

9.3. Typical interatomic distances: metals and alloys

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Following the discovery of X-ray diffraction, atomic radii have been discussed and tabulated many times. Teatum, Gschneider & Waber (1960, 1968) derived empirical metallic radii for 12-coordinated atoms; their values were taken, wherever possible, from the elements and adjusted to 12-coordination. These radii have been found to be the most generally useful set for metallic phases and are given in Fig. 9.3.1(a). Although metallic bonding exists only in very few cases, as will be discussed later, it was common to assume that in intermetallics we have a purely metallic bonding character. In general, the bonding situation is much more complex; it is a mixture of metallic, ionic, and covalent bonding. At the present time, it is not possible to predict which bonding situation is formed for a given element–element combination. This rather complex bonding situation in intermetallics has been found to exist in the 3000+ structure types that have been compiled in *Pearson's Handbook* (Villars & Calvert, 1991) and in CRYSTMET (Rodgers & Villars, 1988). For comparison, the covalent radii according to Pauling and the ionic radii of Kordes (1939*a,b*, 1940, 1960) are given in Figs. 9.3.1(b) and (c), respectively (Samsonov, 1968).

Pearson (1979), and also Villars & Girgis (1982), reported a linear dependence between the interatomic distance d_{AB} and the (concentration-weighted) mean metallic radii \bar{R} for compounds crystallizing in over 100 different intermetallic structure types. For demonstration purposes, it is not necessary to make the rather complicated calculation given by Villars & Girgis (1982); instead, Daams (1995) showed this linear dependence by plotting the mean radii of the atoms concerned *versus* half of the mean shortest interatomic distances between these atoms. As an example, for compounds crystallizing in the *hP3* AlB_2 structure type, we have two atoms in the asymmetric unit, and half of the shortest interatomic distance between these atoms (d_{AB}) is $\frac{1}{2} [\frac{1}{3} a^2 + \frac{1}{4} c^2]^{1/2}$. For binary compounds, the mean radius (\bar{R}) is the mean of the metallic radii (Teatum, Gschneider & Waber, 1960, 1968) of the atoms involved. For ternary compounds, we first calculated the mean radius of the atoms mixing on the same position, weighted for their mixing concentration, and then calculated the mean radius of the atoms in the structure. In Fig. 9.3.2(a), this linear dependence is plotted for the binary compounds crystallizing in *hP3* AlB_2 , and it shows that there is a 1:1 dependence, meaning that the mean radius of the atoms involved equals the available space in the structure. The next two examples show that there is not always a 1:1 dependence, but that this linear dependence varies from structure type to structure type, with each of them combining their particular groups of atoms. Fig. 9.3.2(b) shows this linear dependence for the binary 2:1 compounds crystallizing in the *oP12* Co_2Si type. We see that in general the mean radii of the atoms are more than half of the shortest interatomic distances, although a linear relationship still exists. The opposite is observed for compounds crystallizing in the *tP6* Cu_2Sb (see Fig. 9.3.2c), where in general the mean radii are smaller than half the shortest distances. These differences can be understood if we look at the combinations of elements crystallizing in these structure types. In *tP6* Cu_2Sb , we have mainly combinations of rare earths with a *p* element, giving rise to a covalent bonding character with, as a result, smaller radii. In *oP12* Co_2Si , there is no such preference, so we have predominantly a metallic bonding character. Such linear dependencies for each structure type are more precise than those obtained by using Pauling's (1947) general equation for bond numbers, $R_{(1)} - R_{(n)} = 0.30 \log n$, where $R_{(1)}$ is the single-

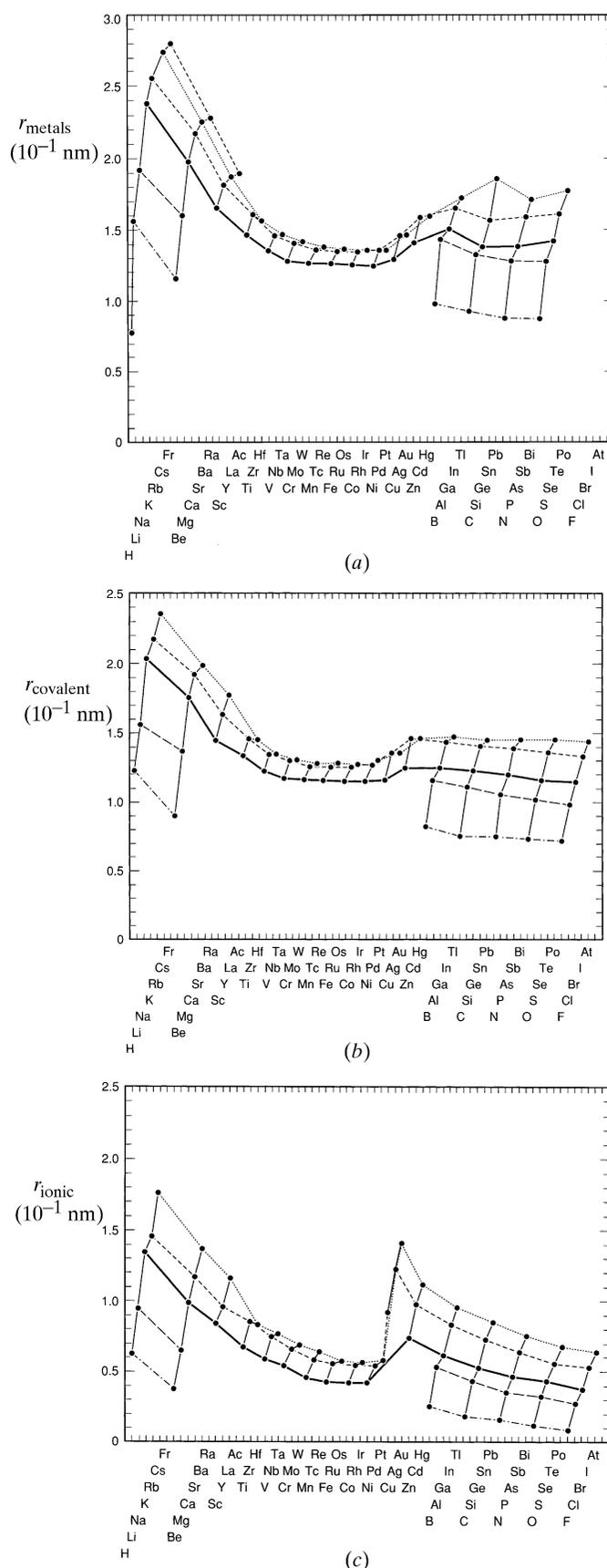


Fig. 9.3.1. (a) The radii for CN=12 after Teatum *et al.* (1960, 1968). (b) The covalent radii according to Pauling. (c) The ionic radii according to Kordes (Samsonov, 1968).

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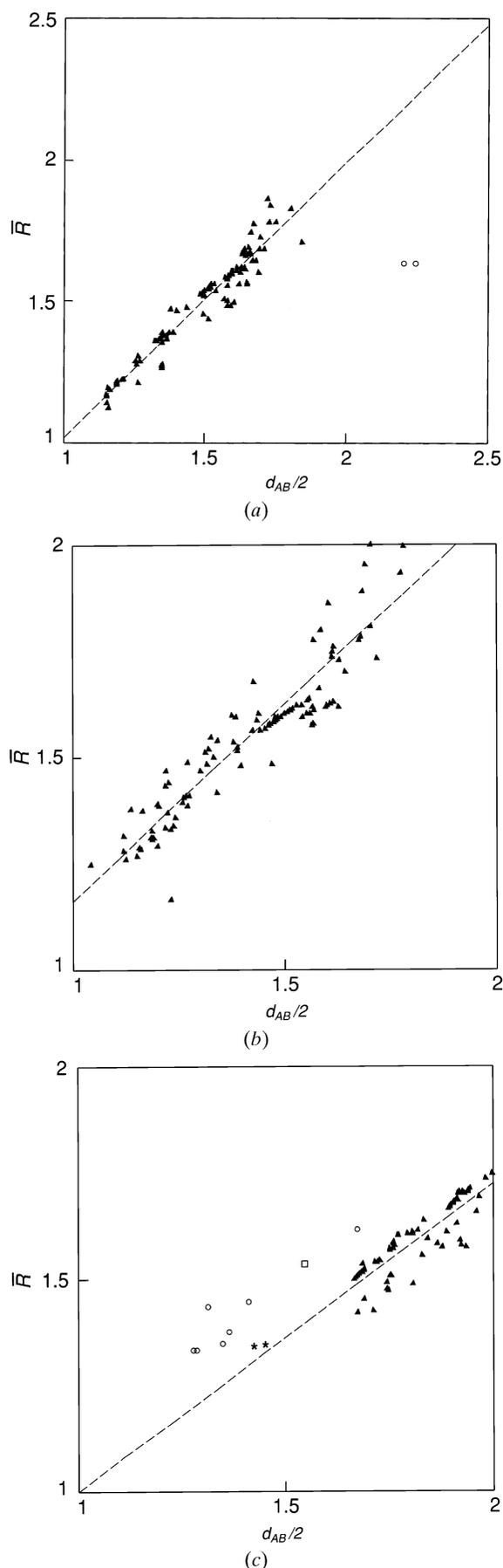


Fig. 9.3.2. (a) Plot of d_{AB} versus \bar{R} for the binary compounds crystallizing in $hP3$ AlB_2 . (b) Plot of d_{AB} versus \bar{R} for the binary compounds crystallizing in $oP12$ Co_2Sb . (c) Plot of d_{AB} versus \bar{R} for the binary compounds crystallizing in $tP6$ Cu_2Sb .

bond radius, and $n = V/12$, with V being the elemental valence, to adjust the radii to coordination numbers other than 12. The adjustment of the radii to the coordination numbers of the structure type of concern is a first approximation adjustment to the structure type. The broken lines in Figs. 9.3.2(a)–(c) are the results of a least-squares analysis.

Much more information about the short-range atomic arrangement, and a deeper insight into the geometry within a structure type, is obtained by looking at the coordination polyhedra (atomic environments AE) instead of looking only at the interatomic distances. These coordination polyhedra or AE not only give geometrical information about an atom and its neighbours but also give the correct coordination number. An AE is determined by using Brunner & Schwarzenbach's (1971) method, in which all interatomic distances between an atom and its neighbours are plotted in a next-neighbour histogram (NNH), as shown in Fig. 9.3.3(a). In most cases, a clear maximum gap is revealed. All atoms to the left of the maximum gap belong to the AE of the central atom; the coordination polyhedron constructed with these atoms is depicted in Fig. 9.3.3(b).

In cases where no maximum gap is found, Daams, Villars & van Vucht (1992) used the maximum convex rule. The maximum convex volume is defined as the maximum volume around only one central atom enclosed by convex faces with all the coordinating atoms lying at the intersection of at least three faces. Systematic studies of all intermetallic structure types

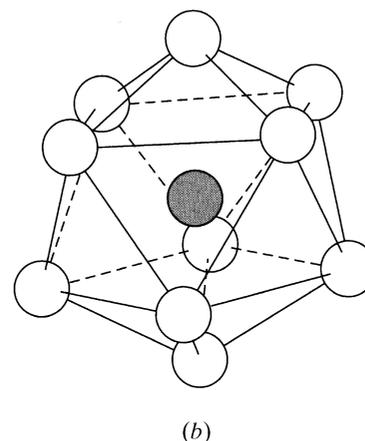
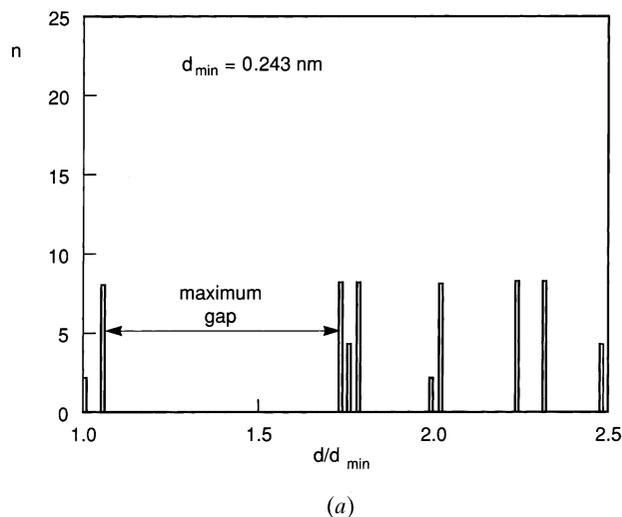
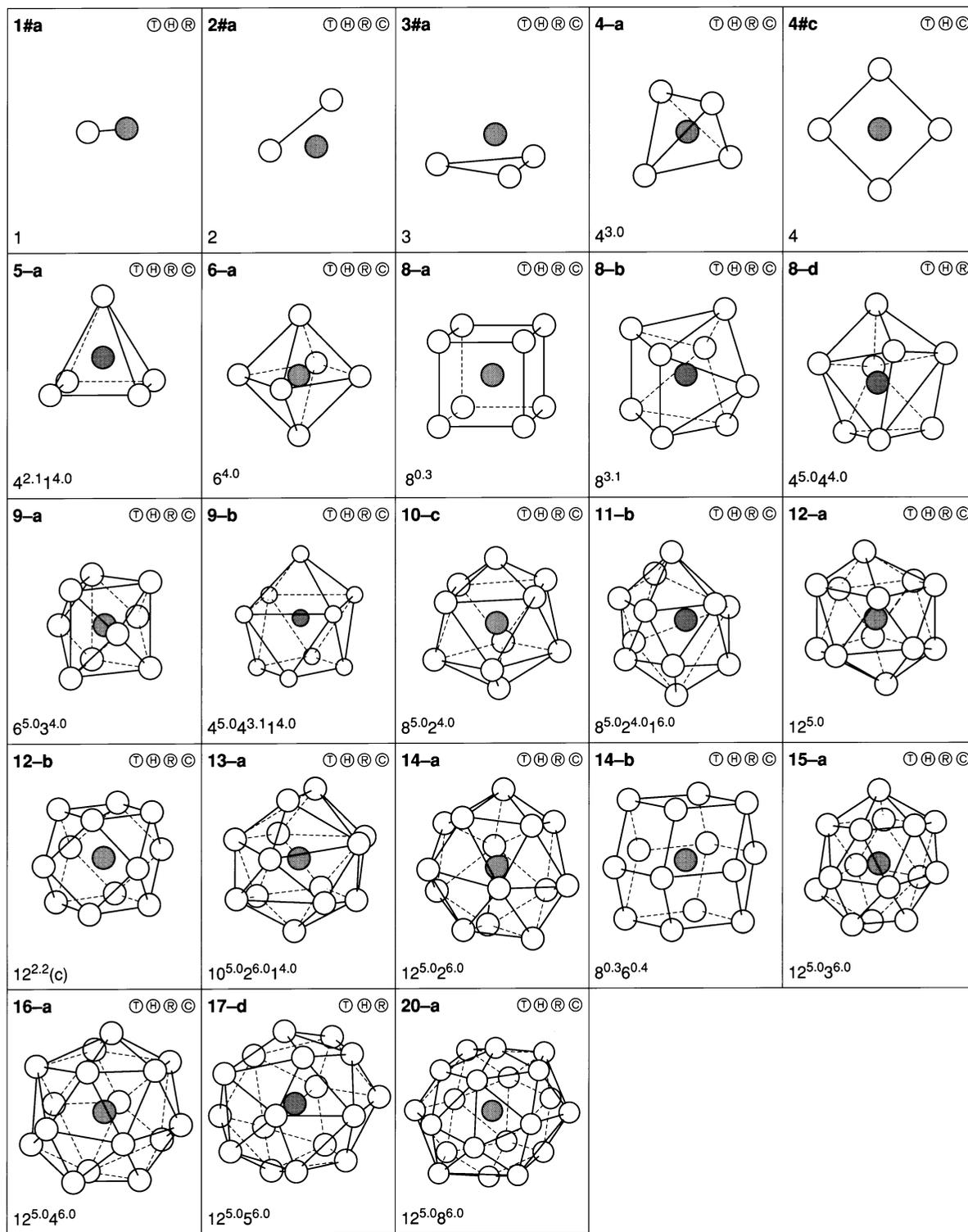


Fig. 9.3.3. (a) A typical example of a next-neighbour histogram (NNH) and (b) the atomic environment (AE) coordination polyhedron belonging to this NNH.

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belonging to the cubic, rhombohedral, hexagonal, and tetragonal crystal systems (Daams & Villars, 1993, 1994, 1997) revealed that 23 AEs, defined as atomic environment types (AETs), are favoured. These 23 most frequently occurring AETs are shown in Fig. 9.3.4(a). In Fig. 9.3.4(b), the AETs are plotted *versus* the number of point sets investigated. Heavily preferred are the tetrahedron (CN4), the octahedron (CN6), the equatorial

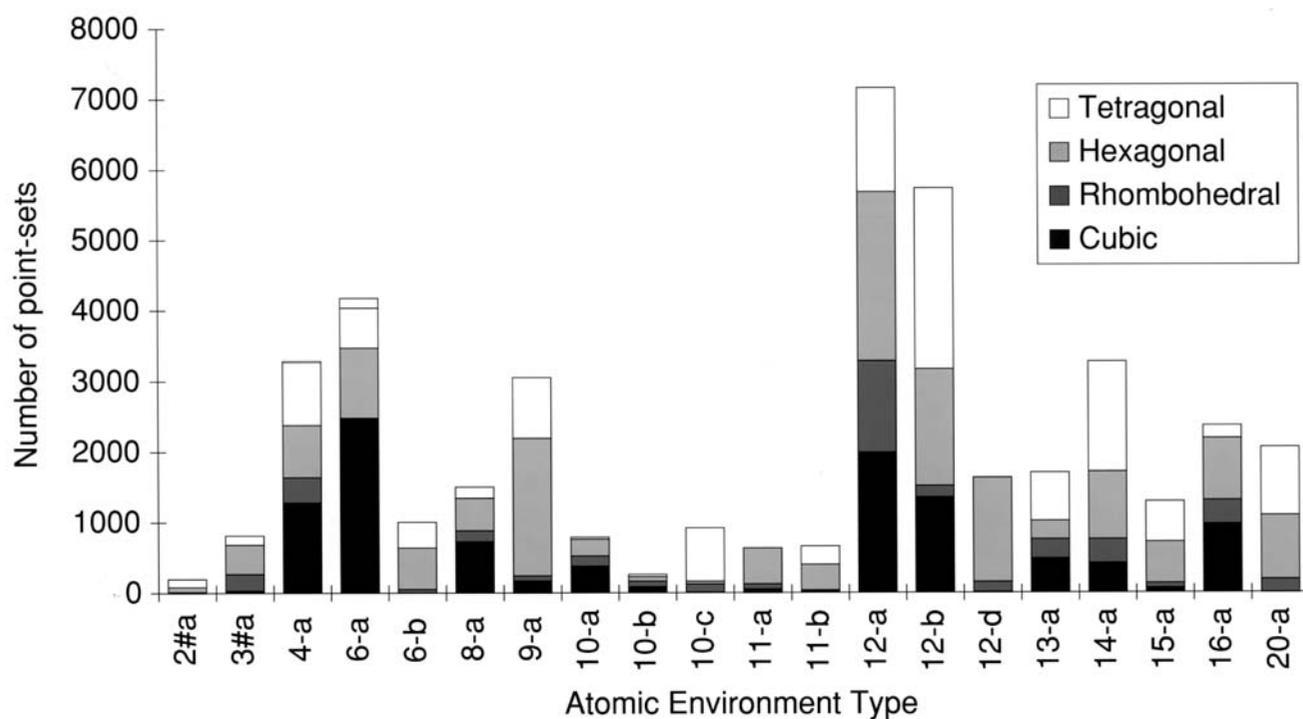
truncated trigonal prism (CN9), the icosahedron (CN12), the cubo-octahedron (CN12), and the CN14 Kasper polyhedron as AEs in intermetallic compounds. We also conclude from the observed AEs that the metallic radii that were published by Teatum *et al.* (1960) are in general not valid for intermetallic compounds. The assumption that the atoms have CN = 12 is probably never met in actual compounds. The above-mentioned



(a)

Fig. 9.3.4. (a) The 23 most frequently occurring atomic environment types (AET) with their polyhedron code (lower left corner of each box). In the upper left corner of each box, the assigned labels are given, consisting of the coordination number followed by a letter (*a*, *b*, ...). At the top right-hand corner, the crystal systems in which the AET occur are marked. (b) A frequency plot of the 23 most frequently occurring AETs *versus* the number of point sets.

Most frequently occurring AETs



(b)

Fig. 9.3.4 (cont.)

systematic analysis shows that we have in general, especially for real intermetallic compounds, low coordination numbers, $CN < 9$, for the p elements, CN numbers between 9 and 14 for the d elements, and $CN > 12$ for the s and f elements. In structure types where we have covalent or ionic bonding, we observe much lower coordination numbers. For example, the atoms of the compounds crystallizing in $cF8$ C1Na have $CN = 6$, and they have the octahedron as an AE.

9.3.1. Glossary

Intermetallic compound: Intermetallic compounds are binary, ternary, quaternary, *etc.* compounds containing the chemical elements other than oxygen, the halides, and the noble gases. Also excluded are compounds containing typical inorganic groups like $-NH$, $-NH_2$, $-N_2$, *etc.* This definition was used for *Pearson's Handbook* (Villars & Calvert, 1991), the *Atlas of Crystal Structure Types* (Daams, Villars & van Vucht, 1991) and the CRYSTMET database (Rodgers & Villars, 1988). This

definition therefore also includes sulfides, selenides, carbides, and nitrides, which most material scientists would not consider to be intermetallic compounds, but, because of their structural similarity, they have been included.

Structure type (or prototype): Based on space-group theory, a crystal structure is completely determined by the following data:
 chemical formula;
 crystal system and unit-cell dimension(s);
 space group;
 occupation number and coordination of the occupied point sets.

Crystal structure types are named by the first intermetallic compound found to be unique in respect of the third and fourth items and are represented by the Pearson symbol followed by the formula of the prototype, *e.g.* $hP3$ AlB₂. The first two letters of the Pearson symbol are identical to the Bravais-lattice type, and the digits give the number of atoms per unit cell.

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9.2.2 (cont.)

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