Thermodynamic properties and phase equilibria of the potassium–indium system by electromotive force measurements

T Takenaka†, A Petric‡ and Marie-Louise Saboungi

Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4837, USA

Abstract. The potassium–indium system has been studied using galvanic cells with potassium beta alumina as the electrolyte. The thermodynamic properties of the liquid solution have been determined between 0 and 52 at.% potassium. There is some evidence for a very weak liquid compound near 35 at.% K, but not at 50 at.% K. Changes are proposed for the potassium–indium phase diagram, including the liquidus temperature and the existence of new compounds.

1. Introduction

The potassium–indium system is one of a group of alloys where charge transfer plays a significant role. The binary constituents of such alloys are always an electronegative metal and an electropositive metal (usually an alkali metal). Ionic alloys are a limiting example of such systems where charge transfer results in positive and negative ionic species in the liquid state forming a 'liquid compound'. One of the more interesting of such compounds is the equiatomic mixture of potassium and lead. Results of resistivity measurements [1], thermodynamic measurements [2], and neutron scattering experiments [3] have suggested the presence of a K_4Pb_4 Zintl-type compound in the liquid phase. A similar structure has been postulated for K–Sn, based on the anomalously high excess heat capacities of these alloys [4]. The question remains whether such a compound might be formed in alloys such as alkali–indium, which contain a group III element. Some evidence for it has been presented by way of a broad maximum in the variations of the electrical resistivity [5] with composition. Thermodynamic evidence for such a compound would be a high excess heat capacity coupled with a high excess stability.

We have derived the thermodynamic properties, including the Gibbs free energy ΔG, the entropy ΔS and the excess heat capacity for K–In over a temperature range of

---

† Present address: Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Katahira-cho, Sendai 980, Japan.
‡ Present address: McMaster University, Department of Materials Science and Engineering, Hamilton, Ontario, Canada L8S 4L7.

390–550 °C from 0 to 52 at.% K. The phase diagram was accurately determined from the measurements.

2. Experiment

Potassium metal having a purity of 99.85 was supplied in sealed ampoules by Callery Chemical Corporation, Callery, PA 16024. High purity indium rods were purchased from Federated Metals Division of Asarco, Inc., Newark, NJ. All results were obtained from EMF (electromotive force) measurements of galvanic concentration cells in a high-purity helium-filled glove box. The cell configuration was as follows:

K–Bi (RE)|K–β alumina|K–Pb (CE)|K–β alumina|K–In (WE)
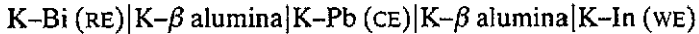
In practical terms, two half cells consisting of a reference electrode (RE) and a working electrode (WE) were immersed in a counter electrode (CE) bath, which was continuously stirred and served as a source/sink for potassium. The composition of the CE was approximately 2 at.% K and the balance lead. The RE was 8 at.% K and the balance bismuth. The reference electrode was calibrated against a pure potassium half cell at the start and checked periodically during the experiment. The dilute alkali metal RE had a longer life and could be used at higher temperatures than could a pure alkali metal cell.

The cells consisted of a K–β alumina tube (15 mm diameter × 30 mm long) which acted as both container and electrolyte. To close the cell, we attached an α alumina annulus to the β alumina tube by means of a Kovar glass joint and then made a mechanical seal with a tantalum plug. Most experiments were begun with a WE containing indium only; potassium was added during the experiment by coulometric titration. This allowed for precise changes to the composition and avoided disturbing the cell once the experiment began. Further details of the experimental procedure are available from earlier publications [2].

3. Results

The EMF was measured either isothermally as a function of composition to determine the Gibbs energy and excess stability or as a function of temperature to obtain the entropy, excess heat capacity, and points on the phase diagram.

3.1. Thermodynamic properties

Equilibrium was difficult to reach in the K–In system for extremely low amounts of K; many repeated attempts and long equilibrium times did not allow us to obtain stable EMF for $X_K < 0.001$. Therefore, we have not derived an experimental Nernst slope. At higher concentrations, the EMFs were stable and reproducible to better than a couple of mV between independent runs.

For $X_K > 0.001$, an activity coefficient γ_K can be calculated from the EMFs by the relation:

$$\ln \gamma_K = FE/RT - \ln X_K$$

where F is the Faraday constant and E is the EMF. Figure 1 shows the variations of
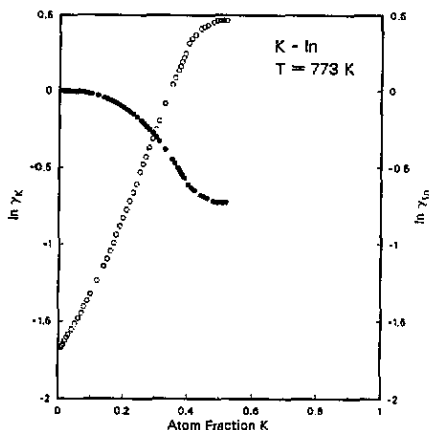
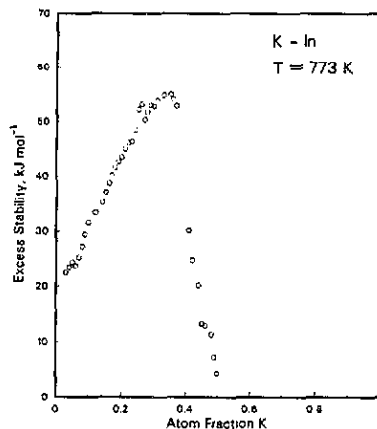Figure 1. Activity coefficients of potassium and indium at 500 °C.

Figure 2. Excess stability function at 500 °C.

$\ln \gamma_K$ and $\ln \gamma_{In}$. Note that $\ln \gamma_{In}$ was deduced from $\ln \gamma_K$ by Gibbs–Duhem integration. The limiting slope of $\ln \gamma_K$, which is defined as:

$$\varepsilon = (\partial \ln \gamma_K / \partial X_K)_{X_K \to 0}$$

was found to be 6.65, 7.02 and 7.80 at 500, 450 and 400 °C, respectively. These values are high compared with systems such as alkali–lead and alkali–bismuth that have limiting slopes between three and five. If the limiting slope is multiplied by RT, a value of 42.8 kJ mol^{-1} is obtained at the three temperatures.

The Darken excess stability function is defined as:

$$\text{ES} = (RT/1 - X_K)(\mathrm{d} \ln \gamma_K / \mathrm{d} X_K)$$

and can be computed directly from the EMFs. The peak in excess stability for three independent cells occurred near 35 at.% K and had a magnitude of 55 kJ mol^{-1} (figure 2). By comparison, excess stabilities of 250 kJ mol^{-1} have been found for liquid K–Pb and 325 kJ mol^{-1} for liquid K–Bi at equiatomic compositions. These is no indication of a 1:1 liquid complex from the excess stability curve for K–In.

The Gibbs energy of mixing has a minimum at 36 at.% K (figure 3), approximately the same composition as the peak in ES. The activity of potassium at this point is 0.39, which is a positive deviation from ideality. Data for the EMF, Gibbs energy, and ES are listed in table 1. Despite the moderate difference in electronegativity, potassium and indium do not form a very stable solution.

The partial entropies were obtained from the slopes of EMF with respect to temperature ($\Delta S_K = F \, \mathrm{d}E/\mathrm{d}T$). The data points were fitted to quadratic polynomials (table 2) from which the entropies and excess heat capacity of mixing ($\Delta C_p = FT \, \mathrm{d}^2(E/T)/\mathrm{d}T^2$) were derived. Values of the partial and integral entropies are given in table 3. Variations of the entropy and excess entropy of mixing are plotted in figure 4. A plot of the excess heat capacity of mixing is shown in figure 5. Although there is no peak in the composition range of this study, a shoulder is evident near 30 at.% K.

3.2. The phase diagram

A change of phase is signalled by a break in the slope of the EMF versus temperature plot. Invariant lines such as the liquidus surface and invariant points such as the eutectic can

Table 1. The EMF, Gibbs energy of mixing, and excess stability of potassium–indium alloys at 500 °C. Values are from one run with composition varied by coulometric titration.

| X_K	E (mV)	ΔG^m (J mol^{-1})	ES (J mol^{-1})
0.0300	339.14	−1183	22484
0.0400	317.79	−1497	23431
0.0500	300.45	−1792	24329
0.0600	286.00	−2070	23694
0.0700	273.42	−2335	25238
0.0800	261.95	−2588	27211
0.0900	251.50	−2829	29465
0.1000	241.55	−3059	31575
0.1200	223.55	−3489	33322
0.1400	206.98	−3881	35269
0.1500	199.20	−4064	37034
0.1600	191.56	−4238	38723
0.1700	184.12	−4403	40129
0.1800	176.81	−4560	41688
0.1904	169.31	−4714	42713
0.2000	162.62	−4848	43509
0.2100	155.75	−4979	45073
0.2200	148.89	−5102	46202
0.2300	142.22	−5216	46387
0.2400	135.69	−5323	48503
0.2535	126.75	−5453	52248
0.2616	121.16	−5524	53174
0.2700	115.87	−5591	50393
0.2800	109.65	−5663	51793
0.2900	103.38	−5727	53027
0.3000	97.25	−5783	52842
0.3100	91.27	−5830	53905
0.3300	79.42	−5899	54806
0.3521	66.79	−5937	54964
0.3600	62.43	−5940	54132
0.3700	57.07	−5938	52889
0.4100	36.39	−5842	30178
0.4100	36.39	−5842	30178
0.4200	33.16	−5800	24755
0.4400	27.26	−5700	20160
0.4502	24.97	−5642	13235
0.4600	22.79	−5583	12896
0.4800	18.57	−5449	11342
0.4900	16.73	−5377	7290
0.5000	15.08	−5302	4295
0.5100	13.62	−5224	−123
0.5200	12.48	−5143	−185
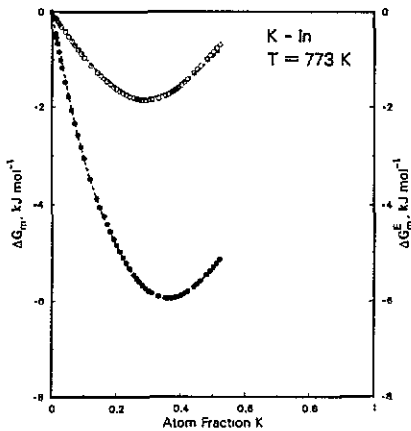
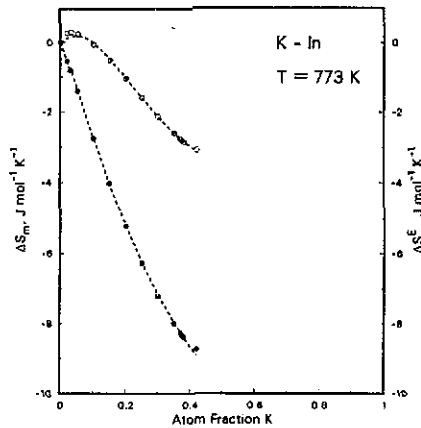**Figure 3.** Gibbs energy of mixing for potassium–indium at 500 °C.

Figure 4. Partial entropies of mixing at 500 °C for the potassium–indium system.

Table 2. Coefficients of the polynomials $E = A + BT + CT^2$ corresponding to the data in the liquid region of figure 6 used to derive entropy and excess heat capacity data. The final column gives the liquidus temperature in degrees Celsius.
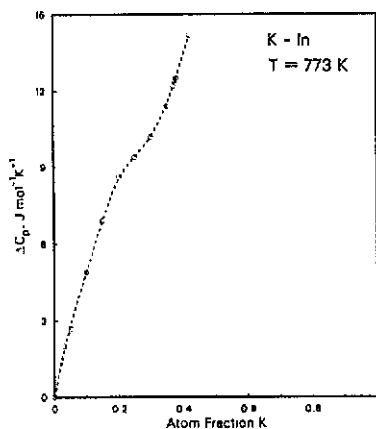
X_K	A	B	C $(\times 10^{-4})$	Liquidus temp. (°C)
0.02	460.22	−0.38053	4.361	—
0.05	387.91	−0.29791	2.536	—
0.10	364.10	−0.40715	3.398	397
0.15	304.51	−0.31528	2.142	421
0.20	277.00	−0.34713	2.421	436
0.25	194.37	−0.15542	5.528	459
0.30	199.95	−0.30709	2.096	475
0.35	135.93	−0.18329	1.023	480
0.355	184.05	−0.37955	2.924	480
0.37	182.56	−0.41074	3.258	480
0.375	1.4298	−0.26179	1.895	479
0.38	1.5706	−0.34318	2.650	478
0.42	1.2023	−0.29456	2.414	470

be determined very precisely by this method since every point is obtained at equilibrium. A compilation of liquidus points is given in table 2.

The K–In system proved more difficult to analyse than was anticipated because of slow equilibration, particularly in the region beyond 35 at.% K. Beginning with pure indium at 400 °C, we observe a single-phase region up to 11.5 at.% K. A two-phase field exists from 11.5 to 20 at.% K, as indicated by a constant EMF reading. The first solid compound appears at 20 at.% K, corresponding to KIn_4, which is in agreement with Thümmel and Klemm [6], but differs from the currently accepted phase diagram [7], which shows a KIn_3 phase.

Table 3. Values of the partial and integral entropies of mixing and the excess heat capacity at 500 °C.

X_K	ΔS_K J mol^{-1} K^{-1}	ΔS J mol^{-1} K^{-1}	ΔC_P J mol^{-1} K^{-1}
0.02	5.360	0.274	1.4
0.03	−0.159	0.298	2.0
0.05	−4.288	0.245	2.7
0.10	−6.481	−0.054	4.9
0.15	−9.752	−0.508	6.9
0.20	−9.752	−1.053	8.6
0.25	−9.786	−1.599	9.4
0.30	−9.405	−2.133	10.2
0.35	−8.085	−2.603	11.4
0.37	−8.192	−2.774	12.2
0.375	−7.750	−2.815	12.4
0.38	−7.826	−2.857	12.5
0.42	−5.127	−3.084	14.2

Figure 5. The excess heat capacity for K–In alloys at 500 °C.

A small drop in EMF occurs at 29–29.5 at.% K with very stable potentials between 22 and 29 at.% (189 mV) and 30 and 32 at.% (183 mV). This could be within experimental error or it could be due to a weak compound that exists over a narrow temperature range with stoichiometry K_2In_5 or K_3In_7.

The strongest compound exists over a considerable range of composition. Following the 400 °C isotherm, the EMF drops from 183 mV just before 33 at.% K to 26 mV at 36 at.% K. The highest melting point of this solid is 480 °C at a composition between 0.35 and 0.36 at.% K. This compound may be designated KIn_2 or K_5In_9.

The final readings taken below the monotectic temperature and above 50 at.% K (the composition is uncertain because of leakage of potassium from the cell) showed an EMF of less than 2 mV, which indicates low solubility of indium in the K-rich liquid. The exact composition of the liquidus cannot be determined due to an error limit of several millivolts. However, it is possible that another solid compound hitherto undetected exists between 42 and 50 at.% K. (Such a compound is found in the Rb–In system at
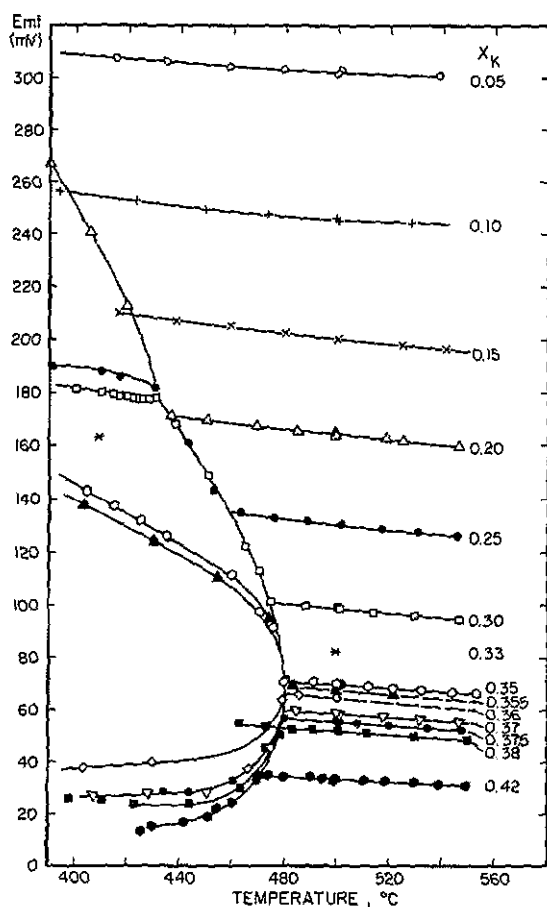
Figure 6. Plot of EMF versus temperature. The discontinuity in slope of each composition corresponds to the liquidus temperature. Data points that extend through the liquidus represent undercooling.

45 at.% Rb). No readings were taken in the liquid beyond 52 at.% K in the region of the miscibility gap.

Figure 6 is an EMF depiction of phase relations between 5 and 42 at.% K. The EMFs in the liquid vary nearly linearly with temperature. When the liquid is cooled into the two-phase region, the EMF follows the liquidus line to the nearest triple point, although undercooling is often observed. Data points below the liquidus correspond to solid–solid equilibria or to a single-phase solid. For example, in figure 5, one sees that compositions between 33 and 38 at.% K cool to form the solid compound K_5In_9. The two triple points at the 180 mV potential correspond to the peritectic reactions that form KIn_4 and K_2In_5/K_3In_7 on the phase diagram in figure 7.

To aid identification of the solid phases, samples having compositions of 25, 30, 40, 50 and 60 at.% K were prepared for XRD. Two preparation techniques were used. The first was to react the components at 250 °C for two or three days. The second was to heat the mixture to 500 °C for one hour, agitate it by shaking, and then furnace cool.

The low-temperature route produced a mixture of three phases, whereas the high-temperature treatment yielded one or two phases. The results were combined, and the following patterns were identified to be representative of equilibrium conditions:
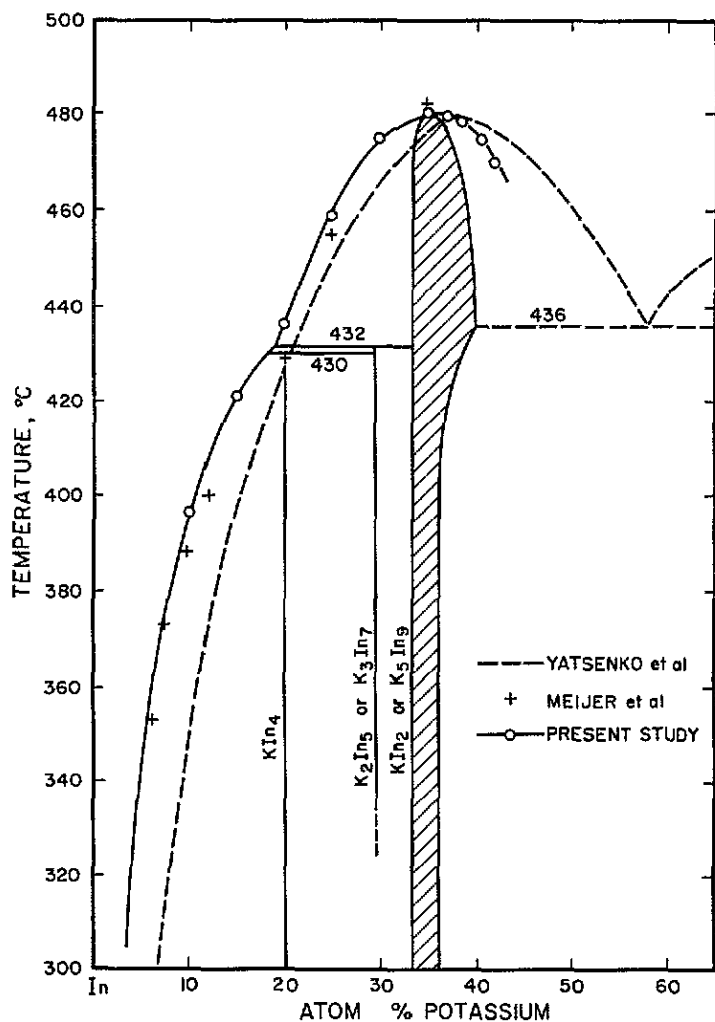
Figure 7. The K–In phase diagram showing changes to the diagram of Moffatt [7].

25 at.% K	KIn_4
30 at.% K	O pattern
40 at.% K	O pattern + T pattern
50 at.% K	T pattern
60 at.% K	T pattern + potassium.

The O pattern corresponds to the strong 33–36 at.% K phase and the T pattern appears to be an as yet unidentified phase in the composition range above 36 at.% K. The weak K_2In_5 phase may exist at 400 °C, but may decompose at lower temperatures and is therefore not found in the x-ray patterns.

The K–In phase diagram has been studied by Thümmel and Klemm [6] and by Yatsenko *et al* [8]. Both studies are consistent with respect to the formation of a

Table 4. Peak values of resistivity and excess stability for liquid alloys of potassium with group III, IV and V metals.

	ρ $\mu\Omega$ cm	X_K	T Kelvin	ES kJ mol^{-1}	X_K	T Kelvin
K–In	480	0.50	723 [5]	55	0.35	77 [5]
K–Pb	1000	0.49	859 [5]	240	0.52	879 [2]
K–Bi	2400	0.75	973 [10]	1050	0.75	1023 [11]

miscibility gap on the K-rich side of the diagram. Meijer *et al* [5] confirm the immiscibility region on the potassium-rich side, but report higher liquidus temperatures on the In side of the diagram. We also find a higher liquidus temperature in this region. A phase diagram incorporating these data is shown in figure 7. Further study is needed to determine the stoichiometry range and thermal stability range of the solid compounds.

4. Discussion

An earlier study of the K–In system has been published by Dergacheva *et al* [9] who used a glass electrolyte to obtain EMF measurements. At compositions up to 15 at.% K, their EMF readings are slightly higher than ours. At a composition of 40 at.% K, their EMF values are about 30% higher and the difference increases to a factor of two or more at higher compositions. Consequently, the values of Gibbs energy, entropy, and excess stability are not in good agreement with this study.

Meijer *et al* [5] have studied the resistivities of these alloys. They found a maximum in resistivity at the equiatomic composition and a corresponding minimum in the derivative of resistivity with temperature. The peaks were attributed to compound formation in liquid KIn. They also noted a trend among Li–In, Na–In, and K–In of a shift in the resistivity peak from the 3:5 composition to the equiatomic composition, similar to alkali–lead alloys.

We have also seen this trend in the thermodynamic properties of alkali–lead alloys, but find different behaviour in this system. The only excess stability peak for K–In occurs at 35 at.% K. There is no corresponding peak, only a weak shoulder, in the excess heat capacity near this composition. Other systems studied previously (alkali–bismuth, alkali–lead, alkali–tellurium) have exhibited coincident peaks of ES and ΔC_p, which may be considered a strong argument in favour of liquid compound formation. A comparison of excess stability and resistivity among various systems is shown in table 4.

In this system, the peak in excess stability is largely a consequence of the asymmetrical shape of the Gibbs energy of mixing. The In-rich side of the phase diagram forms a more stable solution than the K-rich side, which exhibits a tendency to demixing. Therefore, the location of the excess stability peak at 35 at.% K is caused by the asymmetry in the system, and if a liquid compound exists at this point, it will be very weakly bonded. The lack of a peak in ES at 50 at.%, as well as the rise of a miscibility gap beyond 50 at.% K, leads us to discount the existence of a 50:50 KIn liquid compound.

5. Conclusions

Liquid solutions in the potassium–indium system show much less evidence of ionic character than systems having group IV or V electronegative metals. The electrical

resistivity and excess stability have small peak values in comparison with other systems. We find no evidence of an ordered liquid KIn compound. Some changes have been proposed to the phase diagram below 50 at.% K, including a change of stoichiometry from KIn_3 to KIn_4 and the possibility of another solid compound near the mid-composition.

Acknowledgments

References

[1] Calaway W F and Saboungi M-L 1983 *J. Phys. F: Metal Phys.* **13** 1213–23
[2] Saboungi M-L, Leonard S R and Ellefson J 1986 *J. Chem. Phys.* **85** 6072–81
[3] Reijers H T J, Saboungi M-L, Price D L, Richardson J W Jr, Volin K J and van der Lugt W 1989 *Phys. Rev.* B **40** 6018–29
  Saboungi M-L, Blomquist R, Volin K J and Price D L 1987 *J. Chem. Phys.* **87** 2278–81
[4] Reijers H T J 1990 *PhD Thesis* University of Groningen, The Netherlands
[5] Meijer J A, Geetsma W and van der Lugt W 1985 *J. Phys. F: Metal Phys.* **15** 899–910
[6] Thümmel R and Klemm W 1970 *Z. Anorg. u. Allgem. Chem.* **376** 44–63
[7] Moffatt W G 1979 *The Handbook of Binary Phase Diagrams* (Schenectaday, NY: General Electric Company)
[8] Yatsenko S P, Chuntonov K A, Bushmanov V D and Dieva V N 1974 Phase diagrams of the systems Ga–Na, Ga–K, In–K and In–Rb *Struktura Faz, Fazovye Prevrashcheniya i Diagramma Sostoyaniya Metallicheskih Sistem* (Moscow: Nauka) pp 198–201
[9] Dergacheva M B, Kozin L F and Khobdabergenova G R 1978 *Izv. Akad. Nauk.* **18**(5) 21–6
[10] Meijer J A 1988 *PhD Thesis* University of Groningen, The Netherlands p 127
[11] Petric A, Pelton A D and Saboungi M-L 1988 *J. Phys. F: Met. Phys.* **18** 1473–1489