

原子配置パターンによる材料分類

陳 迎 (科学技術振興事業団 研究基盤情報部)
岩田 修一 (東京大学 人工物工学研究センター)
Pierre Villars (Materials Phases Data System (MPDS), Switzerland)

抄録

材料の性質を支配する多くの要因の中で、化学組成と物性間の橋渡し役を果たす結晶構造は、最も重要なものの一つである。多くの結晶構造データを分類し、規則性を抽出することは、材料設計において、非常に重要なステップである。本文では、古典的結晶構造よりもっと共通性のある構造の分類 - 原子配置パターン(atomic environment type)を紹介する。この原子配置パターンの概念と量子構造マップ(Quantum Structural Diagram)の技術を取り入れることにより、化合物の構造と組成との間にいくつかの規則性が発見された。また電子論に基づいた原子配置パターンのメカニズムに関する研究についても述べる。

Classification of Materials by Atomic Environment Types

Ying Chen
Department of Advanced Databases
Japan Science and Technology Corporation (JST)

Shuichi Iwata
Research into Artifacts, Center for Engineering (RACE)
The University of Tokyo

Pierre Villars
Materials Phases Data System (MPDS), Switzerland

Abstract

From the many facts that determine the properties of the materials, the structure of the materials plays a key role on the physical basis. To classify the huge amount of crystallographic data and extract primitives from them is very significant for materials design. On the basis of a new classification of crystal structure - atomic environment type(AET[']) some important regularities between the structure type and the atomic properties of constituent chemical elements and its composition have been revealed by using structural mapping approach. In this paper, the concept of AET['] is briefly introduced, and some calculation results on the microscopic mechanism of AET is presented.

I. Introduction

Materials design is an exciting field of material science nowadays. The challenge is to reveal relationship among chemical composition, structure, and hidden physical properties of the material and to predict constituents of new materials with required properties. From the many facts that determine the properties of the material, the structure plays a key role. Extraction of structural regularities is a very significant step in procedures of materials design.

Given the elements of the periodic table, there are countless combinations that will result in materials with various structures and properties. To design a materials with required properties is, in principle, a completely straightforward problem. The first-principles calculation can be carried out for each possible configuration for given constituent atoms to find the most stable structure, and derive various properties. But the size and time scale of calculation system as well as the number of possibilities to be considered are many orders of magnitude larger than can be managed in a case-by-case calculation. Such kind of systematic approach without doubt can not be applied to the experimental search. On the other side, a large amount of data on compounds are now organized into a number of databases of crystallography, intrinsic properties and phase diagrams, providing a unique opportunity to investigate the structural regularities from a global perspective. What is important for us now is how can we do with a wealth of large databases, namely, "data mining" for "knowledge discovery", which needs a integration of classification, modeling with various techniques. Within several techniques of "data mining" in research of structure primitives, a graphical technique - "structure mapping" is essential owing to its strategic organization of data, then can be thought of a convenient "guide map" for navigation in search for new materials.

II. Review of the structure maps

Conventionally, crystal structures are classified on the basis of symmetry described by space-group theory, such as NaCl type, CsCl type. This kind of classification is called "classical" structural type. The goal of structure maps is to systematize the relationship between composition and structure. It is a procedure to order the huge amount of structural information within a two- or three-dimensional plots, so that the materials with a given structural type are clustered together. Closely related systems have similar values of coordinates and, in general, simple surfaces can be drawn to separate different classes of systems.

Structure maps fall into two basic categories. The first approach orders the empirical data in two-dimensional space, using a single phenomenological coordinates, the typical one is

well known as "Pettifor's map"¹⁾. The second approach uses physical properties as coordinates, such as the maps of Mooser and Pearson²⁾, Phillips and Van Vechten³⁾, Zunger⁴⁾. Although all of these "conventional" maps provide good separation for materials with same structure, the lack of a general framework which can apply to various systems is the obvious restriction.

A new kind of structure map proposed by Villars⁵⁾ with three physical coordinates made a big success for intermetallic compounds. The determination of three most suitable axes as an exemplar of strategic characterization is described as follows:

The starting point was to survey 53 physical properties (experiment and calculation, 182 variables in all due to different definition and measurement) as a function of the atomic number. It was found that there were only five patterns of diagrams of property versus atomic number. The five groups are: size factor, atomic number factor, cohesive-energy factor, electrochemistry factor and valence-electron factor. Selecting one properties from each group, then testing the separating capacity of different combination of these five properties for two most common modifications of binary compounds (NaCl and CsCl) and, finally, three optimal factors have been found - valence electron number N_v , Zunger's pseudopotential radii sum $R = r_s + r_p$ and Martynov-Batsanov's electronegativity χ . The values for 89 elements in periodic table are given in Table 1. Furthermore, for the various

Table 1. Values of the valence electron N_v , the electronegativity χ and the pseudopotential radii sum $R = r_s + r_p$. for elements

H 1																				
2.10																				
1.25																				
Li 1	Be 2															B 3	C 4	N 5	O 6	F 7
0.90	1.45															1.90	2.37	2.85	3.32	3.78
1.61	1.08															0.795	0.64	0.54	0.465	0.405
Na 1	Mg 2															Al 3	Si 4	P 5	S 6	Cl 7
0.89	1.31															1.64	1.98	2.32	2.65	2.98
2.65	2.03															1.675	1.42	1.24	1.10	1.01
K 1	Ca 2	Sc 3	Ti 4	V 5	Cr 6	Mn 7	Fe 8	Co 9	Ni 10	Cu 11	Zn 12	Ga 3	Ge 4	As 5	Se 6	Br 7				
0.80	1.17	1.50	1.86	2.22	2.00	2.04	1.67	1.72	1.76	1.08	1.44	1.70	1.99	2.27	2.54	2.83				
3.69	3.00	2.75	2.58	2.43	2.44	2.22	2.11	2.02	2.18	2.04	1.88	1.695	1.56	1.415	1.285	1.20				
Rb 1	Sr 2	Y 3	Zr 4	Nb 5	Mo 6	Tc 7	Ru 8	Rh 9	Pd 10	Ag 11	Cd 12	In 3	Sn 4	Sb 5	Te 6	I 7				
0.80	1.13	1.41	1.70	2.03	1.94	2.18	1.97	1.99	2.08	1.07	1.40	1.63	1.88	2.14	2.38	2.76				
4.10	3.21	2.94	2.825	2.76	2.72	2.65	2.605	2.52	2.45	2.375	2.215	2.05	1.88	1.765	1.67	1.585				
Cs 1	Ba 2	La 3	Hf 4	Ta 5	W 6	Re 7	Os 8	Ir 9	Pt 10	Au 11	Hg 12	Tl 3	Pb 4	Bi 5	Po 6	At 7				
0.77	1.08	1.35	1.73	1.94	1.79	2.06	1.85	1.87	1.91	1.19	1.49	1.69	1.92	2.14	2.40	2.64				
4.31	3.402	3.08	2.91	2.79	2.735	2.68	2.65	2.628	2.70	2.66	2.41	2.235	2.09	1.997	1.90	1.83				
Fr 1	Ra 2	Ac 3																		
0.70	0.90	1.10																		
4.37	3.53	3.12																		
Ce 3	Pr 3	Nd 3	Pm 3	Sm 3	Eu 3	Gd 3	Tb 3	Dy 3	Ho 3	Er 3	Tm 3	Yb 3	Lu 3							
1.1	1.1	1.2	1.15	1.2	1.15	1.1	1.2	1.15	1.2	1.2	1.2	1.2	1.2							
4.50	4.48	3.99	3.99	4.14	3.94	3.91	3.89	3.67	3.65	3.63	3.60	3.59	3.37							
Th 3	Pa 3	U 3	Np 3	Pu 3	Am 3															
1.3	1.5	1.7	1.3	1.3	1.3															
4.98	4.96	4.72	4.93	4.91	4.89															

combination (sum, difference, product and ratio) of these three properties, the most effective expression of three properties for binary compounds A_xB_y ($x+y=1$, $x < y$) are found - average number of valence electrons, difference of pseudopotential radii sum, and difference of electronegativities. The definitions are

$$\overline{N}_V = x\overline{N}_{vA} + y\overline{N}_{vB}$$

$$\overline{\Delta\chi} = 2x(\chi_A - \chi_B)$$

$$\overline{\Delta R} = 2x(R_A - R_B)$$

The expression for ternary and quaternary system also can be derived in similar way.

This kind of three-dimensional map using microscopic properties coordinates is called "quantum structural diagram (QSD)". It successfully separated 3,046 AB, AB₂, AB₃ and A₃B₅ binary compounds into 76 structure domains⁵⁻⁷, which revealed some important regularities within binary systems. However, there are some fundamental difficulties when the QSD approach is extended to ternary systems. A new concept is needed.

III. Atomic environment type (AET)

As mentioned previously, early structure maps were all on the basis of "classical" structure types. As reported⁸), a total of 22,000 binary, ternary and quaternary compounds are known in experiment up to now. About 18,000 of them whose structures have been determined include about 2,750 structural types. The fundamental difficulty in extending QSD to a general organizing principle to all intermetallic compounds is the high number of "classical" structures. The problem is that the "classical" structural type contains information in too much detail. This leads one then to seek a classification which is less detailed, but still contains enough information to identify essential similarities and differences between structures. Such generalized structural types proposed by Villars⁸) are defined on the basis of coordinate polyhedron.

Coordinate polyhedron of an atom position in a structure is defined by the neighbors surrounding it. Notice the fact that a minor distortion of a structure can reduce its symmetry but the resulting deformation of the coordinate polyhedron may be negligible, it can be hoped to achieve a substantial reduction of the number of different structures if the structure classification bases on the coordinate polyhedron. Figure 1 is a depiction of construction of coordinate polyhedron in body centered cubic lattice. Because the coordinate polyhedron describes the environment of an atom in a structure, this kind of classification is called "atomic

environment type (AET)". By observing the occurrence of various polyhedron for 650 classical structure types within 18,000 intermetallic compounds, five groups have been found:

- Single-environment type (single AET): all atoms in a structure have the same coordinate polyhedron
- Two-environment type: with two kind of coordinate polyhedra
- Three-environment type: with three kind of coordinate polyhedra
- Four-environment type: with four kind of coordinate polyhedra
- Ploy-environment type: with five or more kind of coordinate polyhedra

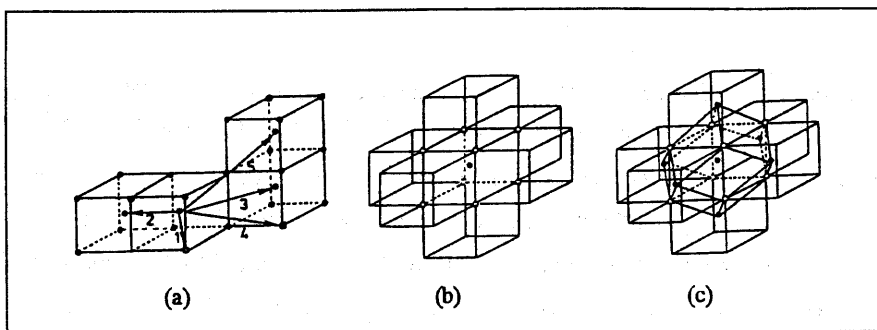


Figure 1. Construction of the coordinate polyhedron in the body centered cubic structure (W type): (a) Representations of the body centered cubic lattice. The numbers indicate the nearest, up to the fifth-nearest atoms respectively. (b) The first coordination polyhedron which is a cube (CN8), and (c) the second coordination polyhedron which is a rhombic dodecahedron (CN14).

It has also been found that for binary, ternary and quaternary intermetallic compounds, there are 47 classical structures belong to the single-AET group, and about 400 and 200 classical structures belong to Two- and Three-AET group respectively.

Examination of the 47 single-AET of structures (with 2,511 representatives), shows that the total number of different AET's is surprisingly small - only 8 AET's. What's amazing is 95% of 2,511 representatives with single-AET only belong to 4 AET's so called "most common AET". They are tetrahedron (CN4), octahedron (CN6), cubooctahedron (CN12) and rhombic dodecahedron (CN14), as shown in Figure 2. It can be concluded then the new classification of structural type reduced the number of structures remarkably to make it possible for ones to find something within them.

Then the quantum structural diagram based on the atomic environment types is constructed. The three dimensional QSD's are represented by a set of $\overline{\Delta R}$ vs. $\overline{\Delta \chi}$ sections with certain regions of value of $\overline{N_V}$. 2,511 intermetallic compounds with single-AET have been

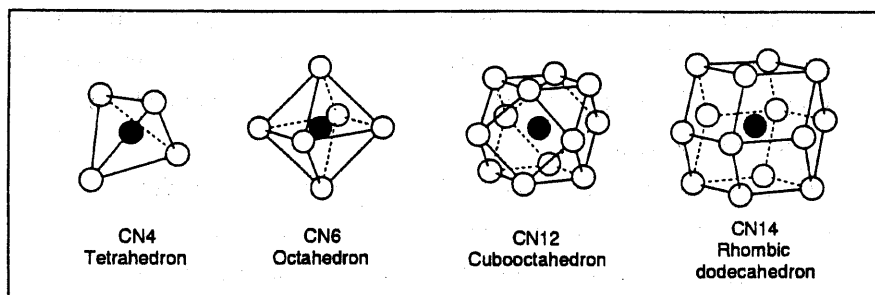


Figure 2. Four most common atomic environment types (AET's)

successfully separated into four most common AET's in an accuracy of 97%. Three sections are shown in Figure 3, corresponding to $\overline{N}_v < 2.74$, $2.75 < \overline{N}_v < 3.24$ and $3.25 < \overline{N}_v < 3.74$. The same procedure are carried out for two-, three-, and four- AET binary compounds.

The quantitative success of the new structure map suggests that the most closely related aspects of crystal geometry and chemistry are accurately represented by the general AET and QSD coordinates, based on valence electron number, electronegativity and pseudopotential core radius. Some regularities between the structure of a compound and the atomic properties of its composition have been revealed, which provides a highly accurate summary of information in the crystallographic database in a readily accessible form. With the QSD, the general structure type -AET of a compound can be predicted from knowledge of its composition alone. Conversely, if a compound with particular structural features is desired, the QSD can be used to identify promising compositions as a direct assistance to experimentalists. Rabe, Phillips and Villars have done excellent work by applying this approach to the problems of stable quasicrystal, high T_c ferroelectrics and high T_c superconductors ⁹).

IV Investigating the microscopic mechanism of AET -Calculated structure maps

The structure maps approach provides an effective way for knowledge discovery from databases with the new concept of classification. However, the ambiguities in the mechanism and in the boundary determination will cause problems in practical application.

To solve these problems, the calculated structure maps are produced from systematic calculation on the structural stability of atomic environment types. A simple model has been presented for studying the structural stability of AB intermetallic compounds ¹⁰).

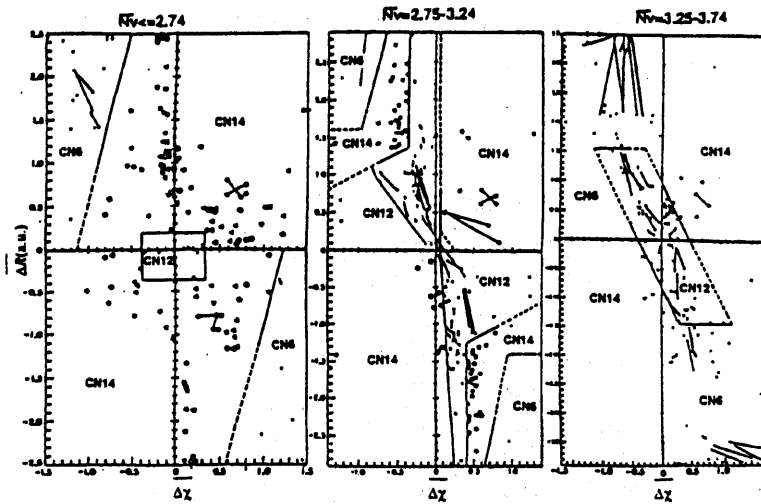


Figure 3. Three sections of the quantum structural diagrams with lower \overline{N}_V

Relative stability of the four most common AET's (as shown in Fig.3) for s-s, s-p and p-d bonded system has been systematically calculated within a tight binding model. The calculated three-dimensional structure map using the difference of valence electron orbital energy of atom ΔE , the distance between atoms d and the average number of electrons per atoms \overline{N} shows a good agreement with corresponding semi-empirical quantum structural diagram (QSD). Figure 4 is one of the calculation results.

The calculation shows that the electronic factor (valence electron count and bonding state) and size factor (relative sizes of atoms) are very important to determine the environment type of the system. The approach used here provides a possibility to classify intermetallic compounds into AET with systematic tight-binding calculation by extending to different kind of interaction systems.

V. Concluding Remarks

As a consequence of large efforts to get better explanation on sophisticated subject of materials, materials information becomes huge and complex with many layers of descriptions with respect to structures and compilation levels from raw data to design data. To increase the efficiency in the successful search for new materials, the main efforts should go towards creating an internationally accessible and compatible information, a prediction system, integrating all databases as well as generally valid principles/models and high-quality regularities.

The "data mining" will become more and more important owing to its role to bridge processing and properties during this procedure.

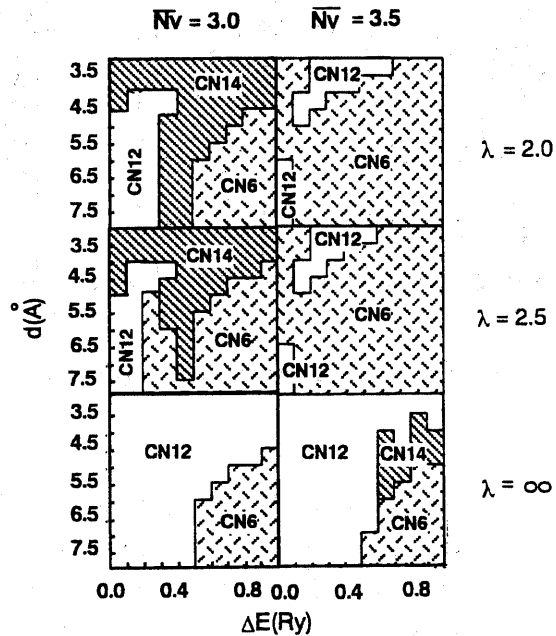


Figure 4. Calculated structure maps of p-d bonded AB compounds using the difference of valence electron orbital energies of atoms ΔE and bond length d (λ is a power index of the repulsive potential term.)

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