 'comparable' variability in the atomic coordinates to that of the cell dimensions and chemical composition.

(IUCr, 2014). It does not say that isostructural compounds have to have the same number of different constituents.
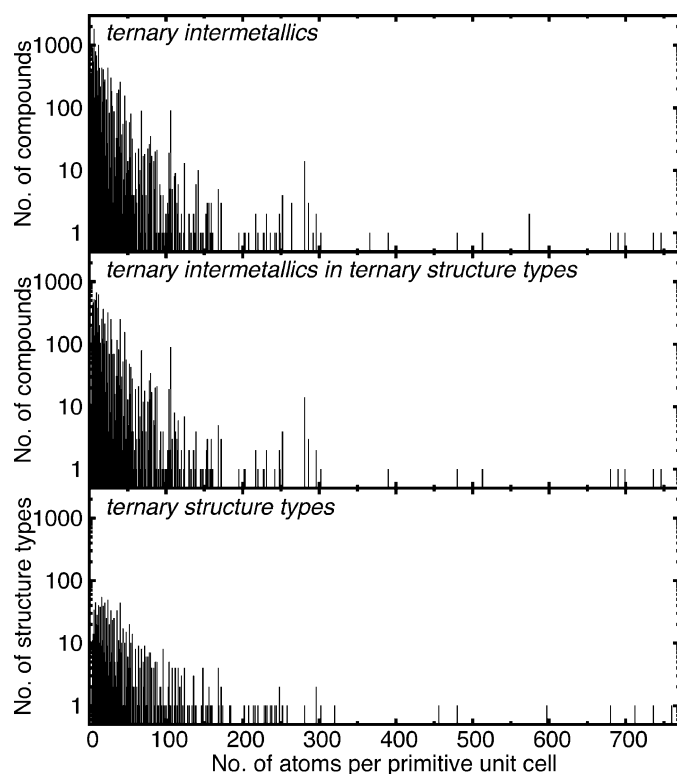
Figure 2
Unit-cell size distributions of the 13 026 ternary compounds (top), 8145 ternary compounds crystallizing in ternary structure types (middle) and 1095 ternary structure types (bottom). All plots have been truncated at a maximum of 770 atoms per *primitive* unit cell, excluding four structures: $hP1164$-Cr$_{10.7}$Fe$_2$Al$_{80.8}$, $hP1192$-Cr$_{10.7}$Fe$_{8.7}$Al$_{80.6}$, $cF5908$-Ta$_{39.5}$Cu$_{3.9}$Al$_{56.6}$ and $cF23134$-Ta$_{39.1}$Cu$_{5.4}$Al$_{55.4}$.

Table 2
The 20 most-common structure types among the 1391 structure types of the 13 026 ternary intermetallics (IMs), each representing at least 1% of the IMs.

Compounds with inherently disordered or pseudo-ternary structures are marked by entries in the Flag column: those with fewer different Wyckoff positions than components (*i.e.*, a maximum of 2) are marked 's' (solid *s*olution) and those with more constituents than the prototype compound of the structure type are marked 'd' (short for isostructural *s*ubstitution *d*erivate), respectively. Additional columns give the ranks that the respective structure types hold among all 20 829 intermetallics, as well as among the 6441 binary intermetallics.

Rank	Structure type	No. of IMs	% of IMs	Flag	All IMs	Binary IMs
1	$cF24$-Cu$_2$Mg	523	4.0	s	1	5
2	$hP9$-ZrNiAl	462	3.5		5	—
3	$oP12$-TiNiSi	388	3.0		8	—
4	$cF16$-Cu$_2$MnAl	333	2.6		7	—
5	$tI10$-CeAl$_2$Ga$_2$	289	2.2		11	—
6	$cP4$-Cu$_3$Au	274	2.1	s	3	3
7	$hP12$-MgZn$_2$	265	2.0	d	6	7
8	$cP2$-CsCl	212	1.6	s	4	2
9	$tI26$-ThMn$_{12}$	210	1.6	d	13	34
10	$hP6$-CaIn$_2$	203	1.6	s	15	91
11	$tP10$-Mo$_2$FeB$_2$	193	1.5		19	—
12	$hP6$-CaCu$_5$	192	1.5	d	10	9
13	$oS16$-CeNiSi$_2$	187	1.4		21	—
14	$oI12$-KHg$_2$	187	1.4	s	14	15
15	$cF12$-MgAgAs	166	1.3		18	—
16	$hP3$-AlB$_2$	153	1.2	s	20	30
17	$hR57$-Zn$_{17}$Th$_2$	151	1.2	d	17	29
18	$cF184$-CeCr$_2$Al$_{20}$	143	1.1		25	—
19	$cF96$-Gd$_4$RhIn	138	1.1		26	—
20	$hP18$-CuHf$_5$Sn$_3$	135	1.0		27	—
	Total	4804	36.9			

Indeed, a considerable number of structure types of ternary intermetallics are binary. These ternary compounds are partially inherently disordered if the binary structure types can be described with only two independent Wyckoff positions in the respective space group, *e.g.*, $cF24$-Cu$_2$Mg, $cP4$-Cu$_3$Au, $cP2$-CsCl *etc*. Many binary structure types, however, exhibit three or more independent atomic sites, making them not inherently binary.

We have investigated the most common binary structure types with three Wyckoff positions with respect to the distribution of the three chemical elements on the different positions. The majority of the representative compounds feature a high degree of disorder. Some are pseudo-binary compounds, with two of the three constituents occupying the site(s) of one of the binary components in a purely statistical manner. In other cases, all three sites are occupied distinctly, but only by a narrow margin, *e.g.*, by different mixing ratios of the same elements. In still other cases, distinct occupancies of the different sites are reported, but could not be thoroughly confirmed by X-ray diffraction due to their very similar scattering factors (*e.g.*, Cu and Zn or Cu and Co *etc.*).

However, a few structures that are ordered derivatives of binary prototype structures are also known. One example is that of two ternary representatives of the $hP12$-MgZn$_2$ structure type exhibiting fully ordered occupancies of the

Wyckoff positions ($2a$, $4f$, $6h$ – occupied by Zn, Mg and Zn, respectively, in the prototype structure): $hP12$-Lu$_2$CoAl$_3$ and $hP12$-Er$_2$CoAl$_3$ (Oesterreicher, 1973). Despite the fact that the respective study was carried out based on X-ray powder diffraction patterns, the significantly differing scattering factors of the element pair Co–Al should allow for a good distinction of their positions in the unit cell (Co on $2a$, Lu/Er on $4f$, Al on $6h$). Also, four ordered variants of the $cF24$-Be$_5$Au structure type ($4a$, $4c$, $16e$ – Au, Be, Be, in the prototype structure) were found among ternary intermetallics: REMgNi$_4$ with RE = Y, Ce, Pr and Nd (Kadir *et al.*, 2002) (RE on $4a$, Mg on $4c$, Ni on $16e$).

The 20 most common structure types of ternary intermetallic compounds are given in Table 2. They represent more than 130 intermetallic phases each, in total 36.9% of all ternary intermetallics covered in this study. Contrary to the binary compounds (Dshemuchadse & Steurer, 2015), no pseudo-unary sphere packings are found among the most common structure types. However, there are ten binary structure types among the top 20, comprising 49.3% of the intermetallic phases in this subset, which have to be considered as solid solutions or compounds with derivative structures. There are also quite a few ternary compounds that crystallize in binary structure types, although none of the three subsystems feature this structure type. This means that a meta- or unstable binary compound crystallizing in a binary structure type can be stabilized by the addition

Table 3
The top 45 compositions of ternary intermetallics, $A_aB_bC_c$ (with $a > b > c$), representing 20 or more intermetallics each.

The number of intermetallic phases and of different structure types (STs) is given for the general stoichiometry and the number of intermetallics for each permutation of a, b, c with $M(A) < M(B) < M(C)$ for $A_aB_bC_c$: $a \geq b \geq c$ (I), $a \geq c \geq b$ (II), $b \geq a \geq c$ (III), $c \geq a \geq b$ (IV), $b \geq c \geq a$ (V), $c \geq b \geq a$ (VI). Values in italic represent cases where compounds are counted twice or six times due to equalities $a = b$, $a = c$, $b = c$, or $a = b = c$, respectively. These cases are highlighted in the 'Comment' column.

Rank	$A_aB_bC_c$ $(a > b > c)$	No. of IMs	No. of STs	I	II	III	IV	V	VI	Comment
1	ABC	1495	62	*1495*	*1495*	*1495*	*1495*	*1495*	*1495*	*a = b = c*
2	A_2BC	841	80	*119*	*119*	*334*	*388*	*334*	*388*	*a > b = c*
3	A_2B_2C	677	41	*257*	*70*	*257*	*70*	*350*	*350*	*a = b > c*
4	A_4BC	324	14	*130*	*130*	*95*	*99*	*95*	*99*	*a > b = c*
5	A_6B_2C	186	9	40	56	0	88	0	2	—
6	A_5B_3C	161	18	2	96	1	37	18	7	—
7	A_3B_2C	160	32	3	23	14	17	62	41	—
8	A_3BC	159	22	*0*	*0*	*6*	*153*	*6*	*153*	*a > b = c*
9	$A_{20}B_2C$	141	3	0	0	0	1	0	140	—
10	A_6B_6C	131	17	*0*	*4*	*0*	*4*	*127*	*127*	*a = b > c*
11	A_5B_2C	108	13	64	29	2	1	5	7	—
12	$A_{13}B_4C_3$	106	6	0	0	0	3	0	103	—
13	$A_9B_3C_2$	104	7	1	0	0	2	10	91	—
14	A_5BC	94	6	*0*	*0*	*29*	*65*	*29*	*65*	*a > b = c*
15	$A_{43}B_6C_4$	86	1	0	0	0	86	0	0	—
16	A_4B_2C	86	22	0	6	0	19	29	32	—
17	$A_5B_3C_2$	82	17	6	1	1	1	0	73	—
18	$A_4B_3C_2$	82	22	0	7	4	23	0	48	—
19	$A_4B_4C_3$	76	9	*1*	*6*	*1*	*6*	*69*	*69*	*a = b > c*
20	A_8B_4C	75	7	0	2	1	8	0	64	—
21	$A_{10}B_2C$	67	7	0	0	0	4	0	63	—
22	$A_{12}B_4C$	66	4	0	0	0	32	0	34	—
23	$A_4B_3C_3$	64	3	*4*	*4*	*0*	*60*	*0*	*60*	*a > b = c*
24	$A_{16}B_7C_6$	60	1	0	1	0	0	18	41	—
25	A_9B_2C	58	7	0	0	1	3	40	14	—
26	$A_{14}B_3C_2$	58	4	0	8	0	0	0	50	—
27	A_8B_2C	56	2	0	0	0	32	0	24	—
28	$A_3B_2C_2$	56	12	*31*	*31*	*2*	*23*	*2*	*23*	*a > b = c*
29	$A_{23}B_7C_4$	49	2	49	0	0	0	0	0	—
30	$A_5B_4C_2$	49	15	0	35	0	5	1	8	—
31	$A_{13}B_6C$	48	2	0	0	48	0	0	0	—
32	$A_3B_3C_2$	47	20	*8*	*21*	*8*	*21*	*18*	*18*	*a = b > c*
33	$A_6B_3C_2$	42	10	0	1	18	7	6	10	—
34	$A_{10}B_5C_4$	37	3	0	0	0	37	0	0	—
35	$A_7B_6C_4$	36	3	0	3	0	0	33	0	—
36	$A_8B_4C_3$	31	6	0	0	0	6	24	1	—
37	$A_{12}B_6C$	29	1	29	0	0	0	0	0	—
38	$A_{12}B_4C_3$	27	2	0	0	0	0	0	27	—
39	A_4B_3C	27	17	0	5	5	10	3	4	—
40	A_9B_4C	22	4	12	0	0	0	10	0	—
41	A_6B_4C	22	10	0	3	0	3	5	11	—
42	$A_7B_3C_2$	21	8	0	0	0	13	7	1	—
43	A_3B_3C	21	12	7	8	7	8	6	6	*a = b > c*
44	A_8B_3C	20	2	0	9	11	0	0	0	—
45	$A_{21}B_{10}C_4$	20	2	0	0	0	0	0	20	—

of a third component, for instance by changing the electron concentration decisively. There are several known examples of ternary compounds crystallizing in, for example, the binary Laves phase prototype $hP12$-MgZn$_2$ (Stein *et al.*, 2005). Some characteristics of the most frequent ternary and binary structure types listed in Table 2 have already been discussed in the previous paper (Dshemuchadse & Steurer, 2015).

Concerning the symmetry, of the 14 Bravais lattice types, only nine are represented among the 20 most frequent structure types: oP, oS, oI, tP, tI, hR, hP, cP, cF. Excluding the ten binary structure types, only six are left: oP, oS, tP, tI, hP, cF. Notably, the highly symmetric Bravais lattices cP or cI are not among the top ten ternary prototype structures.

4. Common stoichiometries

If the compositions of all 8145 ternary intermetallics with ternary structure types are normalized and rounded off to three digits after the decimal point, 998 different stoichiometries result. 671 occur exactly once, 327 more than once: 253 occur 2–9 times, 29 occur 10–19 times and 25 occur 20–70 times. The 671 unique stoichiometries are not equivalent to the 562 unique structure types. In other words, a unique structure type can have a stoichiometry that is also adopted by a non-unique one, and a single non-unique structure type can have representatives with different stoichiometries.

The top 45 of all compositions are given in Table 3. The asymmetry is remarkable, *i.e.*, the assignment of a, b and c in
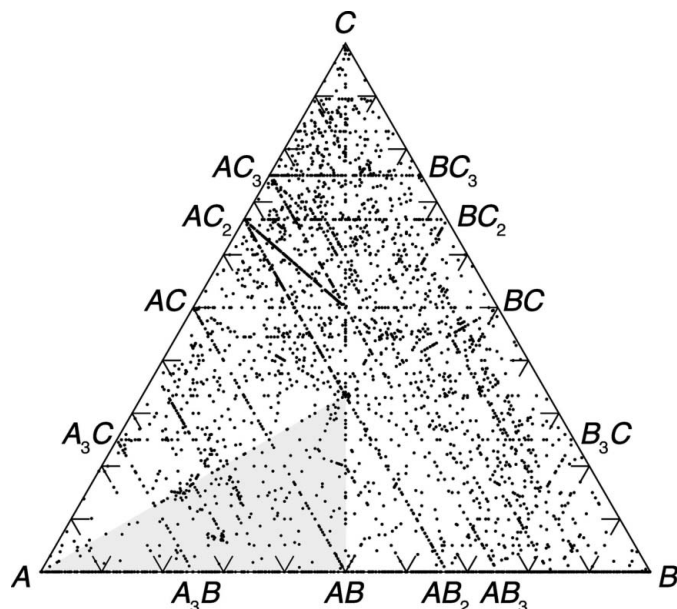
Figure 3
Composition diagram reflecting the stoichiometries $A_aB_bC_c$ of the 13 026 ternary intermetallic compounds [$M(A) < M(B) < M(C)$] (top). The shaded triangle represents one-sixth of the concentration diagram and results from ordering all three elements according to $a > b > c$. The following plots (Fig. 4) show all points projected into this part of the diagram – the 'reduced' composition (or just concentration) diagrams – thus avoiding bias from assigning the elements by their Mendeleev numbers and avoiding compositional ambiguity.

the formula $A_aB_bC_c$ [$M(A) < M(B) < M(C)$]. For instance, there are 159 compounds crystallizing in 22 structure types with the composition 3:1:1; for 153 of them AB_3C applies, and for the other six compounds ABC_3 does. This also means that no compound A_3BC with $M(A) < M(B, C)$ is in the database.

Some of the compounds with compositions A_4BC (rank 4), $A_{20}B_2C$ (rank 9), A_6B_6C (rank 10), $A_9B_3C_2$ (rank 13), $A_{43}B_6C_4$ (rank 15) and A_8B_4C (rank 20) have structure types and structures with interesting magnetic properties (Wolff *et al.*, 2001; Thiede *et al.*, 1998), all of them aluminides containing RE and early TM elements. For instance, $A_{43}B_6C_4$ exists in just one structure type with compositions $A_6B_4C_{43}$ [$M(A) < M(B) < M(C)$], the $hP106$-$Ho_6Mo_4Al_{43}$ type. In the 86 different representatives, Ho can be replaced by other RE elements, and Mo by other early TM elements.

1495 compounds with composition ABC are known. Since the PCD contains ternary intermetallics out of 5109 ternary systems, this means that for only slightly less than every third intermetallic system a phase is known with the equiatomic stoichiometry 1:1:1. The most frequent structure types for this composition are $hP9$-ZrNiAl with 462 representatives, $oP12$-TiNiSi with 388 and $cF12$-MgAgAs, the structure type of the half-Heusler phases, with 166 compounds. Of these, 161 are reported as stoichiometric, with $M(A) = 12$–72, $M(B) = 54$–80, and $M(C) = 80$–88. A large subset of the ABC intermetallics has been named REME phases, with RE a rare-earth metal (in most cases), an actinoid, or a group 1–4 element. M is a late transition metal from groups 8–12, and E is an element of groups 13–15 (Bojin & Hoffmann, 2003a,b). Some of the

REME phases are insulators, semiconductors or semi-metals, others have unusual magnetic and electronic properties. For instance, some representatives of the most common $oP12$-TiNiSi and $hP9$-ZrNiAl structure types are heavy-fermion compounds. A large subclass of the REME phases belongs to structural derivatives of the $hP3$-AlB$_2$ structure type, such as $oP12$-TiNiSi, for instance.
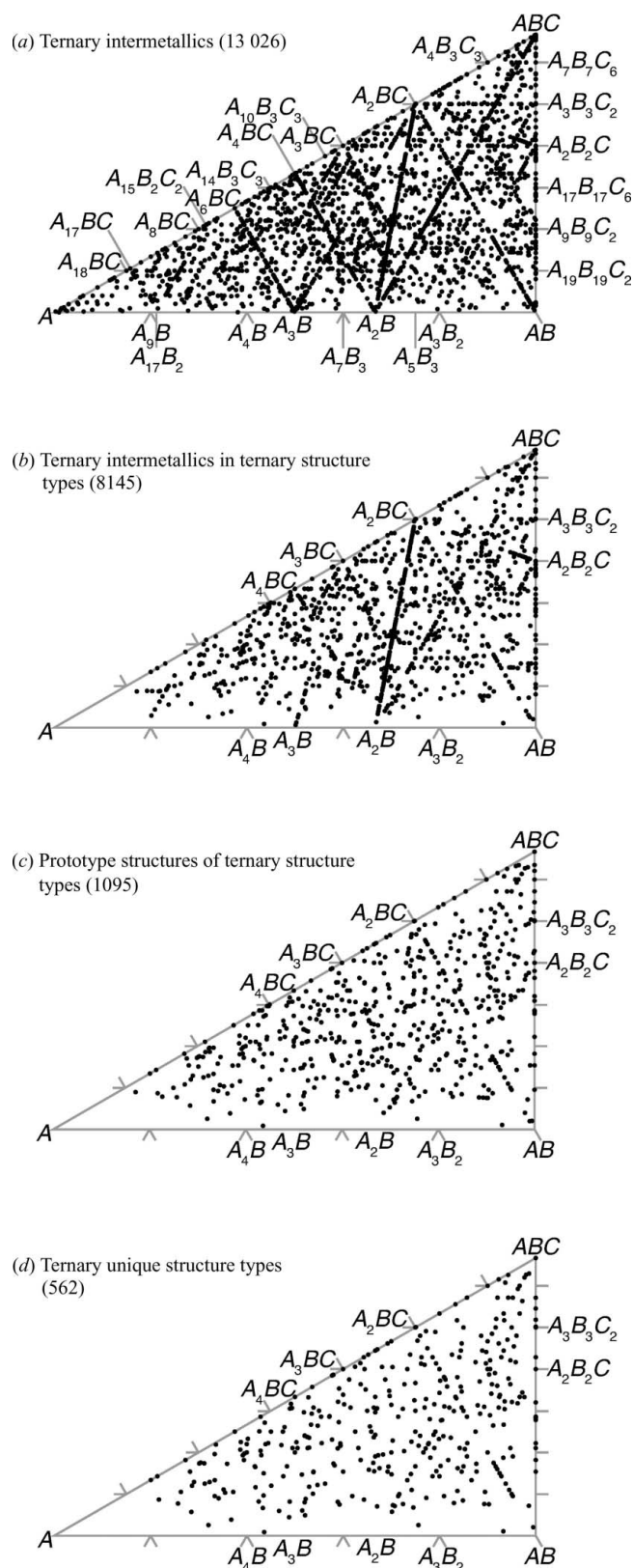
The largest group of compounds with composition A_2BC is formed by the Heusler phases, $cF16$-Cu$_2$MnAl, with 333 representatives, some of them with interesting magnetic, thermoelectric or superconducting properties. 309 out of them are reported to be stoichiometric with 50% of element A with $M(A) = 10$–81 and 25% for each of elements B and C with $M(B, C) = 8$–88 [or $M(B) = 8$–77 and $M(C) = 62$–88 with $M(B) < M(C)$]. Since most of their structures show great compositional flexibility, partial substitution of elements allows for fine tuning of the valence electron concentration and therewith of specific physical properties. For reviews see, for instance, Trudel *et al.* (2010) or Graf *et al.* (2009). Heusler and half-Heusler phases are superstructures of the $cI2$-W structure type.

5. Ternary composition diagrams

The compositions of all 13 026 ternary intermetallics are plotted in Fig. 3. The elements in the general formula $A_aB_bC_c$ are ordered according to $M(A) < M(B) < M(C)$. This diagram clearly shows some asymmetry illustrating that the elements A, B and C cannot be exchanged with one another without destabilizing the respective structure types. To emphasize the role of stoichiometry, the complete data set can be projected into one sixth of the concentration triangle by applying the relationship $a \geq b \geq c$, and neglecting the chemical composition – see Fig. 4(a).

Structure types such as $hP9$-ZrNiAl, $oP12$-TiNiSi and $cF12$-MgAgAs, with altogether 1016 representatives (21.2%), refer to just one single point, ABC, in the concentration diagrams (Figs. 3 and 4). Another prominent point, A_2BC (and permutations), includes the structure types $cF16$-Cu$_2$MnAl and $oS16$-CeNiSi$_2$, with 520 representatives (10.8%). The locations of the ternary representatives of the binary structure types are not exactly at A_2B or AB_2, for instance, but somewhere in the inner part of the concentration triangle, at $A_2B_xC_y$, $A_xB_2C_y$ or $A_xB_yC_2$ with $x + y = 1$ or at $(A_xB_y)_2C$, $(A_xC_y)_2B$ or $A(B_xC_y)_2$ due to the broad distribution of their compositions of the general type $A_xB_yC_z$.

A prominent example for the element-specific asymmetry is the line AC_2–ABC_2, which clearly – and unexpectedly – differs from BC_2–ABC_2. So, replacing B successively by (AC_2), when starting from ABC_2, can be done in an almost continuous way in contrast to replacing A successively by (BC_2) [$M(A) < M(B) < M(C)$]. Most of the compounds show Bravais lattices of the type oS, and quite a few tP. The most frequent ternary structure types with these symmetries are $oS16$-CeNiSi$_2$ and $tP10$-Mo$_2$FeB$_2$, which both have some compositional flexibility.

(a) Ternary intermetallics (13 026)

(b) Ternary intermetallics in ternary structure types (8145)

(c) Prototype structures of ternary structure types (1095)

(d) Ternary unique structure types (562)

Figure 4
Reduced composition diagrams of ternary intermetallics $A_aB_bC_b$ ($a > b > c$) for (a) all 13 026 ternary intermetallics, (b) for the subset of 8145 compounds that adopt ternary structure types, (c) their 1095 prototype structures and (d) the subset of 562 unique structure types, i.e., those with only one representative. The diagrams do not include binary compounds.

In the composition diagrams in Fig. 4, rows of points are visible connecting compositions with 'simple' stoichiometries. The most obvious ones are:

(1) A_3B–A_6BC (–A_3C),
(2) A_2B–A_4BC (–A_2C),
(3) A_3B_2–A_3BC (–A_3C_2),
(4) AB–A_2BC (–AC);
(5) A_4B–A_3BC–A_2B_2C (straight continuation: –BC_4),
(6) A_3B–A_2BC–$A_3B_3C_2$ (straight continuation: –BC_3),
(7) A_2B–ABC (straight continuation: –BC_2);
(8) A_2B–A_2BC–A_2B_2C–A (straight continuation: –A_2BC_2–C);
(9) A–ABC–AB (straight continuation: –BC).

The lines that appear quasi-continuous mainly indicate compositionally flexible structure types, which allow a wide range of stoichiometries for their representatives. A significant portion of the 13 026 ternary compounds belongs to structure types that are not actually ternary. Of the 20 most common structure types listed in Table 2, ten have a binary prototype structure – although only six are intrinsically binary, meaning that they only have two crystallographically distinct atomic (Wyckoff) positions. Among the 2166 different prototype structures that intermetallic compounds have been found to adopt, 80 are unary, 902 binary, 1095 ternary, 87 quaternary and two quinary. So, only slightly more than half of the prototype structures consist of three different elements, thus matching the number of constituents of ternary intermetallics.

The compositions of the 8145 ternary intermetallics that crystallize in one of the 1095 ternary structure types are plotted in Fig. 4(b), while those of the 1095 prototype structures are shown in Fig. 4(c). 562 of these structure types are unique, meaning that they have only one representative, and their compositions are depicted in Fig. 4(d). In contrast to what one might expect, the most frequent structure types are not exclusively those with a simple stoichiometry, neither the binary ($tI26$-ThMn$_{12}$, $hR57$-Zn$_{17}$Th$_2$) nor the ternary ones ($cF184$-CeCr$_2$Al$_{20}$, $cF96$-Gd$_4$RhIn).

The lines connecting simple compositions are much less densely occupied in Fig. 4(b–d) than in Fig. 4(a). This implies that many of the compounds located on these lines are not true ternary compounds but quasi-binary solid solutions. This might be interesting in itself, but our main objective is to explore the characteristics of genuine ternary compounds. Therefore we are concentrating on the 'thinned-out' data sets underlying Fig. 4(b–d) referring to ternary structure types only.

The ternary representatives of ternary structure types – as shown in Fig. 4(b) – still exhibit distinct lines of points along AB–A_2BC and A_2B–ABC, as well as the very strong one A_2B–A_2BC (–A_2B_2C–A). A few more lines are visible, although much less clearly: A_2B–A_4BC, A_3B_2–A_3BC, A_3B–A_3BC–A_2B_2C, A–ABC–AB.

The prototypes of the ternary structure types, shown in Fig. 4(c), mainly exhibit the lines along AB–A_2BC and A_2B–ABC, with A_2B–A_2BC–A_2B_2C–A vaguely discernible. Among the unique ternary structure types, which can be seen in Fig. 4(d), AB–A_2BC and A_2B–ABC can still be recognized.

By comparing Fig. 4(b) with Fig. 4(c) we can conclude that the structure types on the connecting line $A_2B–A_2BC$ are particularly flexible with respect to stoichiometry. This means that representatives of a given structure type exist in an extended range of stoichiometries. The only rather densely occupied lines remaining in Fig. 4(c) are $AB–A_2BC$ and $A_2B–ABC$. This means that we can formally successively replace B in AB by C in small stoichiometrical steps until we reach the composition A_2BC. Analogously, we can formally replace A in A_2B by C until we arrive at the composition ABC.

6. Four lines of ternary stoichiometries

Fig. 5 shows cuts through the composition diagram of the 1095 prototypes of the ternary intermetallic structure types (see Fig. 4c). In Fig. 5(a–d), the frequencies of structure types are shown along the four main lines: $AB–A_2BC$, $A_2B–ABC$, $A_2B–A_2BC–A_2B_2C–A$, as well as $A–ABC–AB$, which runs along two edges of the triangle. Their location in the full ternary composition diagram, as well as the resulting trajectory in the reduced plot, are depicted in Fig. 5(e). This graph illustrates how the shape of the line $A_2B–A_2BC–A_2B_2C–A$ arises. For these and all other compositional lines in the reduced composition diagram the law of reflection applies when they touch the two boundaries $A–ABC$ and $ABC–AB$.

The horizontal axes in Fig. 5(a–d) display the content of the respective varying element(s). The compositions $AB–A_2BC$ all contain 50% of element A, while the C content increases from 0% to 25% and the B content decreases from 50% to 25%. The compositions $A_2B–ABC$ all contain 33.3% of element B, while the C content increases from 0% to 33.3% and the A content decreases from 66.7% to 33.3%. The compositions $A_2B–A_2BC$ all have A and B contents that correspond to the ratio $a/b = 2/1$, while the C content increases from 0% to 25%. The compositions on the consecutive line segment $A_2BC–A_2B_2C$ all have A and C contents that correspond to the ratio $a/c = 2/1$, while the B content increases from 25% to 40%. The third and last line segment $A_2B_2C–A$ contains compositions with B and C contents in a ratio of $b/c = 2/1$ and A contents increasing from 40% to 100%. For the fourth line, the ratio of elements B and C is $b/c = 1$ in the range $A–ABC$, where the B and C contents increase from 0% to 33.3%.
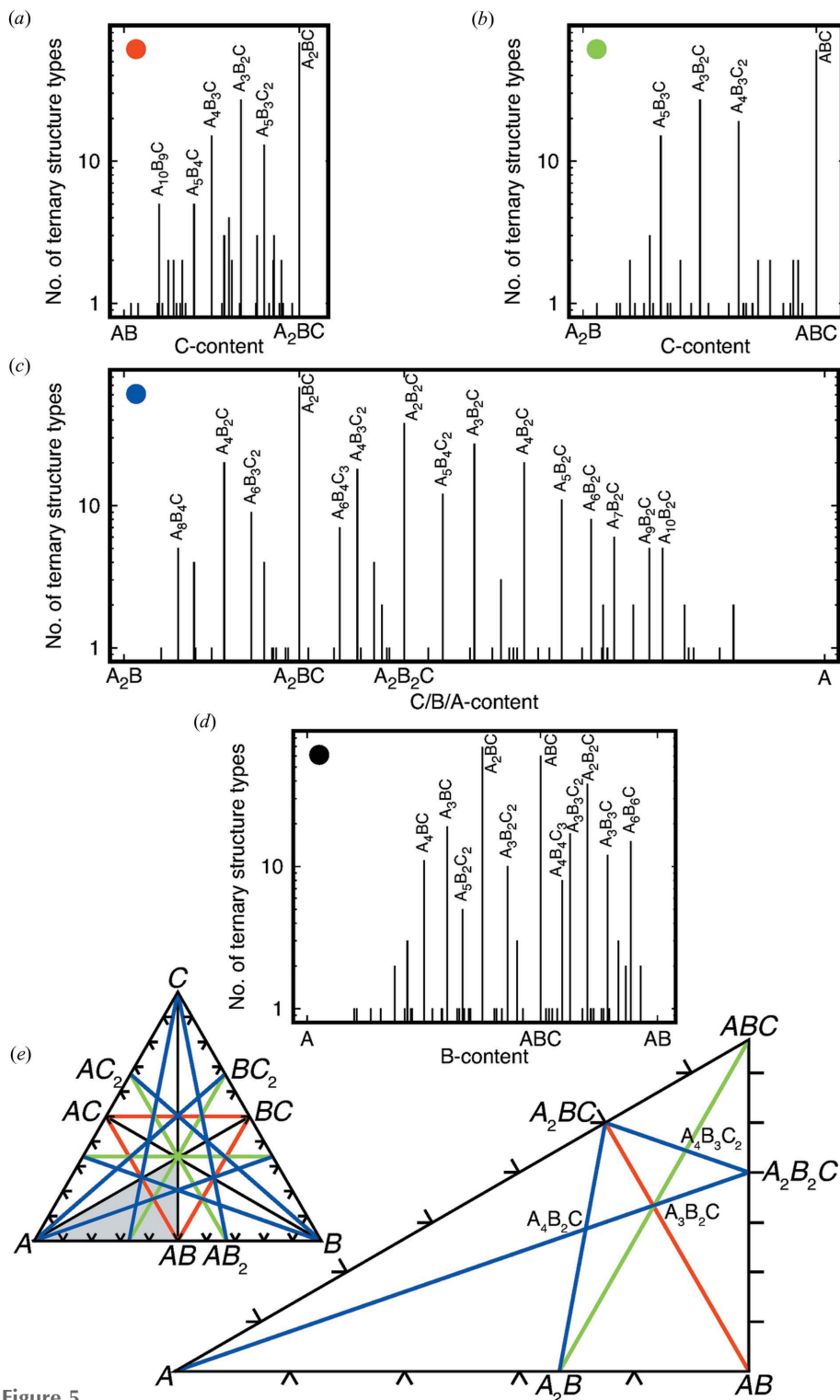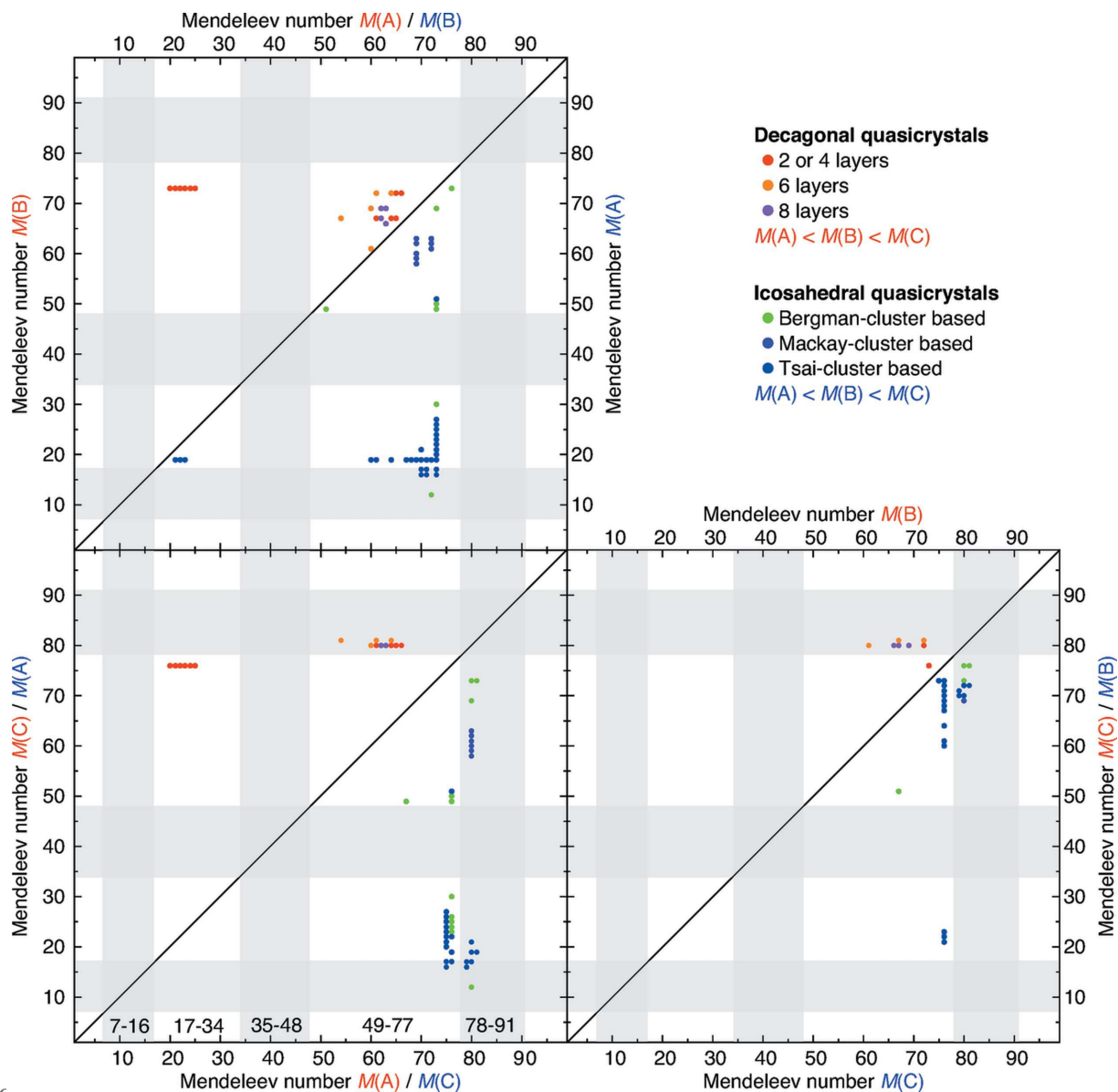

Figure 5
Cuts through the composition diagram of the prototype structures of all 1095 ternary intermetallic compounds. Shown are the lines (a) $AB–A_2BC$, (b) $A_2B–ABC$, (c) $A_2B–A_2BC–A_2B_2C–A$ and (d) $A–ABC–AB$, as well as (e) a schematic view of where the respective lines lie in the full and reduced ternary composition diagrams. Please note the logarithmic scale of the y axes in (a–d).

Figure 6
Chemical compositions of ternary intermetallic quasicrystals. Shown are all ternary systems that form quasicrystals: 21 decagonal and 53 icosahedral ones. The components of all compounds have been assigned to elements A, B and C according to $M(A) < M(B) < M(C)$, but for better illustration the plots are shown with reversed axes for the icosahedral phases. Decagonal phases with two or four layers are shown in red, those with six or eight layers in orange or pink, respectively. Icosahedral phases that are based on Bergman-, Mackay- and Tsai-type clusters are shown in green, purple and blue, respectively. Each two-dimensional M–M plot is projected along the third coordinate. Mendeleev numbers 7–16 mark alkali and alkaline-earth metals, 17–33 rare-earth elements, 34–48 actinides, 49–77 transition metals plus Be (77) and Mg (73), and 78–91 metallic main-group elements.

The second part of the plot always contains the same amount of the A and B components ($a/b = 1$) with values ranging from 33.3% to 50%.

Along the line AB–A_2BC, 172 ternary structure types can be found at 30 different stoichiometries, representing a total of 1570 ternary intermetallics. The maximum value in Fig. 5(a) corresponds to 68 structure types (STs) at composition A_2BC. Additional high values are found at A_3B_2C (27 STs), A_4B_3C (15 STs) and $A_5B_3C_2$ (13 STs). Smaller numbers of structure types are reported at the following compositions: $A_{10}B_9C$ and A_5B_4C (both five STs), $A_{10}B_7C_3$ (four STs), $A_7B_5C_2$, $A_{21}B_{13}C_8$ and $A_7B_4C_3$ (all three STs), with six compositions being featured in two STs each, and 14 in only one ST each.

Along the line A_2B – ABC, 153 ternary structure types are found at 28 different stoichiometries, which represent 2162 ternary intermetallics. The maximum value in Fig. 5(b) corresponds to 60 structure types at composition ABC. Additional high values are found at A_3B_2C (27 STs – where this line, A_2B–ABC, intersects with line AB–A_2BC), $A_4B_3C_2$ (19 STs) and A_5B_3C (15 STs). Composition $A_{12}B_7C_2$ is still featured in three structure types, while six more compositions are adopted by two STs each, and 17 compositions occur only in one structure type each.

The line A_2B–A_2BC–A_2B_2C–A consists of three segments coinciding with a total of 291 ternary structure types at 51 different stoichiometries, representing altogether 3539 ternary

intermetallic compounds [referring to Fig. 4(*c*)]. The turning points at A_2BC and A_2B_2C, which are also the two highest maxima in Fig. 5(*c*), correspond to groups of 68 and 38 structure types, respectively. The intermediate segments contain the following numbers of structure types: 50 in A_2B–A_2BC (excluding A_2BC), 36 in A_2BC–A_2B_2C (excluding both A_2BC and A_2B_2C) and 99 in A_2B_2C–A (excluding A_2B_2C). Additional significant values are found at A_3B_2C (27 STs – where the respective line segment, A_2B_2C–A, intersects with both lines, AB–A_2BC and A_2B–ABC), A_4B_2C (20 STs – where the two line segments A_2B–A_2BC and A_2B_2C–A intersect), $A_4B_3C_2$ (18 STs), $A_5B_4C_2$ (12 STs), A_5B_2C (11 STs), $A_6B_3C_2$ (nine STs), A_6B_2C (eight STs), $A_6B_4C_3$ (seven STs), A_7B_2C (six STs), A_8B_4C (five STs), A_9B_2C (five STs), $A_{10}B_2C$ (five STs), A_6B_3C (four STs), $A_8B_4C_3$ (four STs), $A_6B_5C_3$ (four STs) and $A_7B_4C_2$ (three STs), with five more compositions being adopted by two STs and another 27 by one structure type each.

The fourth and last line A–ABC–AB contains a total of 307 ternary structure types, which occur at 45 different stoichiometries and represent 4882 ternary intermetallic compounds. The first segment, A–ABC, contains 140 structure types, excluding ABC itself, which occurs in 60 structure types, while the second segment, ABC–AB, contains 107 structure types. The maximum values in Fig. 5(*d*) correspond to the following compositions: A_2BC (68 STs), ABC (60 STs), A_2B_2C (38 STs), A_3BC (19 STs), A_3B_3C (17 STs), A_6B_6C (15 STs), A_3B_3C (12 STs), A_4BC (11 STs), $A_3B_2C_2$ (ten STs), $A_4B_4C_3$ (eight STs) and $A_5B_2C_2$ (five STs). Of the remaining compositions, three occur in three STs, three in two STs, and 29 in only one structure type each.

It is remarkable how many unique compositions ($\sim$50%) are located on these relatively densely occupied lines in the concentration triangle. It is also amazing how many different structure types can be found for a given stoichiometry. A_2BC and ABC top the list with 68 and 60 structure types, respectively.

7. Quasicrystals

Quasicrystals (QCs) constitute a special class of intermetallics. They are not covered by the common databases, as their structural information can not be represented by a unit cell in three dimensions. Most quasicrystals are ternary compounds – the rare exceptions being icosahedral phases in the Cd–Ca and Cd–Yb systems. One may now ask: Where are the compositional stability fields of QCs located, compared with those of periodic intermetallics? In some more recent reviews, such composition diagrams have been presented (Steurer & Deloudi, 2008, 2009). Fig. 6 is based on the same data, updated with some quasicrystalline phases discovered during the last few years. Therein, the compositions of ternary quasicrystals from metallic elements are shown analogically to Fig. 1. The compositions of the different types of quasicrystals are color-coded as indicated in the figure. There are more systems exhibiting icosahedral QCs than decagonal QCs; some systems, such as the Al-based and the Zn–Mg-based ones, contain both of them.

It is not surprising that quasicrystals occur in the same systems as periodic crystals, because periodic approximants frequently exist with similar chemical compositions as their quasiperiodic counterparts.

8. Summary

Perhaps the most remarkable results are the following two. Firstly, for only $\sim$6% of all theoretically possible ternary intermetallic systems is at least one ternary phase is known so far. This can mainly be attributed to the lack of thorough studies of the respective ternary phase diagram. Secondly, more than one half of all known structure types are unique. This means that there are not so many ways of arranging three different kinds of atoms in a way that the attractive interactions surpass the repulsive ones, and that unique structure types are structurally rather inflexible, *i.e.*, designed to fit only one compound at one composition.

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