Quantum structure diagrams and structure–property correlations

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Abstract

The existence of large, well-organized databases provides unique opportunities for original research. Some examples are discussed in crystallographic and metallurgical contexts.

One of the purposes of this workshop is to discuss, perhaps for the first time in a metallurgical context, not how structural information on metallic compounds and alloys can be obtained, but what we can do with a wealth of such information after it has been obtained. This problem arose long ago in the context of organic chemistry and was resolved in many different ways. These syntheses of a large database eventually created an enormous conceptual framework which was derived heuristically from the database itself. In these derivations fundamental descriptions based on first principles always played a secondary role, but nevertheless an important one, in simplifying the presentation of the heuristic concepts as they were passed along from one generation to the next. These heuristic syntheses in turn became the foundations of modern biochemistry and genetic engineering.

Our subject here is more modest in its practical consequences but still contains many challenging problems on both the pure and applied levels. Novel properties in both contexts are still being discovered in metals, and one suspects that if a deeper understanding could be achieved, it might well have important practical consequences. Most physical scientists, myself included, have been trained, however, to examine materials one at a time. Parthé's book on tetrahedral compounds [1] remains a classic to this day because it was one of the first books on inorganic materials to organize an entire family of such materials systematically. Global views can be achieved by most of us only with great effort and some pain. However, the analogy with organic chemistry shows that with practice both the effort and the pain can be greatly reduced and can result in substantial rewards. So long as the heuristic approaches lead to new results, the synthetic organization can grow and prosper one step at a time. Moreover, as organic chemistry again teaches us, there is room for many different approaches, each being tested and confirmed by its own successes.

Such is the structural complexity of metals that for many years it appeared that there were at best only a few organizing principles. The most famous of these among metallurgists is probably the Hume-Rothery rules, which describe historically and technologically important alloys such as bronze and brass. Curiously enough, at present theoretical physicists have still not been able to provide a simple basis for these rules and they have just begun to discuss the problems one at a time, beginning with Cu–Zn alloys [2]. The results are both encouraging (in the sense that they agree well with experiment) and discouraging (because they still provide no general insights which could be of global value). Without these insights we can look forward only to very slow, albeit absolutely certain progress. Again in analogy with organic chemistry, heuristic reasoning has already given us genetic engineering, but first-principles calculations still encounter difficulties in treating molecules much larger than ethane or benzene.

In our field I believe that the global heuristic challenge is now well defined because of the very beautiful databases which have been or are being compiled by Villars and his collaborators. So far the only global heuristic solutions to the problems posed by these databases have been presented in the context of what I call quantum structure diagrams. The story of these diagrams has been told before [3–5] and I will not review it here. We have also had considerable success [6, 7] in finding structure–property correlations using diagrammatic methods; in particular, the coordinate sets which are most successful in structural separations produce the most compact groupings of compounds with certain physical properties. These groupings themselves then provide valuable insights to the origins of the properties.

In this brief discussion I wish to stress one important aspect of exploiting a large database. One can select a small portion of the database — octet or tetrahedral semiconductors, as Parthé [1] did, or Van Vechten and I [8] did, long ago — and examine it in detail. Such detailed analysis can be very instructive. However, I believe that the most exciting results will be obtained by finding problems which have the fewest restrictions and which span the largest part of the database. There we will find the greatest surprises and there we can hope to make the most exciting discoveries.

As an example of this situation let us consider the structure and properties of stable quasi-crystals. These are multiple-periodic structures in which the unit cells familiar in crystals are replaced by two kinds of "tiles" which are fitted together in non-periodic series. The size of the tiles is unknown and at present the atomic decoration of the tiles is unknown for any quasi-crystal. Crystalline approximants are known for quasi-crystals, and using one of these approximants — the $Al_6Mg_{11}Zn_{11}$ or ($cI162$) structure type — we were able [7] to generalize from one known stable quasi-crystal, $CuLi_3Al_6$, and two metastable quasi-crystals, $Al_{25}Mg_{36}Zn_{38}$ and $Cu_9Mg_{36}Al_{55}$, to suggest 12 additional candidate compounds. One of these, $Ga_{16}Mg_{32}Zn_{52}$, was soon found to be metastable [7], and when its composition was optimized, it turned out to be [9] the second stable quasi-crystal, $Ga_{20}Mg_{37}Zn_{43}$. Today nine stable quasi-crystals are known [10], with eight containing 60% or more Al. Thus even from a purely phenomenological point of view this prediction for Ga–Mg–Zn was remarkably successful.

The newest stable quasi-crystals, (Fe, Ru, Os)–Cu–Al, are the first to form a family with one element replaceable with other elements from the same column of the periodic table. At the same time in the crystallographic databases [11] there are no Frank–Kasper-type crystals, i.e. no crystals with coordination polyhedra such as icosahedra or dodecahedra with high coordination numbers. The Fe–Cu–Al ternary system has been well studied and it is unlikely that the existence of such corresponding compounds has been overlooked. This situation has puzzled many crystallographers [12]. However, given the complete database [11], instead of trying to force the solution to the new problem to fit the old idea, we can be more open minded and permit the database to tell us the answer. The optimized composition of quasi-crystalline Al–Cu–Fe (chosen because the sizes of Cu and Fe are nearly equal) is $Al_{1-x-y}Cu_xFe_y$ with $x = 24.5$ and $y = 12$, with $x/y = 2.00(2)$. Very close by in composition is crystalline $Al_{70}Cu_{20}Fe_{10}$ also with $x/y = 2.00$, but this is not an icosahedral or Frank–Kasper-type compound so it is not considered as a suitable candidate for a corresponding compound. However, since it is the only candidate available and

the compositions match so well, we should study its structure carefully. It is a layered tetragonal structure with 40 atoms per unit cell and the layers are separated into Al–Fe and Al–Cu. Such layers could be used to construct supertiles, i.e. tiles with very large dimensions which would still give quasi-crystalline diffraction patterns, with the surfaces of the tiles consisting of Al–Fe and Al–Cu layers and the centers occupied by highly coordinated polyhedra [13].

The electronic properties of supertiles could be dominated by these layers, which would be analogous structurally to domain walls in ferroelectrics. Such layers could be highly resistive if they contained a pseudogap in their electronic structure. In fact, the atomic structure of Al–Fe layers in Al_7Cu_2Fe is fairly close to that of AlFe in the CsCl structure, and the band structure of AlFe has been calculated [14]. It shows a pseudogap at $E = E_F$ which is 1.0 eV wide. It is quite interesting that this value of the pseudogap agrees exactly with the cut-off of the linear optical conductance recently measured [15] for quasi-crystalline Al–Cu–Fe. This together with other aspects of the electronic properties (such as the Hall resistance) provides strong support for the supertile model [16].

This story illustrates a general principle, which is that a large database, if utilized with an open mind, can generate many new ideas. When we compare the results obtained in this way with those obtained by routine application of standard methods, the difference is striking. Typically the latter cost decades of man-years of effort compared with a few man-days or man-weeks for the former. In an academic context the latter provides training for graduate students, which may be its good point, but it also emphasizes its weak point. Students are being trained to do science by rote. One of the best antidotes to this in my opinion is to confront them with a large database and ask them to find solutions using whatever methods are most appropriate to the problem at hand. This is the situation as it actually arises in industry and is one that academics should be eager to simulate. In this way they will be able to prepare their students for productive non-academic careers.

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