

# Quantum diagrams and the prediction of new materials

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## Abstract

A statistically based diagrammatic scheme for classifying the full database of crystal structures of binary, ternary and quaternary compounds and the tendency to compound formation in binary and ternary alloy systems is used as the basis for the study of small sets of compounds of special interest. Diagrammatic regularities are observed in stable quasi-crystals, high  $T_c$  ferroelectrics and high  $T_c$  superconductors, reflecting a correlation of these types of order with local structure and stability. Detailed application to quasi-crystals uses these diagrammatic regularities to facilitate the recognition of phenomenological trends and to identify chemical factors which favor quasi-crystal formation. This provides severe constraints on compositions at which quasi-crystals or crystalline approximants are likely to form. Several computerized search strategies which utilize the diagrammatic conditions to identify compositions for experimental investigation are outlined.

## 1. Introduction

Data from the scientific literature on the occurrence and structure of crystalline compounds are now organized into a number of crystallographic databases, providing a unique opportunity to investigate the factors which influence structure and stability from a global perspective. To display, access and extract general principles from this enormous amount of information, a graphical method such as the “quantum diagram” method is essential. Useful conclusions about individual compounds or small sets of compounds can also be drawn from this type of analysis. In this paper we review the application of this approach to three sets of interesting compounds: quasi-crystals, ferroelectrics and superconductors. These unusual types of order can be argued to be related to local structure and stability, with the further assumption that the factors which determine structure and stability in ordinary compounds are also operative for these materials. Analysis of the diagrammatic regularities exhibited by these materials yields physical insight into their occurrence as well as diagrammatic conditions which can aid in the prediction of new examples.

## 2. Review of the quantum diagram technique

The complexity of the systems under consideration dictates the use of the quantum diagram technique [1–3], which is a procedure to display data graphically and identify trends in the full database of 22 000 intermetallic compounds [4]. This global organization

of structure and stability data involves three-dimensional diagrams in which each system is represented by a point whose coordinates are determined by its composition. Closely related systems have similar values of diagrammatic coordinates and, in general, simple surfaces can be drawn to separate different classes of systems.

The goal of the “quantum structural diagrams” (QSDs) is to systematize the relationship between composition and structure. It has been shown that binary compounds can be effectively classified according to their structure type [5] with diagrammatic coordinate definitions  $\Delta\bar{X} = |X_A - X_B|$ ,  $\Delta\bar{R} = |R_A - R_B|$  and  $\Sigma N_v = N_{vA} + N_{vB}$ , where  $X$  is the Martynov–Batsanov electronegativity [6],  $R$  is the pseudopotential core radius [7] and  $N_v$  is the valence electron number. These atomic parameter scales  $R$ ,  $X$  and  $N_v$ , although chosen from a large number of scales solely for their separation efficacy, have clear relevance to bonding. For ternary compounds, structure type is not a useful diagrammatic classification principle because most ternary structure types have only a few representatives. Instead, we use the “generalized structure type”, which labels a crystal structure by the number and type of local coordination environments [1]. With a generalization of the binary coordinate definitions and separate diagrams for one-, two-, three- and four-environment structure types, excellent separation is achieved. A total of 2483 one-environment binary, ternary and quaternary compounds have been separated to the 97% level [1] and 4721 one-, two-, three- and four-environment binaries to 96% [2].

Different combinations of atomic parameters are used as coordinates in the construction of the “quantum formation diagrams” (QFDs), which systematize the relationship between composition and compound formation. Each ternary alloy system is represented by a point with coordinates

$$\left\langle \frac{T_{>}}{T_{<}} \right\rangle = \frac{1}{3} \left( \frac{T_{m,C}}{T_{m,A}} + \frac{T_{m,B}}{T_{m,A}} + \frac{T_{m,C}}{T_{m,B}} \right)$$

$$\langle |\Delta R| \rangle = \frac{1}{3} (|R_A - R_B| + |R_A - R_C| + |R_B - R_C|)$$

$$\langle |\Delta N_v| \rangle = \frac{1}{3} (|N_{vA} - N_{vB}| + |N_{vA} - N_{vC}| + |N_{vB} - N_{vC}|)$$

where  $T_m$  is the elemental melting temperature and  $T_{m,A} < T_{m,B} < T_{m,C}$ . A ternary alloy system is classified as compound forming if it contains at least one true ternary compound, and compound non-forming if it contains no ternary compound at any stoichiometry [3]. A simple surface separates compound-forming from compound-non-forming ternary alloy systems. For 7200 experimentally investigated ternary systems the accuracy of separation is 94%.

The QSDs and QFDs provide a highly accurate summary of information in the crystallographic database in a readily accessible form. QSDs and QFDs are used routinely to catch errors in database sources and compilation [8]. With the QSD the general structure type 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. In the vicinity of the separation surfaces, two or more general structure types are energetically competitive, which can yield predictions for structural phase transitions in temperature and pressure [9, 10]. In first-principles total-energy studies, neighboring structure type regions can be used to generate hypothetical structures, and diagram violators identified as systems for study of the exceptional contributions to the energetics which determine the structure. In the QFD, compound formation implies the existence of at least one ternary compound but gives no information on the number of compounds or their stoichiometries. Compound non-formation, on the other hand, is quite a strong condition, predicting no compound formation at *any* stoichiometry. In general, quantum diagrams can be thought of as a rather large-scale road-map of the database, in that they cover a lot of territory, though not in great detail, and are quick and easy to use to find out what is nearby and where one is in relation to the whole.

The quantum diagram technique provides a systematic approach to studying small groups of compounds [11]. Through the computation of their diagrammatic coordinates, particular classes of materials such as quasi-

crystals, ferroelectrics and superconductors, which are of great physical interest but have too few known representatives to support an independent statistical analysis, can be related to known compounds for which the factors governing structure and stability are relatively well understood and assumed to be similar. The results not only include a better understanding of the physics of these compounds but also provide practical strategies for the prediction of new materials of direct assistance to experimentalists in this area.

### 3. Diagrammatic analysis of quasi-crystals, superconductors and ferroelectrics

In each of the three cases we consider, the analysis starts with the computation of diagrammatic coordinates for the compounds of interest and the investigation of any regularity in their distribution on the diagram. For these unusual types of order the existence of diagrammatic regularities implies at least that the same factors which control local structure and stability in ordinary compounds also determine the tendency to these types of order, and probably a direct connection as well. The diagrammatic conditions satisfied by known examples can, as discussed further below, also be used to aid in the prediction of new materials.

Our QSD analysis of stable quasi-crystals has been described fully in refs. 11 and 12. There are 10 known stable quasi-crystals:  $\text{CuLi}_3\text{Al}_6$ ,  $\text{Ga}_{20}\text{Mg}_{37}\text{Zn}_{43}$ ,  $\text{A}_{15}\text{Cu}_{20}\text{Al}_{65}$  ( $\text{A} \equiv \text{Fe, Ru, Os}$ ),  $\text{Cu}_{15}\text{Co}_{20}\text{Al}_{65}$ ,  $\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$ ,  $(\text{Mn, Re})\text{Pd}_2\text{Al}_7$  and the recently discovered  $\text{Al}_{43}\text{Mg}_{43}\text{Pd}_{14}$  [13]. For the first nine the diagrammatic coordinates are computed and plotted on the QSD as shown in Fig. 1. All 10 quasi-crystals, including  $\text{Al}_{43}\text{Mg}_{43}\text{Pd}_{14}$ , fall into the restricted range  $-0.6 \leq \overline{\Delta X} \leq 0.3$  and  $-0.2 \leq \overline{\Delta R} \leq 0.7$ , which we designate the QSD quasi-crystal condition.

Our QSD analysis of high  $T_c$  superconductors has been described in refs. 11, 14 and 15. The results are reproduced in Fig. 2, with the size and electronegativity differences  $\overline{\Delta X}$  and  $\overline{\Delta R}$  in Fig. 2(a) and the Matthias plot [16]  $T_c$  vs.  $\overline{N}_v$  in Fig. 2(b). A total of 67 superconductors with  $T_c > 10$  K are well localized into three separate islands, labelled A, B and C. Each island is characterized by a particular range of  $\overline{N}_v$ ,  $\overline{\Delta X}$  and  $\overline{\Delta R}$ . Island A is dominated by binary high  $T_c$  superconductors in the *cP8*  $\text{Cr}_3\text{Si}$  (A15) structure, but it contains compounds in five other structure types as well. Island B contains cubically and hexagonally packed simple AB binaries. Finally, island C contains chevel, perovskite and the recently discovered cuprate superconductors, as well as  $\text{LiTi}_2\text{O}_4$ .

Our QSD analysis of ferroelectricity [17] is based on a database containing a total of 175 ternary ferro-

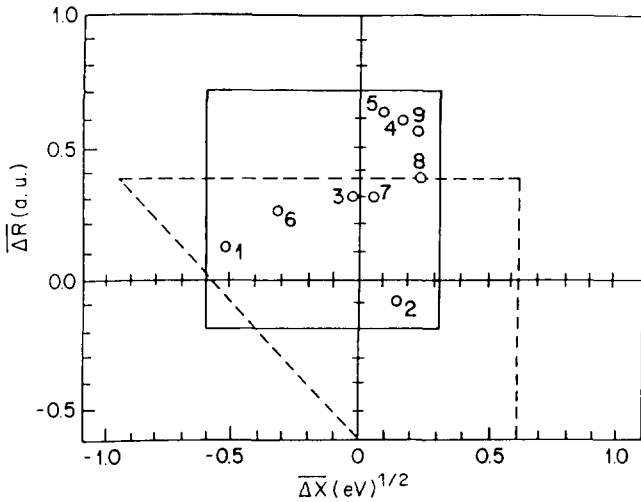


Fig. 1. The distribution of the nine stable quasi-crystals on the QSD, projected along the  $N_v$  axis. The numbering of the stable quasi-crystals is (1)  $\text{CuLi}_3\text{Al}_6$ , (2)  $\text{Ga}_{20}\text{Mg}_{37}\text{Zn}_{43}$ , (3)  $\text{Fe}_{15}\text{Cu}_{20}\text{Al}_{65}$ , (4)  $\text{Ru}_{15}\text{Cu}_{20}\text{Al}_{65}$ , (5)  $\text{Os}_{15}\text{Cu}_{20}\text{Al}_{65}$ , (6)  $\text{Cu}_{15}\text{Co}_{20}\text{Al}_{65}$ , (7)  $\text{Co}_{15}\text{Ni}_{15}\text{Al}_{70}$ , (8)  $\text{MnPd}_2\text{Al}_7$  and (9)  $\text{RePd}_2\text{Al}_7$ . The dashed line shows a portion of the boundary of the  $\Delta\bar{X}$ - $\Delta\bar{R}$  box defining the quasi-crystal condition of ref. 19, based on *c*/162 compounds and corresponding quasi-crystals only. The solid line shows the box used in the present analysis.

electric and antiferroelectric oxides, which were divided into three sets. The first set,  $F_1$ , with 50 representatives, contains ternary compounds with  $T_c > 500$  K, while the second set,  $F_2$ , with 22 representatives, contains ternary compounds with  $300 < T_c < 500$  K. Finally, the third set,  $F_3$ , with 103 representatives, contains pseudoternary and quaternary ferroelectric and antiferroelectric oxides with  $T_c > 500$  K. Values of the QSD coordinates  $\Delta\bar{X}$ ,  $\Delta\bar{R}$  and  $N_v$  were computed for all three sets of materials. The calculation of  $\Delta\bar{X}$  and  $\Delta\bar{R}$  for the pseudoternaries

and quaternaries with  $T_c > 500$  K (set  $F_3$ ) is performed by combining the two most chemically similar elements into a single "element" with weighted average  $N_v$ ,  $X$  and  $R$ . The resulting  $\Delta\bar{X}$  and  $\Delta\bar{R}$  values for the ternaries, pseudoternaries and quaternaries with  $T_c > 500$  K (sets  $F_1$  and  $F_3$ ) are confined to one very small region of the QSD as shown in Fig. 3. The area occupied by the set  $F_1$  is particularly small, while the inclusion of set  $F_3$  requires a slight displacement of the left-hand boundary to larger values of  $|\Delta\bar{X}|$ . This figure also shows a Matthias population plot for  $T_c$  vs.  $N_v$  for the 153 compounds belonging to sets  $F_1$  and  $F_3$ . This shows a very narrow peak, even narrower than is found for superconductors, for which such plots are usually made. The narrowness of this peak is consistent with the excellent localization in the  $(\Delta\bar{X}, \Delta\bar{R})$  diagram.

#### 4. Quasi-crystals: discussion

We have studied the implications and applications of QSD localization most thoroughly for quasi-crystals because of the availability of diagrams for the intermetallic compound database [1, 2]. For information about the behavior of compounds in the region occupied by stable quasi-crystals, we look at QSD structural separations of compounds which, like the *c*/162 crystalline approximant, have four inequivalent local coordination environments. We studied 814 binary and ternary compounds in the four-environment structure types listed in ref. 2. A total of 270, or 51%, of the 535 compounds with icosahedral environments fall within the  $\Delta\bar{X}$ - $\Delta\bar{R}$  range, while only seven, or 2.5%, of the 279 non-icosahedral compounds fall in this range,

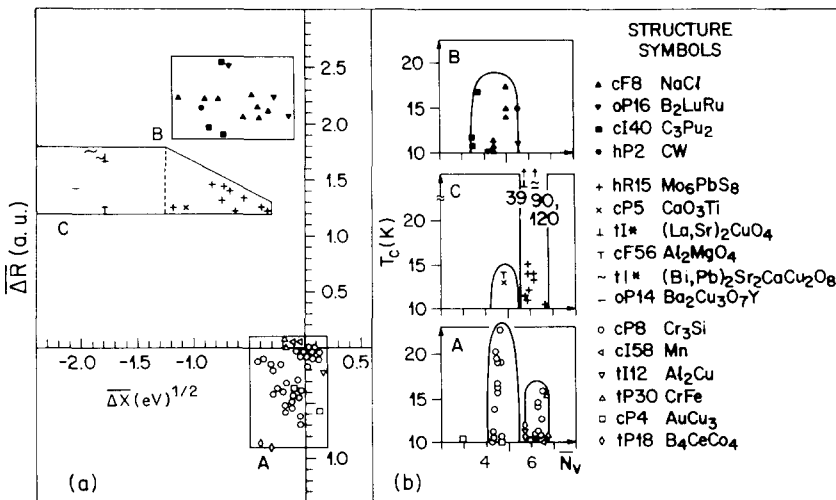


Fig. 2. QSD for 67 high  $T_c$  (above 10 K) superconductors. For the cuprate superconductors in island C, minor differences in the layer compounds (addition or subtraction of one layer) or in substitutional doping shift the points only very slightly.

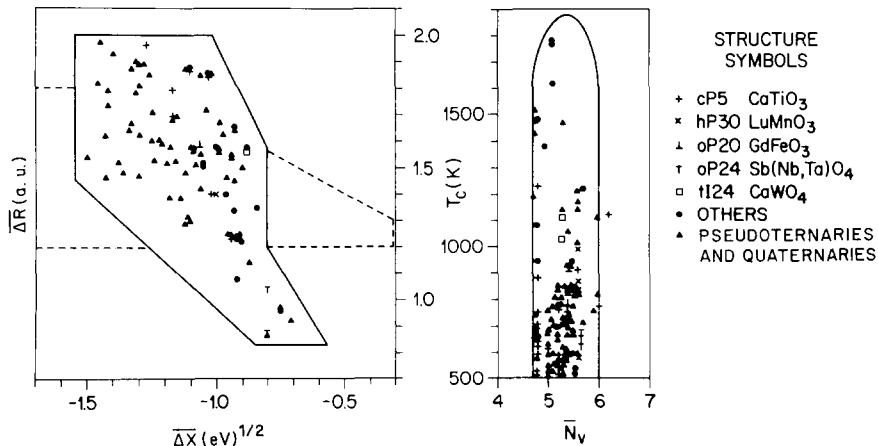


Fig. 3. QSD for 153 high  $T_c$  (about 500 K) ferroelectrics and antiferroelectrics. Pseudoternaries and quaternaries with  $T_c > 500$  K (set  $F_3$ ) are represented by solid triangles; the ternaries with  $T_c > 500$  K (set  $F_1$ ) are represented by a variety of symbols distinguishing different structure types as specified in the legend. Note that all scales are expanded by a factor of 2 relative to Fig. 2. The outline for island C from Fig. 2 is indicated by a dashed line to facilitate comparison of ferroelectric with superconducting domains.

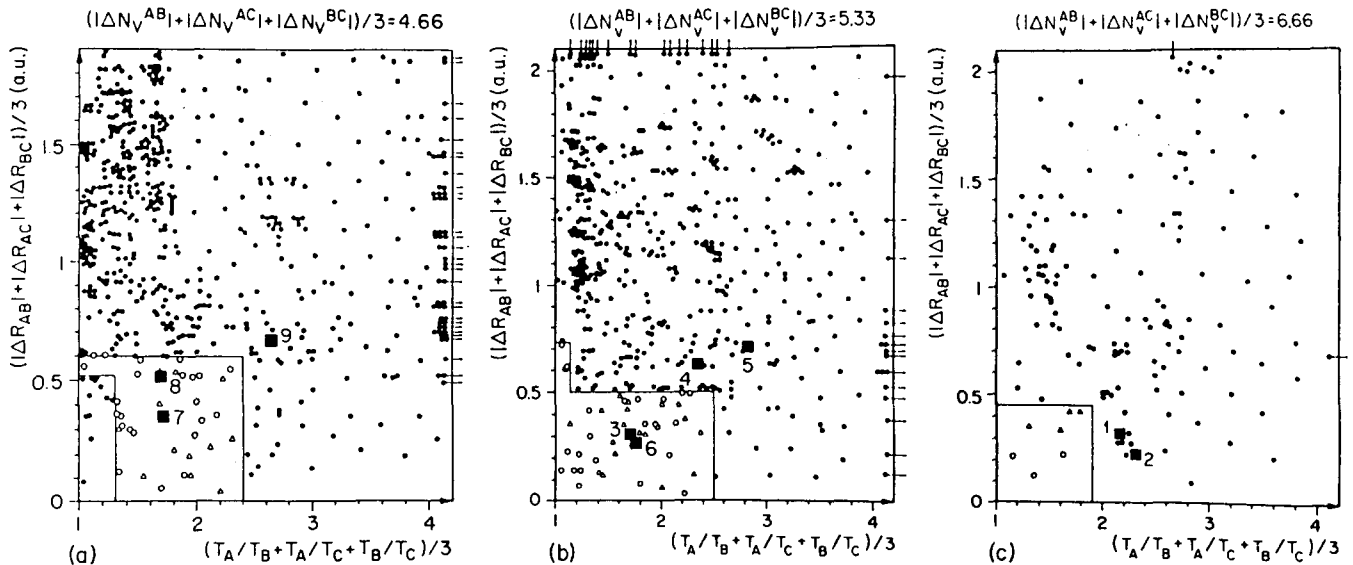


Fig. 4. (a) The  $\langle |\Delta N_v| \rangle = 4.67$  section of the QFD, showing the distribution of stable quasi-crystals in relation to the boundary separating compound formation (filled circles) from compound non-formation (open circles and triangles). The numbers adjacent to the solid squares identify the quasi-crystals as listed in Fig. 1. (b) Same as (a) but with  $\langle |\Delta N_v| \rangle = 5.33$ . (c) Same as (a) but with  $\langle |\Delta N_v| \rangle = 6.67$ .

showing that this region, independent of  $\bar{N}_v$ , is primarily associated with the formation of icosahedral compounds. From this we conclude that *long-range quasi-crystalline order is driven by a tendency to local icosahedral order*. This principle has been the basis for many searches for new quasi-crystals through the modification of known crystalline compounds with local icosahedral arrangement, and for nearly all model systems constructed to exhibit quasi-crystalline ground states [18].

Systems in or near the compound-non-forming region of the QFD should contain conflicting contributions to

total energies of crystalline compounds, generally resulting in the suppression or elimination of compound stability. For the ternary alloy systems in which the 10 stable quasi-crystals form, the regularities on the QFD are quite striking. As shown in Fig. 4, they are clearly located either in or near the compound-non-forming region, which we take as the QFD quasi-crystal condition. All four systems falling well inside this region are notable in that they are among the few (less than 6%) known violators of the ternary QFD. The physical interpretation of the QFD condition is that *long-range*

quasi-crystalline order is possible only with the suppression of factors favoring long-range periodic order.

## 5. Prediction of new materials

A step-by-step procedure for the diagrammatic analysis of small databases can be summarized as follows: (1) compile the database; (2) compute coordinates and construct diagrams; (3) look for regularities and formulate diagrammatic conditions; (4) examine diagrammatic conditions using the diagrams for the full database to extract physical interpretations and possibly to refine or extend the conditions. To use this analysis to aid in the discovery of new materials, an additional step is added; (5) generate a large number of candidate compositions for new materials and screen them using the diagrammatic conditions to yield a "short list" suitable for experimental investigation.

Predictions for new quasi-crystals have been produced by screening two kinds of candidate composition lists: new combinations based on compositions of known quasi-crystals [11, 12, 19, 20] and known intermetallic compounds as possible crystalline approximants [11, 12]. The predictions in ref. 19, based on the new combinations approach, led to the discovery of four new metastable quasi-crystals [21].

One of the main advantages of diagrammatic screening is that it can be performed very quickly for a large list of compounds. However, it is not sufficiently selective to be used as the sole criterion. The diagrammatic conditions are necessary but not sufficient, being satisfied by a large number of ordinary compounds, and imply merely that quasi-crystalline order, for example, is competitive with other structures within the rather low resolution of the method. Informed construction of the list to be screened is of great importance and should be performed with the application of additional non-diagrammatic conditions based on generalizations from known examples or from some physical ideas, such as a structural model (for quasi-crystals see ref. 22).

## 6. Conclusions

In conclusion, the theoretical prediction of new materials is a challenging problem. Empirical approaches using large databases, such as that described in this paper, should be used in combination with first-principles calculations to construct lists of candidates and narrow them down to find the most promising materials

for experimental investigation. This integrated empirical-first-principles approach holds the most promise for the future development of expert systems for the prediction of new materials.

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