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Dimension of the Gibbs function topological manifold: 2. Thermodynamically stable binary quasicrystals: Reality or artefact?

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Abstract In complex systems with at least three independent components, one-phase normal states may transform into exotic states. The former are represented by a non-branching tree, while the latter are represented by a branching tree. The transformation takes place through a non-congruent two-phase equilibrium. Until recently, researchers using this process were able to obtain stable quasicrystals with three, four, or more components. It therefore seemed justified to suppose that exotic states constituted quasicrystals. In 2000, however, Tsai's team discovered two stable binary quasicrystals formed through a congruent process. Virtually no reports on other stable binary quasicrystals have been obtained since that discovery despite considerable effort on the part of researchers. The graph-based representation of equilibrium states rules out the existence of exotic one-phase equilibria (i.e., stable quasicrystals) in binary systems. A question arises: What types of systems did Tsai discover?.

Keywords Graph theory · Thermodynamic equilibrium · Stable quasicrystals

Mathematics Subject Classification 80A10 · 80A50 · 52C23

1 Introduction

Previously in this work, it was shown that the values of the Gibbs function (1):

$$G \equiv G(p, T, x_1, x_2, \ldots, \tilde{x}_C) \equiv H - TS \tag{1}$$

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which determines the location of the thermodynamic equilibrium state in a closed isotherm–isobar system, where p denotes pressure, T denotes temperature, and the molar fraction $x_1, x_2, \ldots, \tilde{x}_C$ denotes chemical composition (the tilde over the last value means that for closed systems: $\tilde{x}_C = 1 - (x_1 + x_2 + \cdots + x_{C-1})$), form a two-dimensional piecewise smooth topological manifold (2-D) [1]. This occurs because $C-1$ constraints, i.e., equations derived from the Gibbs–Duhem theorem (*viz.* Equation (11) in the previous part of this work), are imposed onto a set of arguments with $C + 1$ dimensions ($C - 1$ molar fractions plus 2 for pressure and temperature). This manifold is two-dimensional regardless of how complex the thermodynamic system is. Consequently, the values of two geodesic coordinates determine the location of a point on this manifold. Let X, Y denote the geodesic coordinates. There likely exist many methods of laying out geodesic lines on a Gibbs function 2-D topological manifold. In our publications, X equalled molar enthalpy H (1) and Y equalled -TS, where S denoted molar entropy [1]. The Gibbs function can be written using geodesic coordinates:

$$G^{(k)}(X, Y) = \begin{cases} X^{(k)} + Y^{(k)} & C = 1 \\ \sum_{i=1}^{C} x_i \mu_i^{(k)} \equiv \sum_{i=1}^{C} g_i^{(k)} \left(X^{(k)}, Y^{(k)} \right) & C > 1 \end{cases} \tag{2}$$

where the superscript $k = 1, 2, \ldots, P$ enumerates individual phases of the system and μ_i, g_i denote the chemical potential (3) and the weighted chemical potential (4) of the i-th component, respectively:

$$\mu_i^{(k)} = \left(\frac{\partial G^{(k)}}{\partial x_i} \right)_{p, T, x_j} \tag{3}$$

$$g_i^{(k)} = \left(\frac{\partial G^{(k)}}{\partial \ln x_i} \right)_{p, T, x_j} \tag{4}$$

Individual smooth sections of the topological manifold correspond to the appropriate phases of the system [1]. These sections are glued along the phase transformation line. One pair of values X, Y corresponds to each point on the smooth part of the section of the manifold. Two pairs of values of geodesic coordinates X, Y correspond to a point located on the gluing line (one pair is located on one section and the other is located on the other glued section).

Let the thermodynamic equilibrium state be represented by the set of parameters:

$$\chi_0 \equiv (p_0, T_0, x_{10}, x_{20}, \ldots, \tilde{x}_{C0}) \tag{5}$$

The mapping of this state onto the reference state

$$\chi^* \equiv (p^*, T^*, x_1^*, x_2^*, \ldots, \tilde{x}_C^*), \tag{6}$$

which, as has been shown previously in this work, is an invariant state, creates the set of $C + 1$ points $R_i^{(k)}$ on the surface of the manifold [1], where:

$$R_i^{(k)} = \left(X^{(k)}(\chi_i), Y^{(k)}(\chi_i) \right) \ldots \quad i = 1, 2, \ldots, C + 1 \tag{7}$$

and the i-th set of parameters χ_i denotes the set for reference state χ^*, the value of the appropriate parameter from the set χ_0 is located at position i in the reference state (*viz.* Equation (18) in the previous part of this work). Each point $R_i^{(k)}$ constitutes one degree of freedom. The value of the Gibbs function in the equilibrium state, calculated relative to the reference state, is equal to the integral of $dG^{(k)}$ over the minimal path connecting the individual degrees of freedom, where

$$dG^{(k)} = \begin{cases} dX^{(k)} + dY^{(k)} & C = 1 \\ \sum_{i-1}^{C} \left[\left(\frac{\partial g_i^{(k)}}{\partial X^{(k)}} \right) dX^{(k)} + \left(\frac{\partial g_i^{(k)}}{\partial Y^{(k)}} \right) dY^{(k)} \right] & C > 1 \end{cases} \tag{8}$$

Either of the following may be true for this integration:

(a) None of the $C + 1$ degrees of freedom lies on the phase transformation line;
(b) At least one degree of freedom lies on the phase transformation line(s).

In the first case, the integration path creates a connected graph without cycles, i.e., a tree. Each of the C edges connecting the individual degrees of freedom (tree vertices) is equal to the weighted chemical potential (4) of the appropriate component in the system. The state graph is located on a smooth section of the topological manifold. This manifold represents a phase of the system and constitutes the only face of the graph. Two types of one-phase thermodynamic states can be distinguished for systems with three or more components. The first type corresponds to the one for unary and binary systems represented by non-branching trees. The second type corresponds to systems represented by branching trees and usually comprises many subtypes. Figure 1a shows state graphs for a one-phase quaternary system. States represented by non-branching trees have been termed *normal states* (graph a_0 in Fig. 1a), while those represented by branching trees have been termed *exotic states* (graphs a_1 and a_2 in Fig. 1a).

In the second case, the degree(s) of freedom located on the phase transformation line represent(s) pairs of glued vertices connected with one or more edges. The gluing occurs because points with different geodesic coordinates $R_i^{(k)}$, $R_i^{(l)}$, as long as they are located on the phase transformation line, represent the same geometric location. As a result of the degrees of freedom having been glued together, one or more cycles appear by means of integration. Thus, the state graph will include cycles or, in special cases, loops. Previous in this work it has been shown that the individual faces of such a graph represent the appropriate phases of the system. Consequently, the composition of a given phase is determined by a sequence of edges (i.e., weighted chemical potentials (4) of individual components) that form a given face. In other words, the situation corresponds to the states of multi-phase systems. Figure 1b shows several two-phase state graphs for systems with $C = 4$. Note that the two-phase state graphs include cycles with C edges that represent a state in which both phases are qualitatively or even quantitatively identical (graph b_0 in Fig. 1b). Equilibrium processes represented by such graphs include congruent processes (if the phase composition is quantitatively identical) and non-congruent processes (if the phase composition is quantitatively different).
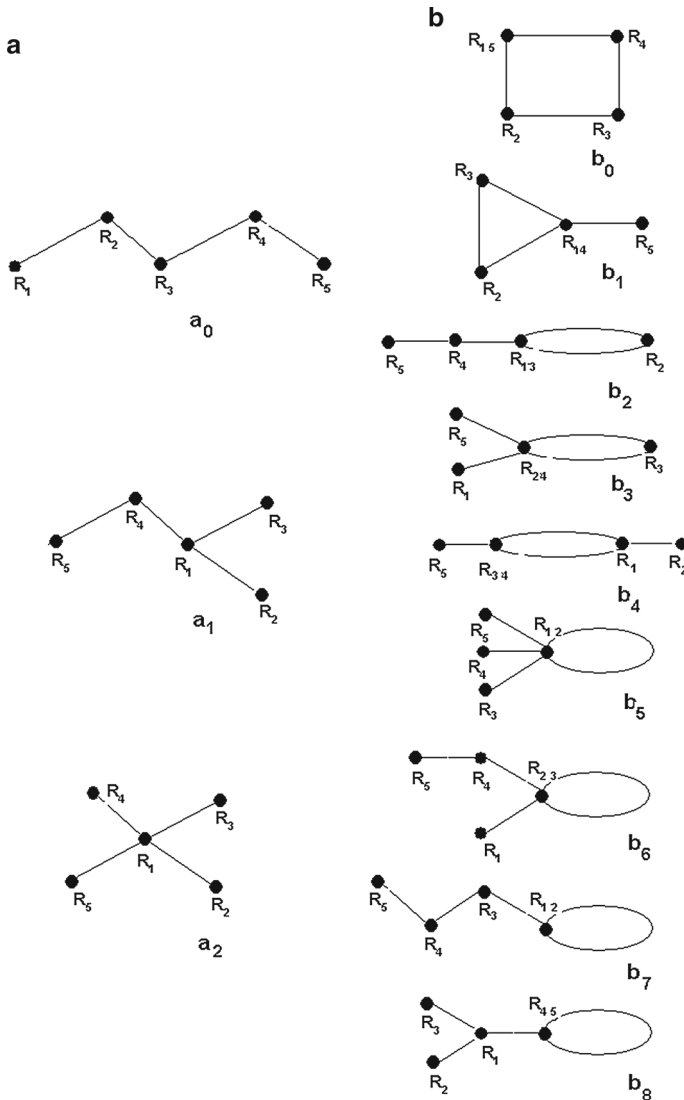
Fig. 1 Example state graphs for quaternary systems. For clarity, the edges representing individual components (A, B, C, and D) are marked with the same type of a line. **a** One-phase state graphs (a_0, a_1, a_2). **b** Two-phase state graphs (b_0, b_1, b_2, b_3, b_4, b_5, b_6, b_7, b_8); the two-parameter vertices R_{ij} were created by gluing the vertices R_i and R_j in the appropriate graphs from Fig. 1a. The gluing (as well as the taking apart) of vertices represents a phase transformation

The remaining two-phase state graphs represent states in which the two phases have different compositions. These graphs only represent non-congruent processes (graphs b_1, b_2, b_3, b_4, b_5, and b_6 in Fig. 1b). Of course, one-phase systems (normal and exotic) will, in the appropriate conditions, transform into two-phase systems, which in turn can be transformed back into one-phase systems, usually different from the

original systems. Such transformations are applied in practice to create new types of phases that often display an atypical arrangement of molecules. This is why it is worth analysing the conditions that graph theory imposes onto phase transformations.

2 Theory

In 1984, Shechtman's team discovered phases forming in Al–Mn alloys that displayed a rotational symmetry forbidden for three-dimensional structures [2]. However, these phases, termed *quasicrystals*, were uninteresting from the perspective of thermodynamics for the simple reason that they were thermodynamically unstable. Nonetheless, researchers later noticed that adding a third component or more into the metastable quasicrystals stabilised them. The first thermodynamically stable quasicrystal $Al_{65}Cu_{20}Fe_{15}$, discovered by Tsai's team [3], began a series of investigations that resulted in the discovery of numerous other stable ternary and quaternary quasicrystals. To date, researchers have described quasicrystals that form in such systems as Al–Ni–Co, Al–Cu–Co, Al–Cu–Co–Si, Al–Mn–Pd, Al–Li–Cu, Al–Pd–Mn, or Zn–Mg–RE (RE = La, Ce, Nd, Sm, Gd, Dy, or Y) [4–6]. The single fact that such phases are thermodynamically stable is a sufficient to motivation for investigating them from the perspective of phenomenological thermodynamics. From the discovery in 1987 until 2000, researchers observed that stable quasicrystals form by means of non-congruent solidification in systems with three or more components [7–10]. Graph-based representation of states describes phase transformations through the gluing or taking apart of state graph vertices. Let us consider such a transformation occurring in quaternary systems (Fig. 2). A quaternary liquid, the state of which is represented by a non-branching tree, transforms into one of six possible two-phase states (b_0, b_1, b_2, b_3, b_6, or b_7) when cooled to an appropriate temperature, as Fig. 2 shows. Some of these two-phase states transform into exotic one-phase states represented by either of the branching trees a_1 or a_2 when an appropriate change in thermodynamic parameters is induced. Note that exotic states are created only in non-congruent processes. A congruent equilibrium represented by a cycle with four edges (b_0) can only transform into a one-phase normal state (a_0), and never into an exotic state. On a side note, one of the five non-congruent equilibria, b_7, is an exception: it does not transform into an exotic state, in contrast to a vast majority of such equilibria. Notice that this two-phase exception, just as the congruent equilibrium graph b_0, is represented by graphs that cannot form from exotic state graphs (a_1 and a_2). This constitutes an argument in favour of the assumption that in thermodynamics, the state of quasicrystals is represented by a branching tree. A second argument in favour of this proposal is the fact that stable quasicrystals, just like branching trees, are observed in systems with at least three components. In the more than 10 years since the discovery of stable quasicrystals, the thesis that the thermodynamic state of these systems is represented by a branching tree seemed correct. No stable quasicrystals in binary systems were found despite extensive research. Such research was well-justified: phase diagrams for binary systems are better known, and many more of them were found than diagrams for more complex systems. Researchers attempted to explain the lack of stable binary quasicrystals by conducting model theoretical studies [11–13]. Widom et al. [11] noticed that 'a binary Lennard-Jones alloy in
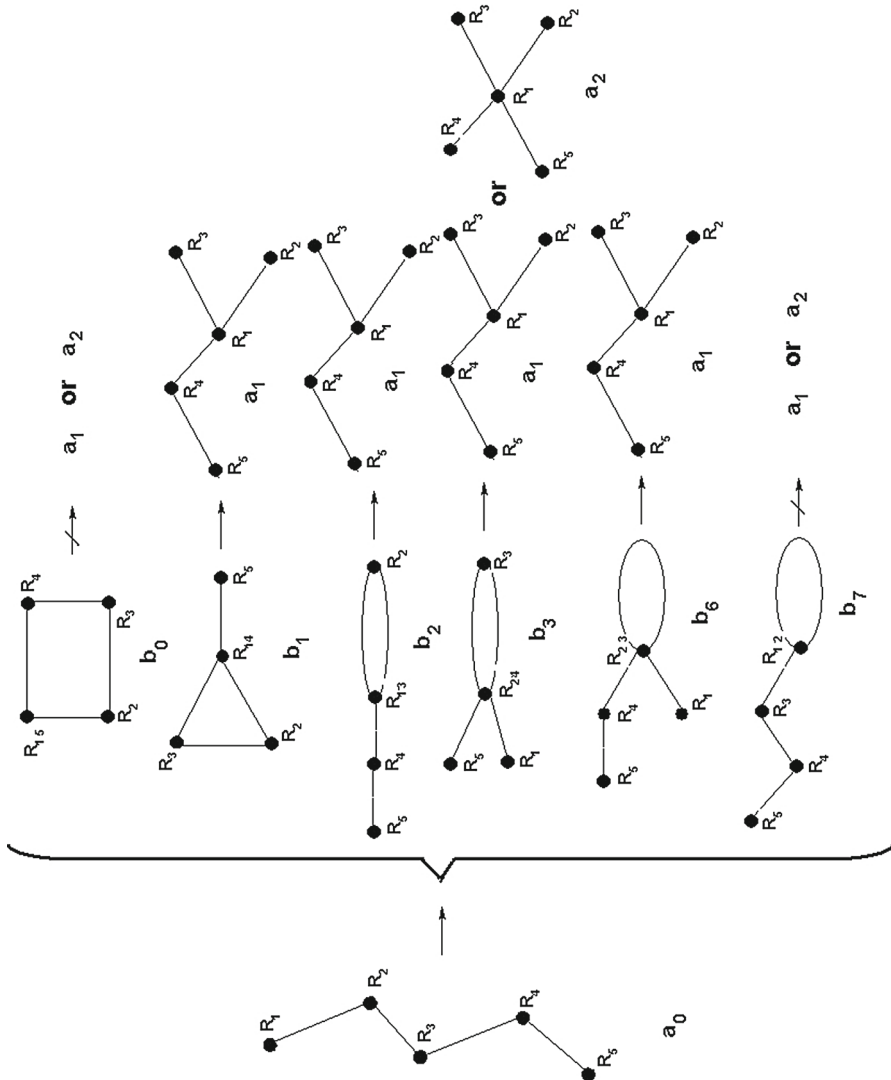
Fig. 2 State graphs that describe the transformation of the one-phase quaternary normal state a_0 into an exotic one-phase state (a_1 or a_2). The transformation takes place through two-phase states for which state graphs are created by gluing a pair of vertices in a non-branching normal state tree. The non-congruent majority of two-phase states (b_1, b_2, b_3, b_6) may transform into an exotic one-phase state (a_1 or a_2). Such a transformation is represented by the taking apart of the appropriate vertices in a two-phase system graph. The two-phase congruent state b_0 and the exceptional non-congruent state b_7 do not transform into exotic states. Such two-phase states cannot be created from one-phase exotic states (a_1 and a_2)

two dimensions exhibits an entropically stabilized quasicrystal state', i.e., 'quasicrystal compounds exhibit crystalline states at low temperatures, then transform into the quasicrystal at intermediate T before melting at higher temperatures'. Of course, the results of model studies on 2-D systems can differ considerably from those on 3-D

systems. Nonetheless, Widom et al. [11] made the important observation that entropy is a stabilising factor for quasicrystals. Cataldo et al. [12,13] analysed the stability of real, i.e., three-dimensional, binary quasicrystal structures using 'molecular-dynamic simulation' and 'generalized effective liquid approximation'. Their study indicated that 'hard-sphere icosohedral quasilattice is metastable with respect to the crystal and fluid structures'. The series of theoretical study results that were unfavourable to the existence of stable binary quasicrystals ended in 2000, when Tsai's team [14] published an article on their discovery of two 'stable binary icosohedral quasicrystals'. One of these crystals was composed of $Cd_{5.7}Yb$, the other of $Cd_{5.7}Ca$. Atypically, the systems formed through congruent solidification. Tsai's discovery seemed to dispel the myth that stable quasicrystals must comprise at least three elements. The great number of known phase diagrams for binary systems created the illusion that the road to synthesising new stable binary quasicrystals had opened. In time, the fact that it was merely an illusion became apparent. Since 2000, hundreds of binary systems have been researched that could potentially form stable quasicrystals. Unfortunately, even when quasicrystal phases formed in some of these systems, they were metastable. It was only in 2010 that Goldman's team reported [15] synthesising a stable quasicrystal composed of $Sc_{12}Zn_{88}$. In sum, within 15 years, only three, rather than 'a great number', of quasicrystals were found. One can hardly avoid making the ironic remark that stable quasicrystals, if they exist, are extremely rare. Thus, the following questions arise:

- Why does configuration entropy (especially the entropy of phason fluctuation) so rarely and so poorly constitute a stabilising factor for binary quasicrystal phases in moderate temperatures, despite the claims by Widom et al. [11,16–18]?
- Why does entropy constitute a stabilising factor for quasicrystals in three systems but not in other systems?
- Do Tsai's and Goldman's discoveries [14,15] of stable quasicrystals in binary systems bring an end to the thesis that the states of quasicrystals are represented by branching trees (which, it needs to be emphasised, appear only for systems with at least three components)?

Answering these questions requires us to accept that the stable binary quasicrystals discovered by Tsai and Goldman [14,15] are not, in fact, binary! None of the truly binary quasicrystals, beginning with the Al-Mn discovered by Shechtman [2], are stable, while the stable quasicrystals discovered by Tsai and Goldman are not actually binary. This is due to the isotope composition of natural elements used for synthesising quasicrystals. Some of these elements, such as Al, Mn, and Sc, are composed almost entirely of a single isotope. Other elements, such as Cd, Yb, and Zn, are in their natural state composed of several isotopes with similar ratios. For instance, natural Zn is a mixture of three isotopes in the 0.49:0.28:0.19 proportion; Cd is mixture of as many as six isotopes in the 0.13:0.13:0.24:0.12:0.29:0.07 proportion; and Yb primarily includes five isotopes in the 0.14:0.22:0.16:032:0.13 proportion [19]. Thus, the three stable 'binary' quasicrystals are, in fact, quasicrystals with 11, 7, and 4 components, respectively. In other words, they constitute pseudobinary systems; the truly binary quasicrystals, such as the Al–Mn discovered by Shechtman's team, are only metastable. The isotope composition of a given thermodynamic phase has a negligi-

Table 1 Metals with a melting point lower than about 1,500 K that in their natural state comprise at least two isotopes with comparable shares	E	$[E_1]:[E_2]:\ldots$	N(E)
	Sb	0.57:0.43	2
	Ce	0.88:0.11	2
	Eu	0.48:0.52	2
	Ga	0.60:0.40	2
	In	0.04:0.96	2
	Li	0.07:0.93	2
	Cu	0.69:0.31	2
	K	0.93:0.07	2
	Rb	0.72:0.28	2
	Ag	0.52:0.48	2
	Tl	0.30:0.70	2
	Si	0.92:0.05:0.03	3
	Mg	0.79:0.10:0.11	3
	Ni	0.68:0.26:0.04	3
	Pb	0.24:0.22:0.52	3
	Ca	0.97:0.02:0.01	3
	Zn	0.49:0.28:0.04:0.19	4
	Ba	0.02:0.07:0.08:0.11:0.72	5
	Gd	0.15:0.20:0.16:0.25:0.22	5
	Ge	0.20:0.27:0.08:0.37:0.08	5
	Yb	0.03:0.14:0.22:0.16:0.32:0.13	6
The second column provides the fractions of individual isotopes, beginning with the lightest one. The third column provides the total number of such isotopes for a given element. The table was created based on data in [16]	Cd	0.13:0.13:0.24:0.12:0.29:0.07	6
	Hg	0.10:0.17:0.23:0.13:0.30:0.07	6
	Sn	0.15:0.08:0.24:0.09:0.33:0.05:0.06	7
	Nd	0.27:0.12:0.24:0.08:0.17:0.06:0.06	7
	Sm	0.03:0.15:0.11:0.14:0.07:0.27:0.23	7

ble effect on energy differences between phases due to the small difference in mass between individual isotopes. On the other hand, isotope composition has a significant effect on the entropy of individual phases. Of course, the entropies of mixing for both the crystal phase and the quasicrystals phase are the same. However, configuration and vibrational entropies may differ between the two phases. For crystal structures, the number of equivalent energy configurations that differ in the arrangement of the individual isotopes of a given element is much lower than for less structured entities (quasicrystals, liquids, glass, etc.). Therefore, it is obvious that isotope composition, by means of configuration entropy, is a stabilising factor for the quasicrystal phase relative to the crystal phase. It seems peculiar that such an effect (the influence of isotope composition on the thermodynamic stability of quasicrystals) has not been observed thus far. The issue of whether the difference in entropy would suffice to allow, in certain thermodynamic conditions, the quasicrystal phase to stabilise relative to the crystal phase should be resolved through theoretical calculations for model binary systems. These calculations should take into account that one or two compo-

nents have different isotope compositions. Regardless of when such calculations are going to be conducted, it can already be stated that the experimental discovery of three stable pseudobinary quasicrystals confirms the influence of isotope composition on phase stability. The proposal that isotope effects are responsible for the thermodynamic stability in pseudobinary quasicrystals leads to a considerable decrease in the number of elements that can form such phases. Table 1 lists about 20 elements with a melting point lower than about 1,500 K. The isotope composition of these elements allows one to hope that a pair of these elements may, with good likelihood, form stable pseudobinary quasicrystals. The phrase 'good likelihood' means one may expect that synthesising stable quasicrystals could be easier using elements listed in the table rather than such elements as Al, Mn, or Sc, i.e., those that comprise one isotope in their natural state. Initially, scientists who investigated quasicrystals considered the potential existence of unary quasicrystals. Today, we realise that quasicrystals constitute systems with at least three components, and as a result, the existence of such phases seems absurd. However, if we replace the term *unary* with *pseudounary*, the notion becomes less absurd. Thus, while searching for stable unary quasicrystals is futile, the futility diminishes if the search is conducted by investigating phase transformations in metals that in their natural state have at least three isotopes with high shares.

3 Conclusions

1. Stable quasicrystals may form through non-congruent processes in systems with at least three components. In phenomenological thermodynamics, branching tress represent the state of such phases.
2. Such a representation of the thermodynamic state of quasicrystals supports the hypothesis that the quasicrystal arrangement of matter may constitute the ground state in some complex systems, i.e., it may be stable at 0 K.
3. The three stable binary quasicrystals obtained by Tsai and Goldman [11,12] are, when the isotope composition of the elements is taken account, quasicrystals with 11, 7, and 4 components, respectively, i.e., they constitute pseudobinary phases.
4. Isotope compositions are a stabilising factor for the three quasicrystals obtained by Tsai and Goldman by means of configuration entropy and vibrational entropy.
5. Difficulties in obtaining stable "binary" quasicrystals may have resulted from the fact that a large number of the researched systems were truly binary, i.e., composed of two metals with only one isotope each (e.g., Al–Mn), which cannot form stable quasicrystals.

Appendix

In August 2013 team of Professor A.I. Goldman published [20] information about the synthesis of 7 stable quasicrystals in systems RE–Cd, where RE = Gd, Tb, Dy, Ho, Er, Tm, Y. Easy to see that these systems are pseudobinary (respectively: 11, 7, 10, 7, 10, 7, 7 components), so in accordance with the thesis of this work may create a stable quasicrystals. Professors A.I. Goldman and P.C. Canfield thanks for the information on their recent research [20].

References

1. J. Turulski, J. Math. Chem. doi:10.1007/s10910-014-0439-5
2. D. Shechtman, I. Blech, D. Gratias, J. Cahn, Phys. Rev. Lett. **53**, 1951 (1984)
3. I.P. Tsai, A. Inoue, T. Masumoto, J. Mater. Sci. Lett. **6**, 1403 (1987)
4. I.P. Tsai, A. Inoue, T. Masumoto, Jpn. J. Appl. Phys. **27**, 1587 (1988)
5. A.P. Tsai, MRS Bull. **22**, 40 (1997)
6. A.P. Tsai, Acc. Chem. Res. **36**, 31 (2003)
7. P. Gille, B. Bauer, M. Hahne, A. Smontara, J. Dolinsek, J. Cryst. Growth **318**, 1016 (2011)
8. R. Popescu, A. Jianu, M. Manciu, R. Nicula, R. Manaila, J. Alloys Compd. **221**, 240 (1995)
9. S. Katrych, Th Weber, M. Kobas, L. Massuger, L. Palatinus, G. Chapuis, W. Steurer, J. Alloys Compd. **428**, 164 (2007)
10. L. Barbier, D. Gratias, Prog. Surf. Sci. **75**, 177 (2005)
11. H.K. Lee, R.H. Swendsen, M. Widom, Phys. Rev. B **64**, 224201 (2001)
12. H.M. Cataldo, C.F. Tejero, Phys. Rev. B **52**, 13269 (1995)
13. H.M. Cataldo, Philos. Mag. B **79**, 1603 (1999)
14. A.P. Tsai, J.Q. Guo, E. Abe, H. Takakura, T.J. Sato, Nature **408**, 537 (2000)
15. A.I. Goldman, A. Kreyssig, S. Nandi, M.G. Kim, M.L. Caudle, P.C. Canfield, Philos. Mag. **91**, 2427 (2011)
16. W. Steurer, in *Ninth International Conference on Quasicrystals*, Stable clusters in quasicrystals - fact or fiction? Ames (2005)
17. Marc de Boissieu, in *Ninth International Conference on Quasicrystals*, Stability of Quasicrystals: Energy, Entropy, and Phason Modes. Ames University, Ames (2005)
18. Ch. Henley, in *Ninth International Conference on Quasicrystals*, Clusters, Phason Elasticity, and Entropic Stabilization: A Theory Perspective. Ames (2005)
19. J. Emsley, *The Elements*, 2nd edn. (Clarendon Press, Oxford, 1991)
20. A.I. Goldman, T. Kong, A. Kreyssig, A. Jesche, M. Ramazanoglu, K.W. Dennis, S.L. Bud'ko, P.C. Canfield, Nat. Mater. **12**, 714 (2013)