ISSN 1063-7745, Crystallography Reports, 2012, Vol. 57, No. 7, pp. 984–987. © Pleiades Publishing, Inc., 2012.

CRYSTALLOGRAPHIC SOFTWARE

Search for Low-Temperature Solvents Using Nonplanar Tie-Lines

V. I. Lutsyk[a], A. E. Zelenaya[a], and A. M. Zyryanov[b]

[a] *Institute of Physical Materials Science, Siberian Branch, Russian Academy of Sciences, Sakhyanova ul. 6, Ulan-Ude, 670047 Russia*
e-mail: vluts@pres.bscnet.ru
[b] *Buryat State University, Ulan-Ude, 670000 Russia*

Received December 20, 2010

Abstract—The technique of searching for the point of quaternary eutectics is imitated by constructing a series of two-dimensional vertical cross sections (method of tie-lines) by the example of a model of eutectic-type T–x–y–z diagram without solid-phase solubility. Errors that arise when mapping cross sections of experimentally studied diagrams are analyzed.

DOI: 10.1134/S1063774512070164

INTRODUCTION

Computer models of T–x–y–z diagrams make it possible to clearly visualize geometric structures in both the concentration projection and projections that take into account temperature; in addition, they provide different vertical and horizontal cross sections [1, 2]. Having understood the structural regularities of a T–x–y–z diagram under study, one can predict the form of two-dimensional cross sections based on their position in the concentration projection with respect to the liquidus elements; thus, errors in their construction can be excluded [3].

We will imitate the tie-line method to search for the invariant-point coordinates by the example of a model of T–x–y–z diagram of eutectic type without solid-phase solubility.

MODEL OF T–X–Y–Z DIAGRAM OF EUTECTIC TYPE WITHOUT SOLID-PHASE SOLUBILITY

This diagram contains four hypersurfaces of liquidus Q_I, 24 ruled hypersurfaces (12 hypersurfaces with a one-dimensional simplex generator Q^r_{IJ} and 12 hypersurfaces a two-dimensional simplex generator Q^r_{IJK}), and a horizontal hyperplane at the quaternary-eutectics temperature T_ε (Fig. 1a, table) [4]. There are four two-phase regions $L + I$ ($I = A$, B, C, D), six three-phase regions $L + I + J$, and five four-phase regions ($L + A + B + C$, $L + A + B + D$, $L + A + C + D$, $L + B + C + D$, $A + B + C + D$) between the hypersurfaces. To construct a computer model of a diagram, we used the kinematic way of describing hypersurfaces [1, 2, 5], in which the coordinates of points of four initial components (I), six binary eutectics (e_{IJ}), four ternary eutectics (E_{IJK}), and a quaternary eutectic (ε) are set as the initial data. The initial dataset includes also the corresponding conjugate points of the tie-lines located on the edges of hyperprism: 12 points I_{eIJ} and 12 points I_{EIJK} at the temperature of binary and ternary eutectics (T_{eIJ} and T_{EIJK}) and four points I_ε at the quaternary-eutectics temperature (T_ε). The curvature on the binary and univariant liquidus lines and on the hypersurface was taken into account.

IMITATION OF THE TIE-LINE METHOD

In the conventional tie-line method [6–8], the coordinates of quaternary-eutectics point are sought as follows. First, the three-dimensional vertical cross section mnk, which is parallel to the tetrahedron face BCD and is located before the eutectics, is considered (Fig. 1b). Then, the vertical cross section gf is set on mnk parallel to the side nk to reveal the point (r) on the common simplex generator $A_\varepsilon B_\varepsilon \varepsilon$ of the ruled hypersurfaces Q^r_{ABC} and Q^r_{ABD}, which belongs to the horizontal hyperplane H_ε at the quaternary-eutectics temperature (T_ε). A cross section mh is drawn through the vertex m on the edge BS and the found point r to intersect the tie-line $A_\varepsilon\varepsilon$ (at the point r_ε), which belongs to the ruled hypersurface Q^r_{AB} at the temperature of the horizontal hyperplane H_ε. Then, the cross section Ap, in which the desired point ε lies, is drawn through the tetrahedron vertex A and the point r_ε.

We propose an approach in which one does not need to set the three-dimensional vertical cross section and the where the first two two-dimensional sections (gf and mh) may belong to different planes (Fig. 2a). At the first stage, a two-dimensional cross section located in the projection within one of the liquidus hypersurfaces, is set by two points on the tetrahedron faces. For example, the cross section $s1$(0.6; 0.25; 0.15; 0) – $s2$(0.6; 0.25; 0; 0.15) (Fig. 2b) intersects the hypersurface of the liquidus Q_A (line 1–2), ruled

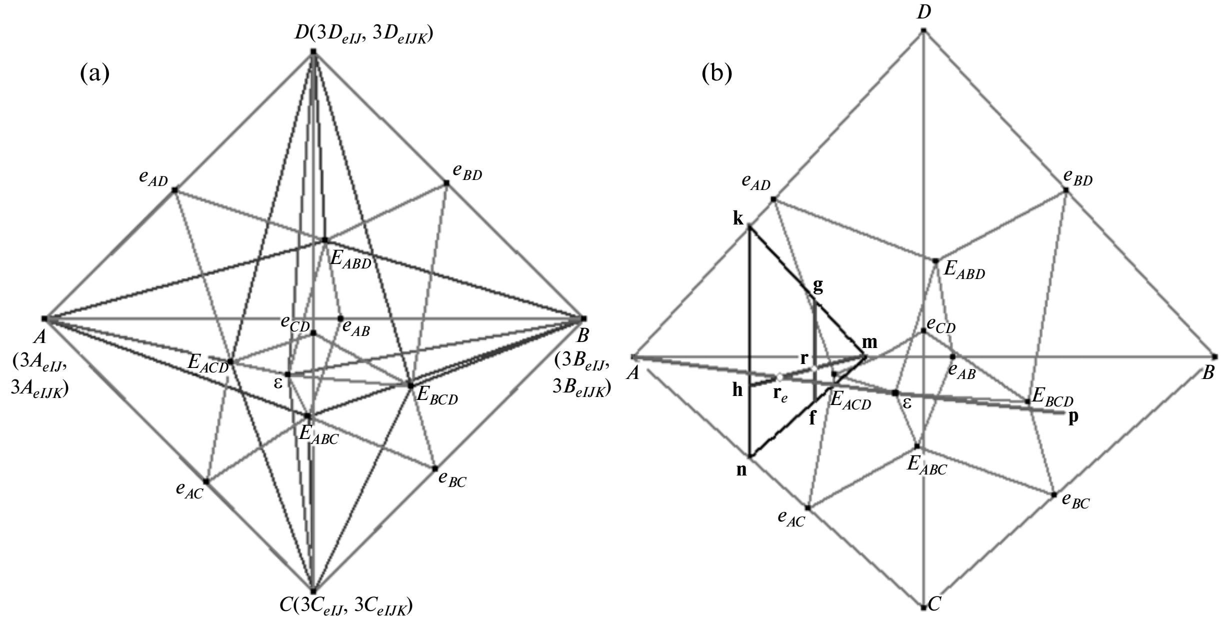

Fig. 1. (a) Model of a T–x–y–z diagram in the XYZ projection and (b) the scheme for constructing cross sections.

hypersurfaces Q^{r}_{AB} (3–4), Q^{r}_{ABC} (5–6) (Fig. 3c), Q^{r}_{ABD} (6–7), and the hypersurface at T_ε (8–6–9). The cross section point $6 \equiv r$ belongs to the common two-dimensional simplex generator $A_\varepsilon B_\varepsilon \varepsilon$ of the ruled hypersurfaces Q^{r}_{ABC} and Q^{r}_{ABD} at T_ε. Having assumed the length of the segment $s1s2$ to be unity when projecting the point r on it (Fig. 2b), we find this point to divide the segment in the ratio of 0.673 : 0.327. Thus, the coordi-

Contours of hypersurfaces of the liquidus Q_I and the ruled hypersurfaces Q^{r}_{IJ} and Q^{r}_{IJK}

Symbol	Contour	Symbol	Contour	
Q_A	$Ae_{AB}e_{AC}e_{AD}E_{ABC}E_{ABD}E_{ACD}\varepsilon$	Q^{r}_{ABD}	$E_{ABD}\varepsilon A_\varepsilon B_\varepsilon B_{EABD}A_{EABD}$	
Q_B	$Be_{AB}e_{BC}e_{BD}E_{ABC}E_{ABD}E_{BCD}\varepsilon$	Q^{r}_{ADB}	$E_{ABD}\varepsilon A_\varepsilon D_\varepsilon D_{EABD}A_{EABD}$	
Q_C	$Ce_{AC}e_{BC}e_{CD}E_{ABC}E_{ACD}E_{BCD}\varepsilon$	Q^{r}_{BDA}	$E_{ABD}\varepsilon B_\varepsilon D_\varepsilon D_{EABD}B_{EABD}$	
Q_D	$De_{AD}e_{BD}e_{CD}E_{ABD}E_{ACD}E_{BCD}\varepsilon$	Q^{r}_{ACD}	$E_{ACD}\varepsilon A_\varepsilon C_\varepsilon C_{EACD}A_{EACD}$	
Q^{r}_{AB}	$E_{ABD}e_{AB}E_{ABC}\varepsilon A_\varepsilon A_{EABC}A_{EABD}A_{eAB}$	Q^{r}_{ADC}	$E_{ACD}\varepsilon A_\varepsilon D_\varepsilon D_{EACD}A_{EACD}$	
Q^{r}_{AC}	$E_{ABC}e_{AC}E_{ACD}\varepsilon A_\varepsilon A_{EACD}A_{EABC}A_{eAC}$	Q^{r}_{CDA}	$E_{ACD}\varepsilon C_\varepsilon D_\varepsilon D_{EACD}C_{EACD}$	
Q^{r}_{AD}	$E_{ABD}e_{AD}E_{ACD}\varepsilon A_\varepsilon A_{EACD}A_{EABD}A_{eAD}$	Q^{r}_{ABC}	$E_{ABC}\varepsilon A_\varepsilon B_\varepsilon B_{EABC}A_{EABC}$	
Q^{r}_{BA}	$E_{ABD}e_{AB}E_{ABC}\varepsilon B_\varepsilon B_{EABC}B_{EABD}B_{eAB}$	Q^{r}_{ACB}	$E_{ABC}\varepsilon A_\varepsilon C_\varepsilon C_{EABC}A_{EABC}$	
Q^{r}_{BC}	$E_{BCD}e_{BC}E_{ABC}\varepsilon B_\varepsilon B_{EABC}B_{EBCD}B_{eBC}$	Q^{r}_{BCA}	$E_{ABC}\varepsilon B_\varepsilon C_\varepsilon C_{EABC}B_{EABC}$	
Q^{r}_{BD}	$E_{ABD}e_{BD}E_{BCD}\varepsilon B_\varepsilon B_{EBCD}B_{EABD}B_{eBD}$	Q^{r}_{BCD}	$E_{BCD}\varepsilon B_\varepsilon C_\varepsilon C_{EBCD}B_{EBCD}$	
Q^{r}_{CA}	$E_{ABC}e_{AC}E_{ACD}\varepsilon C_\varepsilon C_{EACD}C_{EABC}C_{eAC}$	Q^{r}_{BDC}	$E_{BCD}\varepsilon B_\varepsilon D_\varepsilon D_{EBCD}B_{EBCD}$	
Q^{r}_{CB}	$E_{BCD}e_{BC}E_{ABC}\varepsilon C_\varepsilon C_{EABC}C_{EBCD}C_{eBC}$	Q^{r}_{CDB}	$E_{BCD}\varepsilon C_\varepsilon D_{\varepsilon EBCD}C_{EBCD}$	
Q^{r}_{CD}	$E_{BCD}e_{CD}E_{ACD}\varepsilon C_\varepsilon C_{EACD}C_{EBCD}C_{eCD}$			$A_\varepsilon B_\varepsilon C_\varepsilon \varepsilon$
Q^{r}_{DA}	$E_{ABD}e_{AD}E_{ACD}\varepsilon D_\varepsilon D_{EACD}D_{EABD}D_{eAD}$	H_ε	$A_\varepsilon B_\varepsilon C_\varepsilon D_\varepsilon \varepsilon$	$A_\varepsilon B_\varepsilon D_\varepsilon \varepsilon$
Q^{r}_{DB}	$E_{ABD}e_{BD}E_{BCD}\varepsilon D_\varepsilon D_{EBCD}D_{EABD}D_{eBD}$			$A_\varepsilon C_\varepsilon D_\varepsilon \varepsilon$
Q^{r}_{DC}	$E_{BCD}e_{CD}E_{ACD}\varepsilon D_\varepsilon D_{EACD}D_{EBCD}D_{eCD}$			$B_\varepsilon C_\varepsilon D_\varepsilon \varepsilon$

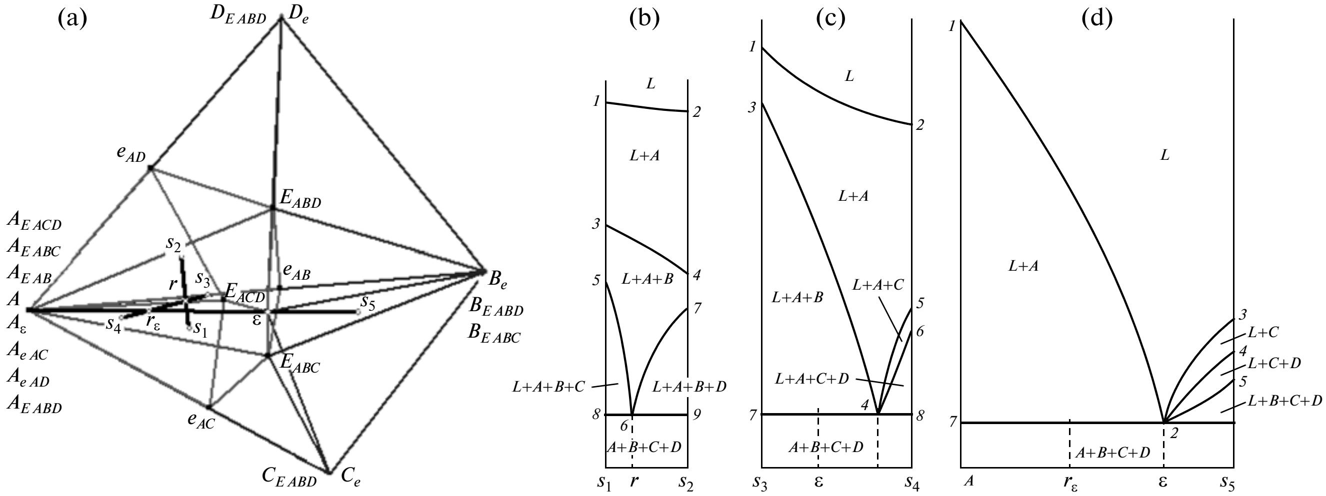

Fig. 2. (a) Schematic diagram of arrangement of the cross sections (b) $s1s2$, (c) $s3s4$, and (d) $As5$.

nates of the point r can be calculated using the matrix transformations [9]

$$\begin{pmatrix} r_1 \\ r_2 \\ r_3 \\ r_4 \end{pmatrix} = \begin{pmatrix} s1_1 & s2_1 \\ s1_2 & s2_2 \\ s1_3 & s2_3 \\ s1_4 & s2_4 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$= \begin{pmatrix} 0.6 & 0.6 \\ 0.25 & 0.25 \\ 0.15 & 0 \\ 0 & 0.15 \end{pmatrix} \begin{pmatrix} 0.673 \\ 0.327 \end{pmatrix} = \begin{pmatrix} 0.6 \\ 0.25 \\ 0.101 \\ 0.049 \end{pmatrix}.$$

At the second stage, a cross section is drawn through the found point r and an arbitrary point $s3(0.6; 0.4; 0; 0)$ of the tetrahedron edge AB to the intersection with the tetrahedron face ACD at the point $s4$ (Fig. 2a). Since the point $s4$ belongs to the tetrahedron plane ACD, $s4_2 = 0$. The other coordinates, $s4_1$, $s4_3$, $s4_4$, are found from the joint solution of the equations of the ACD plane and the straight line $s3r$. The equation of the plane has the form $s4_1 + s4_3 + s4_4 - 1 = 0$. The equation of the straight line in the parametric form can be written as

$$\begin{cases} s4_1 = s3_1 + t(r_1 - s3_1) \\ s4_3 = s3_3 + t(r_3 - s3_3) \\ s4_4 = s3_4 + t(r_4 - s3_4) \end{cases} \Rightarrow \begin{cases} s4_1 = 0.6 \\ s4_3 = 0.101t \\ s4_4 = 0.049t \end{cases}.$$

Let us substitute the found values of $s4_1$, $s4_3$, and $s4_4$ into the equation of plane and calculate $t = 2.667$. Having substituted t into the equation of the straight line, we obtain:

$$\begin{cases} s4_1 = 0.6 \\ s4_3 = 0.2694 \\ s4_4 = 0.1306 \end{cases}.$$

Thus, the coordinates of the point $s4$ are (0.6; 0; 0.2694; 0.1306). The cross section s_3s_4 intersects the liquidus Q_A (line 1–2); the ruled hypersurfaces Q^r_{AB} (3–4), Q^r_{AC} (4–5), and Q^r_{ACD} (4–6) (Fig. 2c); and the one-dimensional segment generator of the ruled hypersurface at the temperature of quaternary eutectics $A_\varepsilon \varepsilon$ at the point $4 \equiv r_\varepsilon$.

Similar to the above-considered case, when projecting the point r_ε, we find it to divide the cross section base in the ratio of 0.78 : 0.22 and then calculate its coordinates:

$$\begin{pmatrix} r_{\varepsilon 1} \\ r_{\varepsilon 2} \\ r_{\varepsilon 3} \\ r_{\varepsilon 4} \end{pmatrix} = \begin{pmatrix} s3_1 & s4_1 \\ s3_2 & s4_2 \\ s3_3 & s4_3 \\ s3_4 & s4_4 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix}$$

$$= \begin{pmatrix} 0.6 & 0.6 \\ 0.4 & 0 \\ 0 & 0.2694 \\ 0 & 0.1306 \end{pmatrix} \begin{pmatrix} 0.22 \\ 0.78 \end{pmatrix} = \begin{pmatrix} 0.6 \\ 0.088 \\ 0.2101 \\ 0.1019 \end{pmatrix}$$

Let us draw a cross section along the ray Ar_ε to its intersection with the BCD face at the point $s5$ (Fig. 2a); here, $s5_1 = 0$. The coordinates $s5_2$, $s5_3$, and $s5_4$ are calculated by joint solution of the equations of the plane BCD and the straight line Ar_ε. The equation of the plane has the form $s5_2 + s5_3 + s5_4 - 1 = 0$. The equation of the straight line in the parametric form can be written as

$$\begin{cases} s5_2 = A_2 + t(r_{\varepsilon 2} - s5_2) \\ s5_3 = A_3 + t(r_{\varepsilon 3} - s5_3) \\ s5_4 = A_4 + t(r_{\varepsilon 4} - s5_4) \end{cases} \Rightarrow \begin{cases} p_2 = 0.088t \\ p_3 = 0.2101t \\ p_4 = 0.1019t \end{cases}.$$

The obtained values of $s5_2$, $s5_3$, and $s5_4$ are substituted into the equation of the plane to find t to be 0.25.

Having substituted t into the equation of the straight line, we determine the coordinates of the point $s5$ as follows: (0; 0.22; 0.5252; 0.2548). The cross section $As5$ intersects Q_A (1–2), Q_C (2–3), Q^r_{CD} (2–4), Q^r_{CDB} (2–5), and H_ε (Fig. 2d). In this cross section, point 2 is the desired point ε, which divides the cross section base in the ratio of 0.74 : 0.26. Its coordinates are found from the expression

$$\begin{pmatrix}\varepsilon_1\\ \varepsilon_2\\ \varepsilon_3\\ \varepsilon_4\end{pmatrix} = \begin{pmatrix}A_1 & s5_1\\ A_2 & s5_2\\ A_3 & s5_3\\ A_4 & s5_4\end{pmatrix}\begin{pmatrix}x_1\\ x_2\end{pmatrix}$$

$$= \begin{pmatrix}1 & 0\\ 0 & 0.22\\ 0 & 0.5252\\ 0 & 0.2548\end{pmatrix}\begin{pmatrix}0.26\\ 0.74\end{pmatrix} = \begin{pmatrix}0.26\\ 0.1628\\ 0.3886\\ 0.1886\end{pmatrix}.$$

The tie-line method can be optimized by drawing the first section through two ternary eutectics.

ERRORS IN MAPPING CROSS SECTIONS OF T–X–Y–Z DIAGRAMS

Based on the location of the cross section, one can draw conclusions on its form and avoid errors in interpreting experimental data. In particular, Gubanova et al. [10] presented a cross section in which one vertex obeys the condition $s1 \in ABD$ (i.e., is located inside the simplex $AE_{ABD}B$) and the other lies behind the line AE_{ABD} in the simplex $AE_{ABD}D$. This cross section should intersect two ruled surfaces with a one-dimensional simplex generator (Q^r_{AB}, Q^r_{AD}), three ruled hypersurfaces with a two-dimensional simplex generator (Q^r_{ABC}, Q^r_{ABD}, Q^r_{ADB}), and a hyperplane (H_ε) at the quaternary-eutectics temperature, which follows from the location of the cross section. At the same time, cross sections of the $s1s2$ type were reported in [10].

When analyzing the Li,Ba,Mg,Zr//F system [11], it was believed that the cross section drawn through the vertex of ZrF_4 tetrahedron and the opposite ternary eutectics Li,Ba,Mg//F contains the quaternary-eutectics point. However, in reality, the quaternary-eutectics point was not found [3]. According to the topological structure of the diagram, the ternary eutectics under consideration should lie on the continuation of the tie-line connecting the vertex of ZrF_4 and the ternary-eutectics point, which corresponds to a particular case of the diagram structure.

CONCLUSIONS

The proposed modification of the tie-line method makes it possible to determine the coordinates of invariant points in T–x–y–z diagrams using three two-dimensional vertical cross sections (that are not related to the same plane) and matrix calculations. This method of constructing models of T–x–y–z diagrams allows one to not only visualize and understand their geometric structure but also, when studying vertical cross sections, to choose their most optimal position and avoid errors in their interpretation.

REFERENCES

1. V. I. Lutsyk, A. E. Zelenaya, and A. M. Zyryanov, Crystallogr. Rep. **54** (Suppl. 7) 1300 (2009).
2. V. I. Lutsyk, A. E. Zelenaya, and A. M. Zyryanov, J. Mat. Methods Technol. **2**, Part 1, 176 (2008).
3. V. I. Lutsyk, Electrochem. Soc. Proc. **PV2002-19**, 386 (2002).
4. V. I. Lutsyk and V. P. Vorob'eva, Geol. Geofiz. **39**, 1218 (1998).
5. V. I. Lutsyk, A. M. Zyryanov, and A. E. Zelenaya, Zh. Neorg. Khim. **53**, 858 (2008).
6. D. A. Petrov, Zh. Fiz. Khim. **14**, 1498 (1940).
7. V. I. Posypaiko, A. S. Trunin, et al., Dokl. Akad. Nauk SSSR, **228**, 811 (1976).
8. V. I. Lutsyk, *Analysis of the Liquidus Surface for Ternary Systems* (Nauka, Moscow, 1987) [in Russian], p. 150.
9. V. I. Lutsyk and V. P. Vorob'eva, Z. Naturforsch. A **63a**, 513 (2008).
10. T. V. Gubanova, I. M. Kondratyuk, and I. K. Garkushin, Zh. Neorg. Khim. **53**, 1184 (2004).
11. G. Li, R. Takagi, and K. Kawamura, Denki Kagaku **59**, 800 (1991).

Translated by Yu. Sin'kov