

Thermodynamic proof of the existence of compounds in the phase diagrams of systems without solid solutions

II. The systems MF—AlF₃ (M = Li, Na, K)

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Application of the Le Chatelier—Shreder equation to the analysis of coordinates of the eutectic point on the liquidus curve of lithium, sodium, and potassium hexafluoroaluminate in the subsystems M₃AlF₆—AlF₃ was used to prove the presence of compounds LiAlF₄, NaAlF₄, and KAlF₄, respectively, in these systems. Further, the existence of a chemical compound in the system KF—AlF₃ in the composition range 75—55 mole % KF is predicted. On the other hand, the possibility of the existence of compounds of the type Li₃Al₃F₁₄ or Li₃Al₂F₉ in the system LiF—AlF₃ was disproved.

С использованием уравнения Ле Шателье—Шредера применительно координатам эвтектической точки на кривой ликвидуса гексафторалюминатов лития, натрия и калия в подсистемах M₃AlF₆—AlF₃ было проведено термодинамическое доказательство присутствия соединений LiAlF₄, NaAlF₄, KAlF₄ и предполагается существование химического соединения в системе KF—AlF₃, в интервале концентраций от 75 до 55 мол. % KF. Одновременно была опровергнута возможность образования соединения типа Li₃Al₃F₁₄ или Li₃Al₂F₉ в системе LiF—AlF₃.

In paper [1] a simple thermodynamic method has been described which allows to prove or disprove the assumption about the presence of chemical compound in a binary eutectic system. The method is based on the analysis of the course of liquidus curve of pure component. This paper deals with the application of the method to the systems of the type MF—AlF₃ (M = Li, Na, K) which are similar in physical and chemical respect. These systems have been studied carefully many times [2] because of their importance in electrolytic production and purification of aluminium or in deposition of surface layers of metals from molten electrolytes. Compounds of the type M₃AlF₆ exist without doubts. However, the published results on the existence of compounds in the subsystems M₃AlF₆—AlF₃ are inconsistent and thus we paid our attention to the analysis of this problem. First we checked the proposed method on the proof of the existence of compound Li₃AlF₆.

Assumptions and relationships used

The method has been explained in detail in paper [1]. It is based on the analysis of liquidus curve of the pure component. The following assumptions are made:

- (i) This pure component forms with its nearest neighbour compound a simple eutectic system without solid solution;
- (ii) the behaviour of this system is not far from ideality;
- (iii) the temperature dependence of the enthalpy of fusion of pure component can be neglected.

The analysis requires knowledge of four experimental data and employment of five thermodynamic relationships:

ΔH_i^f (calor) is the calorimetrically determined change in enthalpy of fusion of pure component,

T_i^f is the temperature of fusion of pure component,

T_i, x_i are the temperature of fusion and the concentration coordinate of a figurative point on the liquidus curve of component i in mixture with the second component. In our consideration we chose the eutectic point for this purpose and it is further denoted by the index E.

$$\ln a_i^E = \frac{H_i^f \text{ (calor)}}{R} \frac{T^E - T_i^f}{T^E T_i^f} \quad (1)$$

a_i^E is the activity of the component i in the eutectic point,

R is the gas constant.

If we assume that the nearest neighbour of pure component is a chemical compound, it is necessary to transform the concentration coordinate of the eutectic point so that the chemical compound forms one component of this new subsystem. As this new subsystem will be again close to ideality, it holds

$$a_i^E = y_i^E = f(x_i^E) \quad (2)$$

y_i^E is the transformed concentration coordinate of the eutectic point in the new subsystem.

The enthalpy of fusion of the pure component i can be calculated according to the relationship

$$\Delta H_i^f = \frac{RT_i^f T_i^E}{T_i^E - T_i^f} \ln y_i^E \quad (3)$$

The calculated value of the enthalpy of fusion ΔH_i^f is denoted in paper [1] with the subscript calc. If the concentration base is chosen correctly (and if the above-mentioned assumptions are fulfilled) then it must hold

$$\Delta H_i^f = \Delta H_i^f(\text{calor}) \quad (4)$$

and

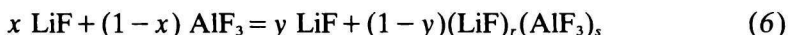
$$a_i^E/y_i^E = D_i \rightarrow 1 \quad (5)$$

D_i is the coefficient of adequacy of choice of the concentration base. Validity of the criteria (4) and (5) indicates or disproves the assumption about the presence of the presumed chemical compound in the system.

The subsystem LiF—(LiF)_r(AlF₃)_s

The proof of the existence of chemical compound as the nearest neighbour of the component LiF in the system LiF—AlF₃ is carried out on the basis of *Rolin's* experimental data [3]: $T^f(\text{LiF}) = 1121 \text{ K}$, $T^E = 984 \text{ K}$, $x^E(\text{LiF}) = 0.845$. According to *Douglas* [4], $\Delta H^f(\text{LiF}) (\text{calor}) = 27\,075 \text{ J mol}^{-1}$.

Transformation of the concentration coordinate of the eutectic point is based on the scheme



It follows that

$$y = \frac{(s+r)x - r}{(s+r-1)x - r + 1} \quad (2a)$$

The choice of compound which would form with LiF a simple eutectic system is based on the assumption that the coefficients r and s are small integers. Calculations carried out for a series of physically possible compounds according to eqns (2a), (3), and (5) are summarized in Table 1.

Table 1

Calculated values of $\Delta H^f(\text{LiF})$ and $D(\text{LiF})$ for the systems of the type LiF—(LiF)_r(AlF₃)_s

System	$y^E(\text{LiF}) = f[x^E(\text{LiF})]$	$\Delta H^f(\text{LiF})/\text{J mol}^{-1}$	$D(\text{LiF})$
LiF—AlF ₃	$x = 0.845$	11 275	0.7898
LiF—LiF·AlF ₃	$(2x - 1)/x = 0.8166$	13 563	0.8173
LiF—2LiF·AlF ₃	$(3x - 2)/(2x - 1) = 0.7754$	17 029	0.8607
LiF—3LiF·AlF ₃	$(4x - 3)/(3x - 2) = 0.7103$	22 900	0.9396
LiF—4LiF·AlF ₃	$(5x - 4)/(4x - 3) = 0.5921$	35 084	1.1272
LiF—3LiF·2AlF ₃	$(5x - 3)/(4x - 2) = 0.8877$	7 975	0.7518

The activity $a^E(\text{LiF})$ calculated according to relationship (1) on the basis of Rolin and Douglas' data equals 0.6674.

As it follows from the results presented in Table 1 the best agreement between the calculated and calorimetric value of the enthalpy of fusion of LiF as well as the best value of the adequacy coefficient $D(\text{LiF})$ is achieved in the system LiF—Li₃AlF₆, which is in agreement with the physical reality. Therefore, it can be stated that the tested method gives unambiguous qualitative and approximately also quantitative information on the presence of the chemical compound as the nearest neighbour of LiF in the system.

The calculated value $\Delta H^f(\text{LiF}) = 22\,900 \text{ J mol}^{-1}$ differs from the calorimetric value $\Delta H^f(\text{LiF}) (\text{calor}) = 27\,075 \text{ J mol}^{-1}$ by 15%. If we take into account the temperature dependence of this quantity, the difference between these two values decreases to 10%. A more detail analysis of this result, viz. the difference between the calorimetric and calculated value of the enthalpy of fusion, will be discussed in another paper. We shall show that the most probable reasons for the observed disagreement are the deviation of the system from ideality with respect to LiF and neglecting dissociation of the complex anion AlF_6^{3-} , which influences the activity of LiF.

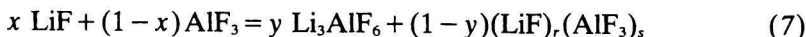
The subsystem Li₃AlF₆—(LiF)_r(AlF₃)_s

The search for a chemical compound which forms a simple eutectic system with lithium hexafluoroaluminate in the subsystem Li₃AlF₆—AlF₃ is based on the analysis of the liquidus curve of Li₃AlF₆. We shall use experimental data published in [5]

$$\Delta H^f(\text{Li}_3\text{AlF}_6)(\text{calor}) = 88\,285 \text{ J mol}^{-1}, \quad T^f(\text{Li}_3\text{AlF}_6) = 1055 \text{ K}$$

$$T^E = 981 \text{ K}, \quad x^E(\text{LiF}) = 0.65$$

The transformation of concentration coordinates of the eutectic point is based on the scheme



It follows that

$$y(\text{Li}_3\text{AlF}_6) = \frac{(r+s)x - r}{(r+s-4)x - r + 3} \quad (2b)$$

The activity of Li₃AlF₆ calculated according to eqn (1) using the above given experimental data equals

$$a^E(\text{Li}_3\text{AlF}_6) = 0.4680$$

Similarly as in the former section we made calculations for a set of physically possible chemical compounds. The results are summarized in Table 2. It follows that the applied method confirms the presence of the compound LiAlF_4 as the nearest neighbour of Li_3AlF_6 in the studied system. The presence of the compound $\text{Li}_3\text{Al}_2\text{F}_9$, which has been suggested by *Pushin* and *Baskov* [6], seems to be from the thermodynamic point of view unprobable. The proof of the existence of compound LiAlF_4 disproves simultaneously the assumption about the presence of the compound of the type $\text{Li}_5\text{Al}_3\text{F}_{14}$ which could be made on the basis of paper [7] or on the basis of physicochemical similarity between the systems $\text{LiF}-\text{AlF}_3$ and $\text{NaF}-\text{AlF}_3$.

Table 2

Calculated values of $\Delta H^f(\text{Li}_3\text{AlF}_6)$ and $D(\text{Li}_3\text{AlF}_6)$ for the systems of the type $\text{Li}_3\text{AlF}_6-(\text{LiF}), (\text{AlF}_3)_x$

System	$y^E(\text{Li}_3\text{AlF}_6) = f[x^E(\text{LiF})]$	$\Delta H^f(\text{Li}_3\text{AlF}_6)/\text{J mol}^{-1}$	$D(\text{Li}_3\text{AlF}_6)$
$\text{Li}_3\text{AlF}_6-\text{AlF}_3$	$x/(3-3x) = 0.619$	55 778	0.756
$\text{Li}_3\text{AlF}_6-\text{LiAlF}_4$	$(2x-1)/(2-2x) = 0.429$	98 410	1.091
$\text{Li}_3\text{AlF}_6-\text{LiF} \cdot 2\text{AlF}_3$	$(3x-1)/(2-x) = 0.704$	40 812	0.664
$\text{Li}_3\text{AlF}_6-2\text{LiF} \cdot 3\text{AlF}_3$	$(5x-2)/(x+1) = 0.758$	32 527	0.619
$\text{Li}_3\text{AlF}_6-3\text{LiF} \cdot 2\text{AlF}_3$	$(5x-3)/x = 0.3846$	111 117	1.217
$\text{Li}_3\text{AlF}_6-5\text{LiF} \cdot 3\text{AlF}_3$	$(8x-5)/(4x-2) = 0.333$	127 869	1.405

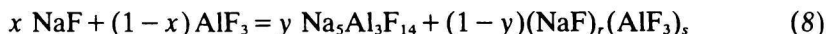
The subsystem $\text{Na}_3\text{AlF}_6-\text{AlF}_3$

The most complicated compound in the subsystem $\text{Na}_3\text{AlF}_6-\text{AlF}_3$ which we know for sure is the incongruently melting chiolite $\text{Na}_5\text{Al}_3\text{F}_{14}$. It forms with another component a simple eutectic system. However, until now there are not unified opinions on the nature of this compound. Some authors claim that it is AlF_3 , the other propose NaAlF_4 . The first direct proof of the existence of the compound NaAlF_4 was given by *Howard* [8] who identified it by an X-ray analysis in condensate of vapours of the mixture of NaF and AlF_3 , the composition of which was close to NaAlF_4 . Soon after that this discovery was confirmed by *Ginsberg* and *Böhmm* [9] and by *Mashovets et al.* [10]. In the phase diagram of the system in question the compound NaAlF_4 was found only when the investigation was carried out in a closed atmosphere [11, 12]. It has been generally assumed that when an open system $\text{Na}_3\text{AlF}_6-\text{AlF}_3$ is investigated the existence of the compound NaAlF_4 cannot be demonstrated.

In paper [13] we presented the experimental proof of the existence of this compound in the phase diagram of the system chiolite— NaAlF_4 studied in an open

atmosphere. Now we shall complete the experimental result with the thermodynamic analysis of the liquidus curve of chiolite (CH) according to the method described above.

If we make the transformation according to the scheme



it holds

$$y(\text{CH}) = \frac{x(r+s) - r}{x(r+s-8) - r + 5} \quad (2c)$$

Instead of eqn (3) we used the relationship

$$\Delta H^r(\text{CH}) = R \frac{T^p T^E}{T^p - T^E} \ln \frac{a^p(\text{CH})}{a^E(\text{CH})} \quad (9)$$

Foster's experimental data [14] on the peritectic and eutectic points were used

$$T^p = 1014 \text{ K}, T^E = 967 \text{ K}, x^p(\text{CH}) = 0.592, x^E(\text{CH}) = 0.535$$

This approach allows to eliminate the unknown value $T^r(\text{CH})$.

According to Cochran [15] $\Delta H^r(\text{CH})$ equals $229\,970 \text{ J mol}^{-1}$. Comparison of this value with calculated $\Delta H^r(\text{CH})$, which are summarized in Table 3, shows that

Table 3

Calculated values of $\Delta H^r(\text{CH})$ for the systems CH—(NaF)_r(AlF₃)_s,
CH stands for chiolite

System	$a(\text{CH}) = f[x(\text{NaF})]$	$a^p(\text{CH})$	$a^E(\text{CH})$	$\Delta H^r(\text{CH})/\text{J mol}^{-1}$
CH—AlF ₃	$x/(5-7x)$	0.692	0.426	83 930
CH—NaAl ₂ F ₇	$(3x-1)/(4-5x)$	0.746	1.457	85 190
CH—NaAlF ₄	$(2x-1)/(4-6x)$	0.411	0.089	266 030

the liquidus curve of chiolite is thermodynamically consistent only if we assume that its nearest neighbour is the compound NaAlF₄.

The subsystem K₃AlF₆—AlF₃

In the subsystem K₃AlF₆—AlF₃ no solid solutions on the base of potassium hexafluoroaluminate have been found. Only the existence of incongruently melting potassium hexafluoroaluminate is stated [16, 17]. Phillips *et al.* [17] investigated by means of X-ray analysis a possibility of formation of the compound K₂AlF₅. The result, however, was negative. With the exception of Pushin and Baskov [6], who

consider a possibility of formation of the compound $3\text{KF} \cdot 2\text{AlF}_3$, prevails the opinion that KAlF_4 forms with K_3AlF_6 a simple eutectic system and that in this system no compound occurs which could be an analogue to chiolite in the system $\text{NaF}-\text{AlF}_3$.

The calculations presented here are based on the experimental data published by *Jenssen* [16]

$$\Delta H^{\text{f}}(\text{K}_3\text{AlF}_6) = 122\,600 \text{ J mol}^{-1}, \quad T^{\text{f}}(\text{K}_3\text{AlF}_6) = 1273 \text{ K}$$

$$T^{\text{E}} = 833 \text{ K}, \quad x^{\text{E}}(\text{K}_3\text{AlF}_6) = 0.55$$

The thermodynamic activity of K_3AlF_6 in the eutectic point, calculated according to the relationship (1) using the above data equals

$$a^{\text{E}}(\text{K}_3\text{AlF}_6) = 0.0022$$

The concentration coordinate of the eutectic point, x^{E} (the mole fraction is given in the system $\text{KF}-\text{AlF}_3$), was transformed according to the scheme

$$x \text{ KF} + (1-x) \text{ AlF}_3 = y \text{ K}_3\text{AlF}_6 + (1-y)(\text{KF})_r(\text{AlF}_3)_s \quad (10)$$

It follows that

$$y = \frac{(r+s)x - r}{(r+s-4)x - r + 3} \quad (2d)$$

As in the former case we made thermodynamic calculations with different chemical compounds of the type $(\text{KF})_r(\text{AlF}_3)_s = \text{Z}$ assuming that the stoichiometric coefficients r and s are low integers and that the figurative points of these compounds are in the concentration range $0 < x^{\text{Z}}(\text{KF}) < 0.55$. The results are summarized in Table 4. It follows that the application of the method disproves the possibility of

Table 4

Calculation of $\Delta H^{\text{f}}(\text{K}_3\text{AlF}_6)$ and $D(\text{K}_3\text{AlF}_6)$ for different systems of the type $\text{K}_3\text{AlF}_6-(\text{KF})_r(\text{AlF}_3)_s$

System	$y^{\text{E}} = f(x^{\text{E}})$	$\Delta H^{\text{f}}(\text{K}_3\text{AlF}_6)/\text{J mol}^{-1}$	$D(\text{K}_3\text{AlF}_6)$
$\text{K}_3\text{AlF}_6-\text{KF} \cdot \text{AlF}_3$	$(2x-1)/(2-2x) = 0.1111$	44 030	0.0198
$\text{K}_3\text{AlF}_6-\text{KF} \cdot 2\text{AlF}_3$	$(3x-1)/(2-x) = 0.4483$	16 076	0.0049
$\text{K}_3\text{AlF}_6-\text{KF} \cdot 3\text{AlF}_3$	$(4x-1)/2 = 0.6000$	10 236	0.0037
$\text{K}_3\text{AlF}_6-\text{KF} \cdot 4\text{AlF}_3$	$(5x-1)/(x+2) = 0.6863$	7 543	0.0032
$\text{K}_3\text{AlF}_6-\text{KF} \cdot 5\text{AlF}_3$	$(6x-1)/(2x+2) = 0.7419$	5 982	0.0030
$\text{K}_3\text{AlF}_6-2\text{KF} \cdot 3\text{AlF}_3$	$(5x-2)/(x+1) = 0.4839$	14 545	0.0045
$\text{K}_3\text{AlF}_6-2\text{KF} \cdot 5\text{AlF}_3$	$(7x-2)/(3x+1) = 0.6981$	7 202	0.0032
$\text{K}_3\text{AlF}_6-3\text{KF} \cdot 4\text{AlF}_3$	$(7x-3)/3x = 0.5152$	13 289	0.0043
$\text{K}_3\text{AlF}_6-3\text{KF} \cdot 5\text{AlF}_3$	$(8x-3)/4x = 0.6364$	9 056	0.0035
$\text{K}_3\text{AlF}_6-4\text{KF} \cdot 5\text{AlF}_3$	$(9x-4)/(5x-1) = 0.5429$	12 240	0.0041
$\text{K}_3\text{AlF}_6-\text{AlF}_3$	$x/(3-3x) = 0.4074$	17 993	0.0054

the existence of an arbitrary compound, even of pure AlF_3 , as the nearest neighbour in the system $\text{K}_3\text{AlF}_6\text{—Z}$. The disagreement between the calculated values $\Delta H^f(\text{K}_3\text{AlF}_6)$ and the calorimetric value and low values of the coefficients $D(\text{K}_3\text{AlF}_6)$ cannot be explained satisfactorily neither by deviation of the system from ideality nor dissociation of the complex anion AlF_6^{3-} , not even by possible inaccuracy in determination of the experimental data.

The only acceptable explanation is that between K_3AlF_6 and the eutectic point there is another, probably unstable, chemical compound Q which has not been observed until yet. Therefore the experimentally found eutectic point $x^E(\text{KF}) = 0.55$ belongs to the subsystem Q—KAlF_4 . For verification of this assumption we shall use again our method.

The calorimetric value of $\Delta H^f(\text{KAlF}_4)$ is not known. *Jenssen* claims [16] that KAlF_4 is formed by the peritectic reaction at $T^p = 853$ K. However, the concentration coordinate of the peritectic point is not given and thus the relationship similar to eqn (8) cannot be used. Therefore we can do only an approximate calculation assuming that this compound melts congruently at the temperature 860 K. We shall use a method based on the additivity of enthalpies of fusion of basic substances

$$\Delta H^f(\text{KAlF}_4) = \Delta H^{f/s}(\text{KF}) + \Delta H^{f/s}(\text{AlF}_3) + \Delta H_{\text{bond}} \quad (11)$$

$$T = 860 \text{ K}$$

The terms in eqn (11) were obtained using the following data

KF [18]

$$C_p^l/\text{J mol}^{-1} \text{ K}^{-1} = 66.94$$

$$C_p^s/\text{J mol}^{-1} \text{ K}^{-1} = 49.71 + 9.29 \times 10^{-3} T/\text{K} - 3.01 \times 10^5 (T/\text{K})^{-2}$$

AlF_3 [19]

$$\Delta H^{f/s}/\text{J mol}^{-1} = 25.94 + 0.02 T/\text{K}$$

We assume that the quantity ΔH_{bond} is given by a number of bonds of the complex anion with respect to one potassium cation. Then

$$\Delta H_{\text{bond}} = \frac{1}{3} [\Delta H^f(\text{K}_3\text{AlF}_6) - \Delta H^{f/s}(\text{KF}) - \Delta H^{f/s}(\text{AlF}_3)] \quad (12)$$

$$T = 1273 \text{ K}$$

Using partial results and putting them in eqn (11) we obtain

$$\Delta H^f(\text{KAlF}_4) = 78\,847 \text{ J mol}^{-1}$$

We shall use this value in our calculations instead of the unknown calorimetric quantity $\Delta H^f(\text{KAlF}_4)$ (calor). By means of eqn (1) we get

$$a^E(\text{KAlF}_4) = 0.6995$$

As we assume the experimentally determined eutectic point $x^E(\text{KF}) = 0.55$ is the intersection of the liquidus curves of compound KAlF_4 and of the unknown compound $\text{Q} = (\text{KF})_r(\text{AlF}_3)_s$. As this compound must lie in the concentration interval limited by the eutectic point and the compound K_3AlF_6 its figurative point must be in the concentration range 55–75 mole % KF. Moreover, it is reasonable to consider only the compounds with stoichiometric coefficients lower or equal to 5. The concentration coordinate of the eutectic point was transformed according to the scheme

$$x \text{ KF} + (1 - x) \text{ AlF}_3 = y \text{ KAlF}_4 + (1 - y)(\text{KF})_r(\text{AlF}_3)_s \quad (13)$$

Then

$$y = \frac{r - (r + s)x}{(2 - r - s)x + r - 1} \quad (2e)$$

Results of the calculations are presented in Table 5. It follows that optimum agreement between $\Delta H^f(\text{KAlF}_4)$ and " $\Delta H^f(\text{KAlF}_4)$ (calor)" and optimum value of the criterion D is achieved when the presumed compound has the composition close to $\text{K}_3\text{Al}_2\text{F}_9$.

Table 5

Calculation of $\Delta H^f(\text{KAlF}_4)$ and $D(\text{KAlF}_4)$ for different systems of the type $\text{KAlF}_4 - (\text{KF})_r(\text{AlF}_3)_s$

System	$y^E(\text{KAlF}_4) = f(x^E)$	$\Delta H^f(\text{KAlF}_4)/\text{J mol}^{-1}$	$D(\text{KAlF}_4)$
$\text{KAlF}_4 - 3\text{KF} \cdot \text{AlF}_3$	$(3 - 4x)/(2 - 2x) = 0.8889$	25 981	0.7869
$\text{KAlF}_4 - 2\text{KF} \cdot \text{AlF}_3$	$(2 - 3x)/(1 - x) = 0.7778$	55 435	0.8993
$\text{KAlF}_4 - 3\text{KF} \cdot 2\text{AlF}_3$	$(3 - 5x)/(2 - 3x) = 0.7143$	74 223	0.9793
$\text{KAlF}_4 - 5\text{KF} \cdot 2\text{AlF}_3$	$(5 - 7x)/(4 - 5x) = 0.9263$	16 889	0.7552
$\text{KAlF}_4 - 5\text{KF} \cdot 3\text{AlF}_3$	$(5 - 8x)/(4 - 6x) = 0.8571$	34 017	0.8161

Conclusion

Despite of simplifications used it can be stated that the proposed method indicates unambiguously the presence of compounds LiAlF_4 , NaAlF_4 , and KAlF_4 in the systems $\text{MF} - \text{AlF}_3$ (M being Li, Na, and K, respectively). The fact that these compounds were not always determined in open systems is not in contradiction with this conclusion. It can be assumed that the tetrafluoroaluminates are compounds which are unstable at normal conditions and they melt incongruently. They exist probably only in a narrow temperature interval and can decompose according to the eutectoid reactions



or



Therefore a direct proof of the existence of pure compounds in the system MF—AlF₃ may be difficult when a common experimental technique is used.

In a mixture with another component, *i.e.* in diluted state, the activity of MAIF₄ is diminished in comparison with the activity of pure MAIF₄, which makes these compounds more stable. Their objective presence in the system influences inevitably position of the eutectic point in the corresponding subsystem.

The conclusion about the possible existence of a new compound K₃Al₂F₉ evokes the necessity of a new thorough investigation of the whole system.

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