

Quantum structural diagrams and high- T_c superconductivity

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Using golden coordinates we have successfully isolated the sixty known superconductors with $T_c > 10$ K into three small volumes which occupy about 1% of elemental configuration space. Two volumes contain the familiar NbN and Nb₃Ge materials, but the third volume contains both the Chevrel sulfide and Bednorz-Müller-Chu oxide materials. Compounds in the third volume with formulas near YBa₂Cu₃O₇ are suggested as promising candidates for new high- T_c superconductors.

The very small differences in interatomic interactions, which are of crucial significance in the discovery and development of new materials, have long been regarded by physicists as beyond the realm of theoretical analysis. Recently, however, powerful first-principles techniques have been developed which have successfully predicted the properties of very simple materials (such as Si) at high pressures.¹ Of more general interest and much more widespread possible application in materials science are the heuristic quantum structural diagrams (QSD) which have evolved from the study of covalent-ionic and covalent-metallic structural transitions in binary solids.² These have proved to be remarkably accurate in separating the crystal structures of thousands of binary³⁻⁵ and even ternary⁶ intermetallic alloys on a global basis. So great has been the success of QSD that it was a significant factor in motivating the creation of the most accurate and complete crystalline structure compilation⁷ presently available. The most dramatic accomplishment of QSD recently has been the prediction⁸ of new stable ternary icosahedral quasicrystals beginning from the knowledge of one such compound, LiCu₃Al₆. From this point four new metastable quasicrystals have so far been found,⁹ and one of these, slowly cooled Ga₁₅Mg₃₇Zn₄₈, has already been shown to be stable,¹⁰ in accordance with the predictions of QSD.

In view of the current interest in the novel superconductive properties of ternary Cu oxides in perovskite-related structures, it is natural to ask what chemical, crystallographic, and/or metallurgical factors are relevant to the very high values of the superconductive transition temperature T_c attained by these materials. Some of these factors are already known, especially the presence of Cu in both 2+ and 3+ valence states.¹¹ However, other factors may also be important, and these could be of great value in the search for new high- T_c materials. We present here an analysis based on QSD which reveals some remarkably simple features of the new materials which are not apparent on a phenomenological or intuitive basis.

Before proceeding to the analysis we would like to counter the most common objection to the application of heuristic global methods to the analysis of the occurrence of superconductivity. It is often argued that the superconductive condensation energy is only of order 10^{-5} eV/atom for $T_c \sim 10$ K, and that this energy is far too

small to be identified in the cohesive energy (of order 1 eV/atom) by any approach, but the most rigorous one (energy-band theory and lattice dynamics adjusted to fit observed vibrational spectra¹²). However, the ability of QSD to predict new stable quasicrystals (where stabilization energies may well be less than 10^{-2} eV) has encouraged us to apply this approach to the study of superconductors with $T_c > 10$ K, on the grounds that even partially effective predictions in the context of ternary ceramics are greatly preferable to no predictions at all. Moreover, even with the simplest phenomenological analysis of structural softening as reflected by lattice-constant bowing in the TM family (T , = Ti, V, Zr, Nb; M = C, N, or O) a successful correlation was achieved¹³ not only for T_c but also for dT_c/dP , the parameter¹⁴ which differentiates (La, Sr)₂CuO₄ from YBa₂Cu₃O₇. We expect to do much better with QSD. Finally we remark that the data base¹⁵⁻²⁶ for superconductors with $T_c > 10$ K is much larger than is generally realized, and from previous experience with 15 compounds⁵ we had good reason to expect the positive results which we have indeed found.

For the present analysis we have used the same elemental quantum configuration coordinates previously applied in studies of ternary intermetallic compounds⁶ and quasicrystals.⁸ We are aware that most oxides are insulators or semiconductors, and that a prerequisite for a high- T_c superconductor is that the material be metallic even if it is near a metal-semiconductor boundary. This distinction (which is easily made in practice) is, however, beyond our present technical capability, which is moreover limited to the analysis of ternary alloys. For materials with four elements, we (of necessity) group the two elements chemically closest and define a pseudoelement with suitably weighted quantum coordinates. This is our most serious approximation and it clearly omits the fine-tuning which produces mixed 2+ and 3+ valence states of Cu, because it combines the Ln³⁺ and (alkaline earth)²⁺ elements into a single pseudoelement. Once this approximation has been made, the analysis proceeds as before.^{6,8}

Our data base consists of 60 strongly superconductive ($T_c > 10$ K) "metals" which are found in only 16 structure types, compared to approximately 2000 existing structure types. The feature common to the 16 structure types in which strong superconductors are found is that they are all relatively simple with only a few inequivalent

sites and bonds. This result is expected both chemically (in terms of resonating bonds²⁷) and in terms of band theory (larger and more symmetric Brillouin zones are more likely to produce Fermi surfaces consisting of fewer pieces which may produce soft phonons and strong electron-phonon coupling through Fermi surface nesting over large areas¹²).

The key to our heuristic method lies in our three carefully chosen elemental quantum configuration coordinates, which were selected³ from a field of 182 candidates. These coordinates have been more than 97% (95%) successful in classifying binary³⁻⁵ (ternary⁶) structures, and they have recently predicted metastable and stable ternary quasicrystals.⁸⁻¹⁰ We therefore refer to these coordinates as golden coordinates. The three coordinates are the suitable averaged⁶ valence-electron numbers \bar{N}_v , orbital radii differences $\bar{\Delta R}$, and metallic electronegativity differences $\bar{\Delta X}$, and with them we find the surprisingly simple result shown in Fig. 1. Strong superconductors are found in only three islands, which we label *A*, *B*, and *C*. More than $\frac{3}{4}$ of the compounds in island *A* are *A15* (*cP8*) compounds with formula T_3M . Many more *A15* compounds are known, but none have $T_c > 10$ K when they lie outside the very small island *A*. Also some compounds lie inside *A*, do not have the *A15* structure, but still have $T_c > 10$ K. This means that the very small regions *A*, *B*, and *C* on the diagram are statistically reliable supplements to structural considerations in searching for high- T_c materials.²⁸ In practice, they are more useful because the location of a material on the diagram is determined only by its composition, whereas its phase diagram and structures are often determined only *after* it has been found to have an interesting property (such as high- T_c superconductivity).

Turning to island *B*, we find that more than half of these boride, carbide, and nitride compounds have the *B1*

(*NaCl*) (*cF8*) structure. In this case a binary compound *TM* which lies in *B* is five times more likely to have $T_c > 10$ K than a binary compound which has the *NaCl* structure but is otherwise unrestricted.

Island *C* contains the compounds of greatest current interest. It was first discovered in connection with the Chevrel phases and it is here that the ternary Cu oxide superconductors are found. Although the perovskite structure is unrelated to the Chevrel structure, the QSD shows that the ternary Cu oxide superconductors are closely related to the Chevrel materials, whose chemistry has been extensively studied in different strongly superconductive compounds.²⁰

The rectangular geometry of the third island shows that the variable golden coordinate for these materials is $\bar{\Delta X}$. We idealize the chemical formulas of $(La, Sr)_2CuO_4$ and $YBa_2Cu_3O_7$ as $(s_2f)(p,d)_3p_7$, where *s* is an alkali or alkaline-earth element, *d* is a transition element (including the Cu and Zn groups), and *p* is any element from the B to F groups. (Here we group the *f* element (Y, La, or any rare earth) with the *s* element to form a pseudoelement in order to analyze the alloy as a ternary.) We next examined all possible ternary compounds $(s_2f)(p,d)_3p_7$ which lie in island *C* with $\bar{\Delta X} < -1.25$, $5.7 < \bar{N}_v < 6.7$, and $1.2 < \bar{\Delta R}$ (a.u.) < 1.65 . The narrow ranges imposed on \bar{N}_v and especially $\bar{\Delta R}$ are the chief factors which enable us to reduce 332 000 candidate compounds to the 234 most favorable combinations shown in Fig. 2. We think that ordinary "chemical common sense" could produce a reduction to about 10,000 combinations, but that any attempt to achieve further reductions without calculations similar to ours would be dangerous. Much experimental effort has already been expended on the combinations $[(Ca, Sr, Ba)_2]Cu_3(O, F)_7$, but according to Fig. 2, these combinations which include F may not be promising. However, many other combinations which include F are

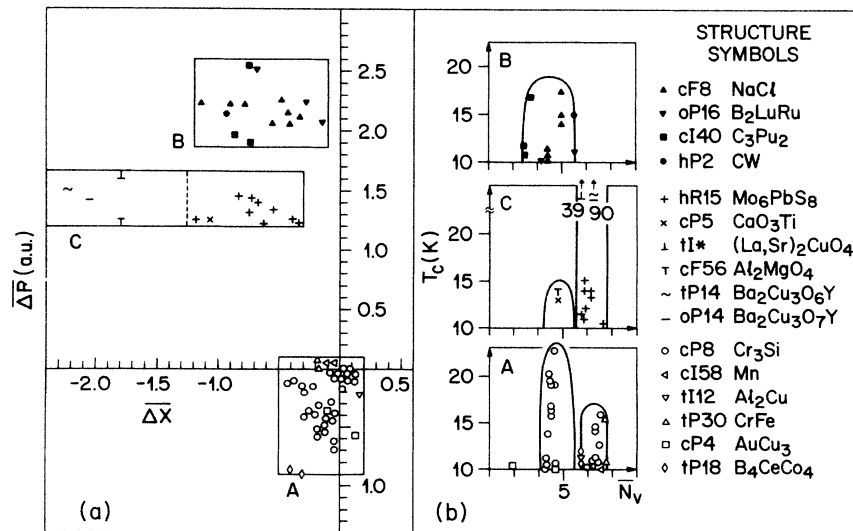


FIG. 1. (a) Projected (with respect to \bar{N}_v) domains of superconductors with $T_c > 10$ K. The golden coordinates $\bar{\Delta X}$ and $\bar{\Delta R}$ are explained in the text, as are the islands *A*, *B*, *C*. (b) Matthias profiles (Ref. 28) of T_c vs \bar{N}_v for islands *A*, *B*, *C*. The crystal structure types are designated on the extreme right using the notation of Ref. 7.

Li		Cl F	Cl N	F	F	O	O	Cl	S	Br	N	N	
Na		I Cl	I Cl	F	F	O	O	Cl	S	Br	N	N	Se
K				F	F	O	O	Cl	S	Br	N	N	
Rb	I			F	F	O	O	Cl	S	Br	N	N	
Cs				F	F	O	O	Cl	S	Br	N	N	
Be	F	F	O	F	O	O	N	N	S	N	N	N	
Mg	F	Br	Cl	Cl	F	Br	O	Cl	O	Br	N	S	
Ca	I	Br	I	Cl	I	F	O	I	O	N			
Sr				F	O	O	O	N		S	N	N	
Ba				F	Br	O	O	N		S	N	N	
				F	Br	O	O	N		S	N	N	
	Cr*	Mn*	Rh*	Fe	Co	Ni	Cu	Ag	Au	Zn	Cd	Hg	

FIG. 2. A tableau of promising pseudoternary (quaternary) candidates for high- T_c superconductors with compositions paralleling $\text{YBa}_2\text{Cu}_3\text{O}_7$. The restrictions imposed on the golden coordinates \bar{N}_v , $\bar{\Delta X}$, and $\bar{\Delta R}$ used to derive this tableau are described in the text. The compositions have the general formula $([2s + f]/3)_3(p, d)_3p_7$ where $f = \text{Y, La, or a rare earth}$. The s elements are listed in the ordinate. On the abscissas are the p, d elements. Because of similar coordinates the Mn* column includes Re, Ru, and Os, the Rh* column includes Ir, Pd, and Pt, and the Cr* column includes Mo, W, O, S, Se, and Te.

favorable, and also other combinations which include the other halides, S, Te, or N. We have presented Fig. 2 in its most general and flexible form, but of course there is nothing in our presentation which precludes the exercise of qualitative considerations, such as a predisposition towards using Cu or Cu alloys for the (p, d) element, to narrow the field further, as may suit individual taste.

We have further analyzed the significance of the A , B , and C islands in Fig. 1 where 60 superconductors with $T_c > 10$ K are localized by plotting the coordinates of 575 superconductors with $1 \text{ K} < T_c < 10 \text{ K}$ on the same map. We find that there is no separation for these "low- T_c " ma-

terials and that the plot appears random (scatter plot). Thus special elemental combinations satisfying stringent restrictions on the golden coordinates (especially \bar{N}_v and $\bar{\Delta R}$) are required to achieve $T_c > 10$ K. We may refer to the region $T_c < 10$ K as the "physical" region, corresponding to T_c attainable in elemental and pseudoelemental materials, while the "chemical" region is $T_c > 10$ K. In the chemical region even the normal-state material properties are unusual, e.g., the Martensitic transformations¹³ and anomalous high-temperature resistivities²⁹ found in island A ; the persistent anion vacancies¹³ in island B ; and, most peculiar of all, the spatial decoupling of superconducting electrons from magnetic ions³⁰ in island C .

The patterns which we have analyzed do not include effects associated with crystal structure (except insofar as crystal structures were the *basis* for choosing our diagrammatic coordinates initially), and they certainly do not include Fermi-surface or lattice vibrational effects associated with specific structural units (such as chains). Moreover, scientists interested in structure and/or property correlations will realize immediately from Fig. 1 that the basic mechanism responsible for superconductivity transcends many of the details of long-range order. In island C , for example, we find PbMo_6S_8 , LiTi_2O_4 (spinel), $\text{BaPb}_{0.8}\text{Bi}_{0.2}\text{O}_3$ (perovskite), and $(\text{La, Sr})_2\text{CuO}_4$ with $\text{YBa}_2\text{Cu}_3\text{O}_7$ (pseudoperovskite), with different structures and different compositions. While it is intuitively plausible that the sulfides and oxides should be related, we know of no other method which does not contain adjustable parameters, which automatically separates these materials from those in island B (borides, carbides, nitrides). Indeed, because islands A , B , and C fill only 1% of elemental configuration space, we believe that they offer to the materials scientist a great improvement in selecting candidate materials over what could be achieved intuitively on the basis of previous experience, no matter how extensive. The exercise which we have carried out to prepare Fig. 2 is but one example of the predictive potential of this new method; we expect others to appear because the technique is very simple and its heuristic value is self-evident.

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