

Structure maps revisited

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VIEWPOINT

Structure maps revisited

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Online at stacks.iop.org/JPhysCM/15/V13**Abstract**

Structure maps have always held out the allure of being useful guides in materials design. A novel method for predicting candidate structure types demonstrates that the Pettifor maps for binary compounds are surprisingly predictive and offers a natural way for extending the predictive power of the maps to higher multicomponent systems.

Twenty years ago a chemical scale was proposed to help order the very large experimental database on the structures of binary compounds within two-dimensional structure maps [1, 2]. Unlike previous maps, which had been constructed by choosing co-ordinates that represented physical properties such as electro-negativity, atomic size or the number of valence electrons, the chemical scale χ was purely phenomenological. It was defined to achieve *a posteriori* the best structural separation of all binary compounds A_xB_{1-x} with a given stoichiometry x within a single two-dimensional map (χ_A, χ_B).

Figure 1 shows the resultant scale, which was set up by requiring that the variation of the chemical co-ordinate χ *within* a group did not overlap and mix with neighbouring groups, so that the Mendeleev-type features of the periodic table were maintained. This constraint excluded the second-row elements, which behave in a chemically distinct fashion from other elements in the same group. As seen from figure 1, χ was also chosen to vary linearly *across* both the transition metal series and the sp valent elements, thereby reflecting the linear behaviour across the periodic table of many properties of free atoms such as the size of their ionic cores or the energy of their valence electrons. The magnitude of the chemical scale was arbitrarily fixed to take the Pauling electro-negativity values for Be through to F. This simple chemical scale produced excellent structural separation of the binary database, as illustrated by the black-and-white maps for 17 different stoichiometries in [3] or the colour map for binary AB compounds inside the back cover of [4].

These maps aroused considerable interest among alloy developers at the time. In 1984 Liu at Oak Ridge National Laboratory had dramatically improved the ductility of the intermetallic Co_3V from 1 to 40% by alloying to change its crystal structure from hexagonal to cubic close-packed [5]. It was hoped that the phenomenological structure maps would guide

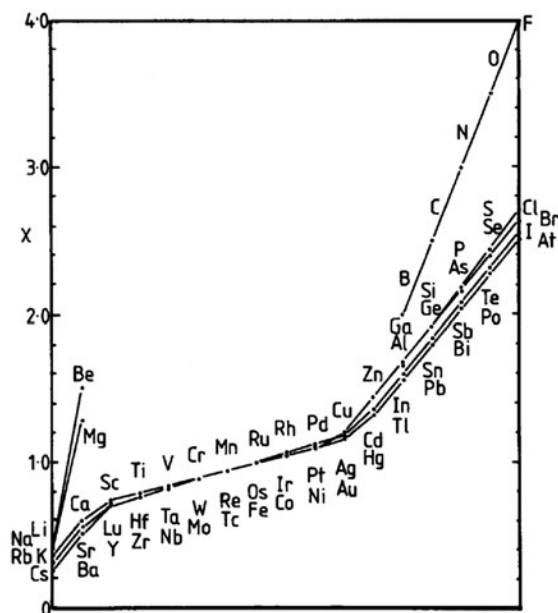


Figure 1. The chemical scale χ from [1].

alloy developers in stabilizing such cubic close-packed pseudo-binary alloys in systems of technological potential such as the titanium aluminides. Alas, this hope has been realized only partially due to four major problems:

- (i) Even if the alloying elements are chosen theoretically to drive the pseudo-binary into the desired structural domain, there is no guarantee that the alloy will exist as a pseudo-binary in nature. This may be due, for example, to the alloying element displaying only very small solubility in the host matrix [7].
- (ii) Even if the alloying elements are successful in stabilizing a cubic close-packed phase, there is no guarantee that the resultant alloy will be much more ductile than the initial binary [9]. This unexpected result is due to many intermetallics such as the titanium aluminides having highly directional bonds that lead to increased resistance to shear and brittle behaviour [8]. This may be inferred from the *neighbourhood map* for TiAl in figure 2 [10], in which TiAl is located at the centre of the map inside the close-packed CuAu domain. We see immediately that, if we replace Ti by isovalent Hf or Zr, then the CrB structure type is stabilized. This structure is characterized by zig-zag chains of boron atoms and highly directional bonds. *Ab initio* density functional calculations confirm that the bonding in TiAl is indeed very anisotropic in its CuAu ground state and that the CrB structure is also the closest-competing metastable phase [11].
- (iii) Even if the domain boundaries can be drawn to demarcate different structures within the known database, how *predictive* are the maps? For example, if we were to remove the data point for HfSn in figure 2 then clearly we would not be able to predict that it takes the FeSi structure type since there are no other known compounds in this map displaying this structure (assuming our information was restricted to the neighbourhood in figure 2).
- (iv) The original binary maps were constructed by hand. How do we *automate* the construction of higher multicomponent maps and analyse the structural data for the many technologically important systems that cannot be treated as simple pseudo-binaries?

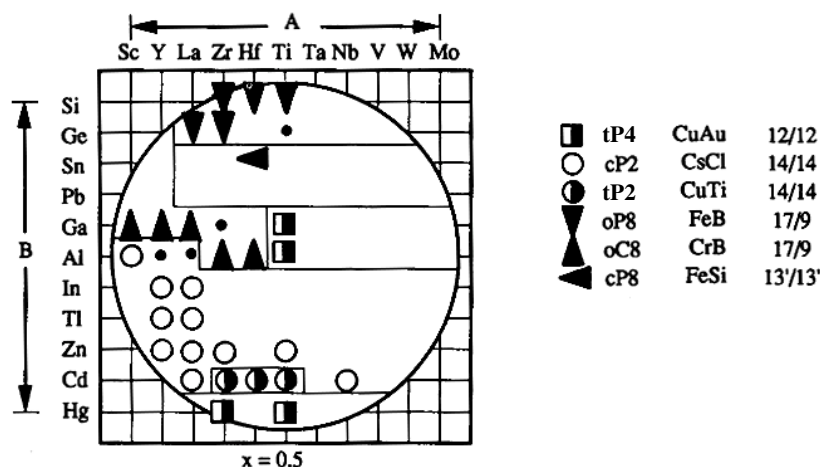


Figure 2. The TiAl neighbourhood map from [10].

The paper by Morgan *et al* [12] in this issue addresses the last two problems. They assessed the predictive capability of the Pettifor maps using a cross-validation technique on the AB and A_3B compounds in the CRYSTMET database [13], which had been ‘cleaned’ to remove those compounds that were recorded as taking two or more conflicting structure types at room temperature. This data-set contained 1540 binary compounds displaying 205 distinct structure types. In order to utilize a neighbourhood map such as figure 2 to predict the structure of the binary compound at its centre, they ranked the nearby structure types via two different methods. The *nearest-neighbour* method listed the candidate structure types according to the distance from the centre of the map at which the given structure type is first observed. The *dominant-neighbour* method listed the candidate structure types according to their frequency of occurrence within a given range from the centre of the neighbourhood map.

They found that the nearest-neighbour method performed marginally better than the dominant-neighbour method and that a candidate list of five structure types was 86% successful in containing the correct structure of the compound at the centre of the map. Moreover, if the 120 compounds that display a unique structure type are removed from the database since they cannot be predicted by the maps, then the predictive success of the Pettifor maps using a candidate list of five structure types rises to 95%. As the authors note, this is an extremely impressive result given the simplicity of the chemical scale¹.

The stage is now set to implement this nearest-neighbour predictive method within the software packages that already exist for constructing and displaying the Pettifor structure maps and neighbourhood maps for binary compounds². Crucially, this predictive scheme can readily be extended on the computer to higher multicomponent systems in multi-dimensional space. Here the ability to list candidate structure types will be critical in helping theorists to complement the sparsity of relevant experimental data with *ab initio* total energy assessments

¹ This predictive success rate falls to 90% if the structure map is constructed using the *uniform* mesh of the Mendeleev numbers (cf [6]). Although they order the elements in essentially the same way as the *non-uniform* mesh of the chemical scale so that topologically the structural domains remain the same, the distance measures used to rank the candidate structure types will change.

² See, for example, the MedeA InfoMaticA software package, which is produced by Materials Design (<http://www.materialsdesign.com/Pages/InfoMaticA.htm>) or the CRYSTMET package produced by Toth Information Systems, where the AB, A_2B and A_3B maps can be downloaded directly (<http://www.TothCanada.com/PettiforMaps/>).

of the competing candidates. This listing of possible structure-types should also help experimentalists speed up their structural analysis of diffraction data from multicomponent systems. However, the key problem remaining to be cracked is the ability to predict reliably and rapidly whether the selected multicomponent system will exist in practice. Only the future will tell whether we can use the *absence* of data in the large bare patches within the structure maps as a predictive guide in this respect!

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