# Icosahedral Quasicrystals and Quantum Structural Diagrams

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Stable crystalline compound analogs of ternary quasicrystals are successfully isolated by quantum structural diagrams, which also predict many possible new quasicrystals. Physical mechanisms responsible for the formation and certain features of quasicrystals are suggested, including the six-dimensionality of the hypercubic protolattices.

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The discovery by Schechtman *et al.*,[1,2] of a metastable metallic phase with long-range icosahedral symmetry and experimentally discrete diffraction patterns, has provoked a wide range of reactions. Scientists have preferred to analyze such phases as crystallographic problems,[3] with an icosahedral structure derived from an irrational cut of a periodic six-dimensional protolattice.[3,4] Mathematicians who model atoms classically as featureless hard spheres, however, have claimed that quasilattices should be regarded as a new metastable phase of solid matter intermediate between crystals and glasses.[5] If this view is correct, the quantum structural diagrams (QSD) which have recently proved so successful in the classification of crystal structures[6] will fail to isolate quasicrystals. However, if these diagrams also are successful with quasicrystals, then the multiple periodicities of these crystals simply constitute a special (but admittedly exotic) kind of crystal structure. A nonnegligible by-product of a successful analysis by QSD will be predictions of new candidates for ternary quasicrystals. Certainly the present paper is the first to predict *ternary* quasicrystal formation by use of primarily quantum-mechanical rather than geometrical considerations.

It is important to distinguish two problems: the question of compound versus noncompound formation, and the structure actually assumed by a given compound. The first question is important for distinguishing metastable compounds from stable ones, and is especially important for quasicrystals where all known examples at present, except one, are metastable. However, the available information base is much greater for known structure types. Thus we address the second question first, taking advantage of the remarkable feature of QSD, which is that they are capable of distinguishing the very small energy differences between stable crystalline phases.

The crucial aspect of diagrammatic analysis is the choice of configuration coordinates. Here great progress has been achieved by the replacement of classical (hard-sphere) atomic radii (based primarily on interatomic spacings in elemental cubic structures) by $l$-dependent radii derived from free-atom term values.[7-9] Satisfactory structural classifications are obtained by use of these radii, an optimized electronegativity coordinate, and the average number of $s$, $p$, and $d$ valence electrons per atom. With these three coordinates 76 structure types of $AB$, $AB_2$, $AB_3$, and $A_3B_5$ crystals including 3086 compounds separate on the QSD with 97% success.[6]

We focus our attention on $CuLi_3Al_6$ (the only known stable quasicrystal),[10] and two electronically and compositionally similar metastable quasicrystals.[11,12] We refer equivalently to these ternaries as DSP or PSD ternaries, and we model all of these as $A_{15}B_{35}C_{50}$, where $A$ ($C$) is a $p$ element (such as Al, Ga, Ge, or Sn), $B$ is an $s$ element (such as Li, Na, or Mg), and $C$ ($A$) is a near-noble metal (such as Ni, Cu, or Zn). To generalize these chemical observations to the ternary metallic context we exploit the recently developed technique of local-environment quantum coordinates.[13] In the binary case each coordinate was the sum ($\phi$) or difference ($\psi$) of elemental coordinates.[6] In the ternary $A_xB_yC_z$ ($x \le y \le z$) case we define the corresponding coordinates

$$\phi = x\phi_A + y\phi_B + z\phi_C, \qquad (1)$$

$$\psi = 2x(\psi_A - \psi_B) + 2x(\psi_A - \psi_C) + 2y(\psi_B - \psi_C). \qquad (2)$$

It has been shown[13] that with these linearly scaled coordinates the binary structure maps for $AB$, $AB_2$, $AB_3$, and $A_3B_5$ compounds all project onto a common structural diagram with closely similar local environments. Therefore these scaled coordinates can be used to describe local environments in ternary compounds, as has been shown for 2500 such compounds.[13]

The question of whether quasicrystals can be isolated on a QSD can now be answered by use of three local environment coordinates weighted according to (1) or (2), with (1) applied to the $s,p$-valence-electron number $N_{VE}$, and (2) applied to the average $s$-$p$ orbital radius ($R = r_s + r_p$), as well as $X$, the electronegativity coordinate.[6] All three of the observed DSP quasicrystal compositions form stable crystals in the ($cI$ 162) $Al_6Mg_{11}Zn_{11}$ structure type.[14] Ten examples of this type are known,[14] and these ten examples are plotted in Fig. 1 and listed in Table I.

The structure type ($cI$ 162) contains 162 atoms in a cubic unit cell with eight inequivalent sites. The ten

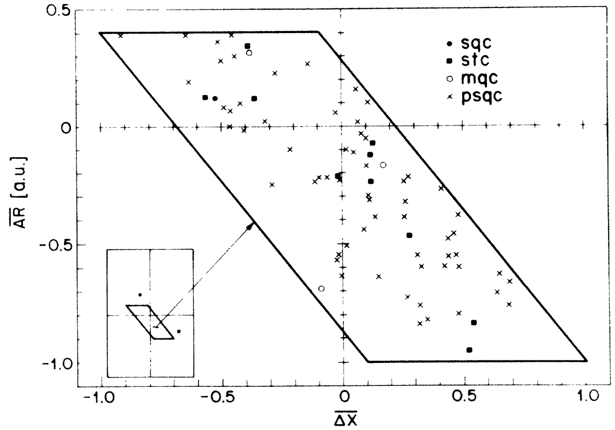

FIG. 1. Quantum structural diagram for icosahedral compounds and quasicrystals. The inset shows the domain spanned by DSP and PSD combinations with average valence-electron concentration $\bar{N}_{\rm VE}$ between 1.3 and 2.5. The two points marked refer to the $(cI\ 160)$ alloys NiLiSi and CuLiSi listed at the bottom of Table I. Abbreviations as in Table I, with also psqc denoting predicted stable quasicrystals.

known examples show that the $p$ and $d$ elements are to some degree interchangeable and occupy icosahedral sites, while the $s$ element occupies the nonicosahedral sites with coordination numbers greater than twelve. In Fig. 1 a cross section of the three-dimensional coordinate space corresponding to an average number of $s,p$ valence electrons between 1.3 and 2.5 is shown.[15] All three quasicrystals and all ten $(cI\ 162)$-structure-type ternary compounds fall in this range, which already excludes 90% of the approximately 100000 possible ternary intermetallic combinations.

Geometrical discussions of $(cI\ 162)$ structure often place primary emphasis on polyhedra centered on the $2(a)$ sites of this structure, based on a bcc lattice.[16,17] Such bias is justified both by the space group and by the fact that two compounds, (Ni,Cu) LiSi, are known[14] which are identical in structure to $(cI\ 162)$, except that the $2(a)$ sites are vacant. The icosahedral coordination shell is undistorted only about these sites. Nevertheless, no geometrical mechanism based on hard-sphere contacts has explained why the $2(a)$ sites are vacant in these two compounds. However, our QSD, which is based on quantum coordinates linearly averaged over all 162 sites, *easily* separates the two $(cI\ 160)$ compounds from the ten $(cI\ 162)$ compounds. Referring to Table I and to Fig. 1, we see that both compounds fall in the cross section $1.3 < \bar{N}_{\rm VE} < 2.5$, but that NiLiSi falls outside the $(cI\ 162)$ domain because $\overline{\Delta R}$ is too large, while CuLiSi is outside because $\overline{\Delta X}$ is too large. This very precise separation of two almost identical ternary structures is characteristic of the accuracy of QSD which has been documented already[6] for a robust base consisting of more than 3000 binary compounds in 76 structures.

The microscopic mechanisms responsible for the formation of PSD quasicrystals can be brought out in the context of Fig. 1. In other alloys [such as $Al_4Mn$, which is based on the $(cP\ 138)$ structure of $Al_9Mn_2Si_2$ and which is not discussed here], the dominant majority $p$ element has usually been Al, which is noted for its nearly-free-electron character, as explained prototypically[18] by the proximity of the nodal $q_0$ in the pseudopotential form factor $V_p(q)$ $[V_p(q_0)=0]$ to $q=2k_{\rm F}$. The appearance of Ga, Si, Ge, and Sn as $p$ elements among the ternary PSD compounds forming in the $(cI\ 162)$ structure shows that these elements may also have sufficient

TABLE I. Combinations of elements forming known DSP ternary icosahedral compounds and quasicrystals. Abbreviations: stc, stable ternary compound; s(m)qc, stable (metastable) quasicrystal. The bar average is compositional, the bracket average combinational (pairwise differences are not compositionally weighted). Note that six configuration coordinates are used in each case, as discussed in the text.

| Material | Structure | $\bar{N}_{\rm VE}$ | $\overline{\Delta R}$ | $\overline{\Delta X}$ | $\langle \lvert \Delta N_{\rm VE} \rvert \rangle$ | $\langle u \rangle$ | $\langle v \rangle$ |
|---|---|---|---|---|---|---|---|
| $Cu_{10}Li_{30}Al_{60}$ | sqc | 2.20 | 0.12 | −0.52 | 6.67 | 2.15 | 0.29 |
| $Al_{25}Mg_{36}Zn_{38}$ | mqc | 2.23 | −0.17 | 0.17 | 6.67 | 1.21 | 0.24 |
| $Cu_9Mg_{36}Al_{55}$ | mqc | 2.46 | 0.32 | −0.38 | 6.0 | 1.40 | 0.24 |
| $Cu_{11}Li_{32}Al_{57}$ | stc | 2.14 | 0.13 | −0.56 | 6.67 | 2.15 | 0.29 |
| $Zn_{17}Li_{32}Al_{51}$ | stc | 2.19 | 0.12 | −0.36 | 7.33 | 1.52 | 0.18 |
| $Al_{25}Li_{32}Zn_{43}$ | stc | 1.93 | −0.24 | 0.12 | 7.33 | 1.52 | 0.18 |
| $Al_{21}Mg_{39}Zn_{40}$ | stc | 2.21 | −0.12 | 0.12 | 6.67 | 1.21 | 0.24 |
| $Ge_{19}Na_{32}Au_{49}$ | stc | 1.57 | −0.84 | 0.54 | 6.67 | 2.65 | 0.73 |
| $Si_{19}Na_{32}Au_{49}$ | stc | 1.57 | −0.95 | 0.52 | 6.67 | 3.13 | 0.83 |
| $Sn_{15}Na_{37}Au_{48}$ | stc | 1.45 | −0.47 | 0.28 | 6.67 | 2.53 | 0.52 |
| $Ga_{16}Li_{32}Zn_{52}$ | stc | 1.84 | −0.21 | 0.01 | 7.33 | 1.77 | 0.18 |
| $Ga_{16}Mg_{32}Zn_{52}$ | stc | 2.16 | −0.07 | 0.13 | 6.67 | 2.22 | 0.22 |
| $Cu_8Mg_{40}Al_{52}$ | stc | 2.44 | 0.34 | −0.39 | 6.0 | 1.40 | 0.24 |
| $Ni_{25}Li_{31}Si_{44}$ | · · · | 2.07 | 0.78 | −0.35 | · · · | · · · | · · · |
| $Cu_{36}Li_{33}Si_{31}$ | · · · | 1.96 | −0.79 | 1.10 | · · · | · · · | · · · |

free-electron character to act as $p$ elements in forming a PSD quasicrystal. The average number of valence electrons per atom is close to 2, which suggests an effective $s^2$ configuration, noted also for the formation of elemental close-packed (nondirectional) structures. The clustering of quasicrystals and related ($cI$ 162) crystals *near the origin* in Fig. 1 suggests a delicately balanced linear compensation in the ternary composition with regard to electronegativity and orbital-radii differences. Such compensation would occur in an element, but then the element would either be close packed (in the absence of Fermi-surface effects) or stabilize in a crystal structure dictated by Fermi-surface effects. In the ternary quasicrystal close packing is suppressed by ternary size differences while Fermi-surface effects are suppressed by chemical fluctuations and multiple periodicity. Thus the energy gain associated with a Fermi surface is reduced and the local increase in density associated with icosahedral order can be the structurally determinative factor.

The question of compound versus noncompound formation has been analyzed for the complex problems presented by the 2100 structure types found in 7200 experimentally studied ternary systems.[19] About 94% of the non-compound-forming ternaries are found to have nearly zero values of two of three additional coordinates for an $ABC$ ternary, these three additional coordinates being $3u = T_A/T_B + T_A/T_C + T_B/T_C$ ($T_A$ = melting point of $A$), $3v = |\Delta r_{AB}| + |\Delta r_{AC}| + |\Delta r_{BC}|$, and the average of the absolute values of the $s,p,d$ valence-electron differences. We now place our three PSD quasicrystals on the corresponding sections of the ternary non-compound-forming diagrams,[19] which are wholly separate and distinct from the diagrams of which Fig. 1 is a two-dimensional section. For example, $CuLi_3Al_6$ has a noncompositionally weighted average $s,p,d$ valence-electron difference of $(10+8+2)/3$. The corresponding diagram is on the lower left of p. 180 in Ref. 19. The remaining average melting-point and orbital-radii coordinates in appropriate units are (2.2, 0.3), which places this compound just *outside* the non-compound-forming region. Both $Al_2Mg_3Zn_3$ and $CuMg_4Al_6$ fall inside non-compound-forming regions and so can only be metastable, as observed.[11,12] The distribution of the ten ($cI$ 162) compounds on the non-compound-forming diagrams is also interesting. The one *closest* to the boundary between compound- and non-compound-forming mixtures is $CuLi_3Al_6$, followed by $Zn_2Li_3Al_5$. This may indicate an increasing tendency towards icosahedral coordination as the boundary is approached.

Next we consider only ternary DSP or PSD combinations with an average valence-electron concentration between 1.3 and 2.5. There are only about 2600 of these, of which only 437 lie in the parallelogram shown in Fig. 1. This number is further reduced to 55 combinations by the requirement that each combination lie as close to the noncompound boundary as $CuLi_3Al_6$. Our final list of promising DSP or PSD ternary combinations for stable quasicrystals is given in Ref. 20. We stress that at this stage we do not expect most of these combinations to exhibit icosahedral crystalline compounds or stable or even metastable quasicrystals. We do expect, however, that the *likelihood* of finding icosahedral structure in one of our combinations is about 100 times larger than in an alloy composition chosen by a geometrical method.

We conclude by discussing the meaning of QSD. Normally, quantum calculations aim for high accuracy in a few systems, but QSD aim for much lower accuracy in $\sim 10^5$ binary and ternary systems. The coordinates that best separate very different cubic binary structures (NaCl and CsCl) with identical cation and anion environments are (surprisingly) the same as the coordinates that best separate closely similar noncubic binary structures with drastically different cation and anion environments (such as FeB and CrB). The present theory is heuristic to the extent that the employed linearized ternary coordinates may vary from problem to problem (sometimes we use $s,p$ valence electrons, and sometimes $s,p,d$) and have been fully optimized only for binaries, but at the same time these are modern *quantum* coordinates,[7-9] not the almost-empty classical hard-sphere coordinates employed in unsuccessful geometrical models.[21] The high success level achieved already by QSD in global surveys of binary and ternary systems[6,18] is the robust basis for our present predictive analysis of quasicrystals. It may well be significant that this success level does not increase smoothly with increasing number of coordinates. For example, in distinguishing among some 600 *three*-dimensional compounds with NaCl and CsCl structures,[6] Villars found that the success level with one, two, or *three* optimized coordinates was 65%, 70%, or *99%*. Thus it may not be entirely accidental that the present characterization of icosahedral structures requires *six* coordinates,[22] just as *six* indices from the protolattice are required to label quasicrystal diffraction patterns.[3,4] We believe that it is only *after* these six global coordinates have been optimized in a ternary alloy that one should begin to apply sphere-packing models to justify or analyze icosahedral coordination.

*Note added.*— Guided by the foregoing theoretical discussion we have made preliminary studies of some of the alloy combinations listed in Ref. 20. The samples were prepared by splat quenching and their structures surveyed by powder diffraction and transmission electron microscopy. Low-angle bands characteristic of icosahedral order[10] were observed in several cases, such as AgMgAl, GaMgZn, ZnLiAl, and AuLiAl. To obtain stable quasicrystals these combinations must be compositionally fine tuned, but these results are promising and they demonstrate the predictive capability of QSD. We also note that stimulating comments were received from C. L. Henley.

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[20] Compounds for which the P and D elements can be interchanged are in italics: AgNaPb, *AlBeCu, AlLiAg, AlLiCd, AlLiCu, AlLiZn,* AlMgAg, AlMgAu, CuCaIn, *GaLiCd, GaLiZn,* GaMgAg, GaMgAu, GaMgCd, GaMgZn, GeBeCu, GeLiAg, GeLiCd, GeLiCu, GeLiZn, GeMgAg, HgLiGa, InBeCu, InCaAu, InMgCd, InMgZn, NiLiIn, NiLiSn, PbCaNi, PbCaPd, PbCaPt, PbLiAg, PbLiAu, PbLiCd, PbLiHg, PbLiZn, PbNaCd, PbNaHg, PdLiIn, PdLiPb, PdLiSn, SiBeCu, SiBeZn, SiMgAg, SiMgCd, SiMgZn, SnBeZn, SnLiAg, SnLiCd, SnLiCu, SnLiHg, SnLiZn, SnMgNi, SnNaCd, SnNaHg. We also mention here combinations which fall inside noncompound-forming regions and inside the parallelogram in Fig. 1, and hence are excellent candidates for forming metastable quasicrystals: InMgAu, SnMgAu, PbMgAu, AlMgCd, GeMgCd, GeMgNi, SiMgNi, AlBeZn, GeBeZn, GeMgZn, NiLiAl, NiLiPb.

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[22] We would argue qualitatively that the information required to specify dimensionality $n$ scales with $n!$, so that agreement between values of $n$ derived in two different ways is about 100 times more significant for $n=6$ than for $n=3$.