

## The density and heat capacity of liquid Li/Na alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 321

(<http://iopscience.iop.org/0953-8984/6/2/004>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 14:33

Please note that [terms and conditions apply](#).

## The density and heat capacity of liquid Li/Na alloys

J Jost, D Heydt, J Spehr and H Ruppertsberg

Fachbereich Werkstoffwissenschaften und Fertigungstechnik, Universität des Saarlandes, Saarbrücken, Federal Republic of Germany

Received 20 August 1993

**Abstract.** Liquid Li/Na exhibits a miscibility gap with a critical temperature  $T_c = 577 \pm 1$  K and a critical composition  $x_c = 36 \pm 1.5$  at.% Na. At temperatures up to about 900 K we observed for the single-phase liquids an ideal behaviour of the molar volume with respect to variations of  $T$  and  $x$ . We studied the shape of the miscibility gap and observed a critical exponent  $\beta = 0.50 \pm 0.015$  in the range  $5 \times 10^{-5} < (T_c - T)/T_c < 2 \times 10^{-2}$ . At  $x_c$  the heat capacity  $c_p$  increases on approaching  $T_c$  with a critical exponent  $\alpha = 0.32 \pm 0.07$  which was observed in the range  $4 \times 10^{-3} < (T - T_c)/T_c < 0.44$ .

### 1. Introduction

Very little information is available on the thermodynamic properties of metallic systems with a miscibility gap in the liquid phase. Until now the variation of the heat capacity  $c_p$  with temperature  $T$  was determined at the critical composition  $x_c$  only in a semi-quantitative way for one single alloy, namely Ga/Hg. For  $\epsilon = (T - T_c)/T_c$  in the range  $5 \times 10^{-5} < \epsilon < 0.02$  Schürmann and Parks [1] observed a critical behaviour of  $c_p$  according to [2]

$$c_p = c_p^0 + (A/\alpha)|\epsilon|^{-\alpha} \quad (1)$$

with a critical exponent  $\alpha = 0.3 \pm 0.1$ , which considerably exceeds the values of 0.125 and 0.110 expected according to the 3D Ising model and the Landau–Ginzburg–Wilson formalism [2]. The classical Landau value is  $\alpha = 0$ .  $A$  is the critical amplitude.

In this paper we present  $c_p(T)$  data for liquid Li/Na at  $x_c = 35$  at.% Na and at 20 at.% Na.  $c_p$  was obtained according to an indirect method, proposed by Lewis and Randall [3] and based on the equation

$$c_p = T(\Delta p/\Delta T)_S(dV/dT)_p \quad (2)$$

allowing  $c_p$  to be obtained from the adiabatic variation of  $T$  with the pressure  $p$  and from the thermal expansion coefficient.

The phase diagram for Li/Na was evaluated by Down *et al* [4] from electrical resistivity data and thermal analysis. The authors confirmed the shape  $x(T)$  of the miscibility gap, which was earlier observed by Kanda *et al* [5] and by Schürmann and Parks [6]. Practically the same shape was found by Feitsma *et al* [7] who fitted the  $x(T)$  data with a polynomial of the order of 7, thus obtaining the following relation between  $T$  (°C) and  $x$  (at.% Na):

$$T = 101.15 + 28.6376x - 1.79722x^2 + 6.37593 \times 10^{-2}x^3 - 1.355154 \times 10^{-3}x^4 \\ + 1.701280 \times 10^{-5}x^5 - 1.161235 \times 10^{-7}x^6 + 3.28902 \times 10^{-10}x^7 \quad (3)$$

which yields  $T_c = 303.2^\circ\text{C}$  and  $x_c = 35.9$  at.% Na.

In addition, the latter authors [7] observed a divergence of the temperature derivative of the electrical resistivity at  $x_c$  on approaching  $T_c$ . An explanation of this effect in terms of critical exponents was given by Ruppertsberg and Knoll [8] in a paper dealing with the distance correlation of concentration fluctuations in liquid Li/Na calculated from a combination of small- and large-angle neutron diffraction investigations.

The shape of the miscibility gap is related to  $\epsilon$  by [2]

$$\Delta x = B\epsilon^\beta \quad (4)$$

where  $\Delta x$  is the difference between the concentrations of the coexisting phases. According to the 3D Ising and Landau–Ginzburg–Wilson formalisms the critical exponent  $\beta$  has values of 0.312 and 0.325, respectively. The classical Landau value is 0.5.  $B$  is the critical amplitude.

For liquid Li/Na the molar volume  $V(x, T)$ , the heat capacity  $c_p$  and the critical exponents  $\alpha$  and  $\beta$  have not yet been determined.

## 2. Experimental procedures

The preparation of the samples from then 3N pure metals and the experimental investigations were performed inside a glove box in a current of continuously purified argon. The composition of the alloys was checked by chemical analysis. Care was taken to obtain complete mixing of the two liquid phases before studying an alloy in the homogeneous liquid region.

The density was measured using the maximum bubble pressure method. An alloy with 96 at.% Na and alloys in nominal steps of 10% from 10 to 90 at.% Na were investigated according to the method which we described in a previous paper [9]. The bubble pressures were in these cases measured at constant temperatures for different positions of the pressure tube, which were changed by hand.

For the investigation of pure liquid Li and Na and of the alloy with  $x_c = 35$  at.% Na an automatized and fully computer controlled technique was used with slowly varying temperature of e.g.  $0.5 \text{ K min}^{-1}$ .  $T$  and  $p$  were controlled every 10 s and 50 ms, respectively. After eight bubbles, which correspond to about 2 min, the height of the bubble tube was varied with a step motor. Its position was controlled with a digitized instrument of 50 mm maximum amplitude and  $1 \mu\text{m}$  resolution. The reproducibility of the results obtained with this technique were much better than with the former method.

Figure 1 shows the  $V(T)$  points obtained for the pure components and for  $x_c = 35$  at.% Na in single automatized runs, and for the other compositions the points obtained in the discontinuous version. The figure also indicates the temperature ranges which were investigated. The molar volumes  $V(x)$  observed at 700 K and their temperature derivatives  $(dV(x)/dT)_p$  are given in figure 2. Following a proposition by Kanda *et al* [10] we also determined as a function of  $T$  the densities  $\rho(T)$  of both liquid phases which coexist below  $T_c$ . These values allow the evaluation of the binodal  $x(T)$  if  $V(x, T)$  is known. Figure 3 shows typical results for  $\rho(T)$  observed on cooling in the continuous mode and starting from a homogeneous alloy of critical composition.

For calculating  $c_p$  according to equation (2) we require in addition to  $(\partial V/\partial T)_p$  the values for  $(\Delta p/\Delta T)_S$ . Our apparatus for measuring the variation of  $T$  during loading and unloading with argon has been described in a previous paper [11]. This apparatus is now computer controlled and equipped with a stirring mechanism for accelerating the mixing of the two phases which would otherwise be very slow.  $\Delta p$  was chosen at about 7 bar, which yields a  $\Delta T$  of the order of 50 mK.

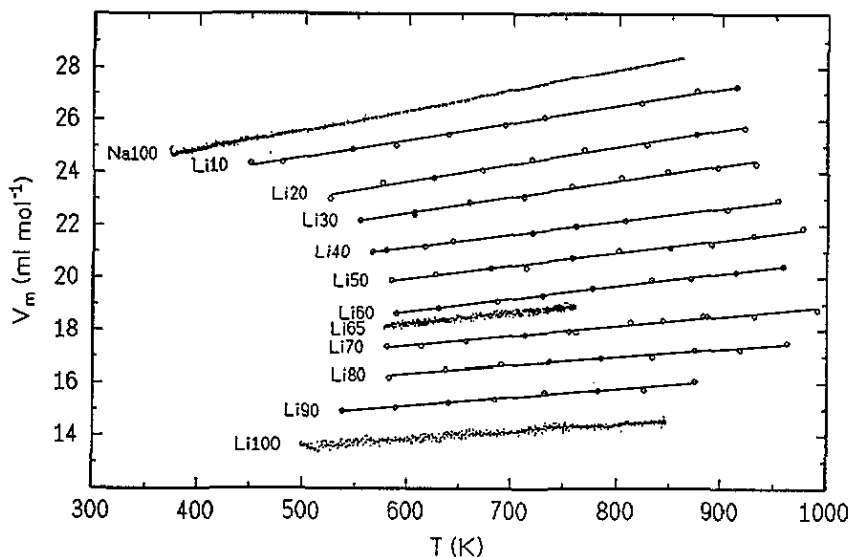


Figure 1. Experimentally obtained clouds of  $V(T)$  points obtained for three compositions by the computer-controlled maximum bubble pressure procedure during continuous variation of  $T$ . The data were obtained during a single run at the given composition. The curves for the other compositions were obtained with discontinuous experiments.

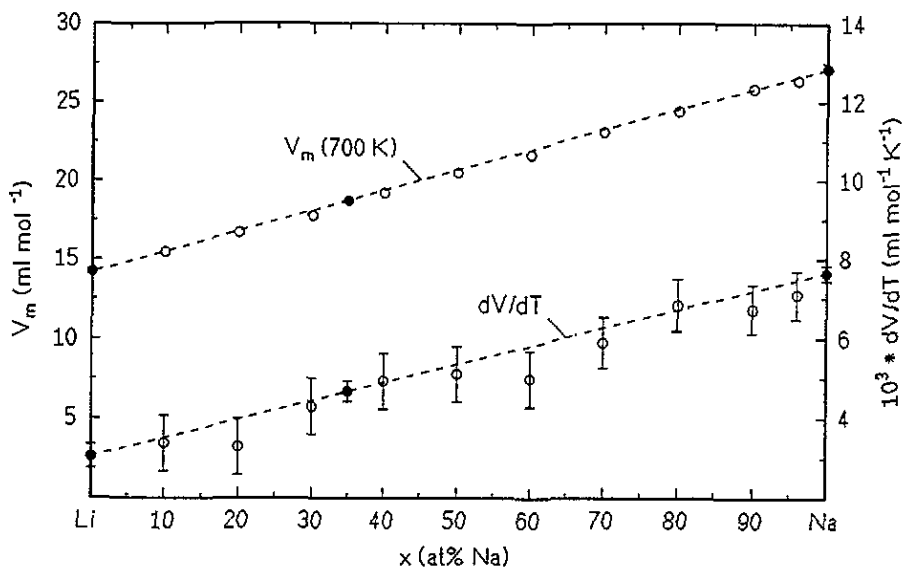


Figure 2.  $V(x)$  at 700 K and  $(dV/dT)(x)$  values obtained from linear least-square fits of the points given in figure 1. Broken lines, linear fits of the results from computer-controlled measurements (full circles).

### 3. Results and discussion

In the homogeneous liquid phase an ideal behaviour, with no indication of any critical

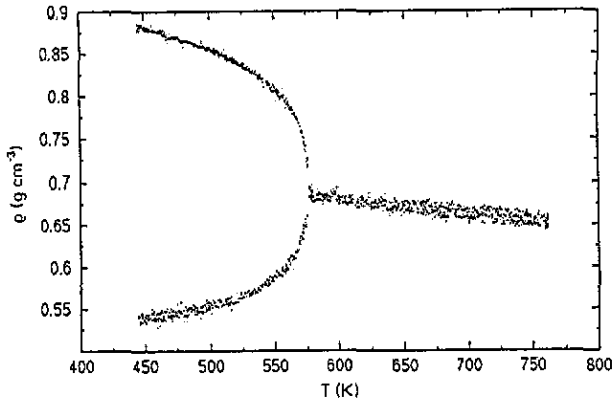


Figure 3.  $\rho(T)$  curves for an alloy with the composition  $x_c = 0.35$  at.% Na, observed on cooling from the single-phase region into the miscibility gap with two coexisting liquid layers.

effects, was observed for the variation of the molar volume with  $x$  and  $T$ :

$$V(x, T) = (1 - x/100)[V_{\text{Li}}^m + (dV_{\text{Li}}/dT)(T - T_{\text{Li}}^m)] + (x/100)[V_{\text{Na}}^m + (dV_{\text{Na}}/dT)(T - T_{\text{Na}}^m)] \quad (5)$$

with  $x$  given in at.% Na. Least-square fits of the experimental results for the automatized measurements, which are partly shown in figures 1 and 2, yield:  $(dV_{\text{Li}}/dT) = (3.1 \pm 0.2) \times 10^{-3} \text{ ml mol}^{-1} \text{ K}^{-1}$ ,  $(dV_{\text{Na}}/dT) = 7.64 \times 10^{-3} \pm 0.07 \text{ ml mol}^{-1} \text{ K}^{-1}$ ,  $V_{\text{Li}}^m = 13.45 \pm 0.09 \text{ ml mol}^{-1}$  and  $V_{\text{Na}}^m = 24.62 \pm 0.09 \text{ ml mol}^{-1}$  at the respective melting points  $T_{\text{Li}}^m = 453.6 \text{ K}$  and  $T_{\text{Na}}^m = 370.9 \text{ K}$ . These values are fairly well confirmed by the results from discontinuous measurements with respect to their increased error range. Equation (5) together with

$$V(x, T) = (1/\rho(T))[x(T)/100 M_{\text{Na}} + (1 - x(T)/100) M_{\text{Li}}] \quad (6)$$

yields  $x(T)$  of the binodal if the atomic weights  $M$  of the two components and the experimentally observed density  $\rho(T)$  are inserted. The results are shown in figure 4 together with the full curve calculated from equation (3). With the exception of the region at large  $x$ , the agreement is excellent. Using the same polynomial as Feitsma *et al* [7] we obtain, instead of equation (3):

$$T = 119.7 + 25.112x - 1.537x^2 + 5.36278 \times 10^{-2}x^3 - 1.123792 \times 10^{-3}x^4 \\ + 1.387888 \times 10^{-5}x^5 - 9.27378 \times 10^{-8}x^6 + 2.54794 \times 10^{-10}x^7 \quad (7)$$

which yields  $T_c = 303.6^\circ\text{C}$  and  $x_c = 36.4$  at.% Na.

We preferred, however, to evaluate a cubic spline through the experimental points for calculating the average  $x(T)$  values, which then yield the  $\Delta x$  values to be inserted into equation (4). An estimation of the relative error  $|(\Delta x/x)|$  of the  $x(T)$  data obtained in this way yields 1.4, 2.6 and 3.5% at  $x = 5, 45$  and  $85$  at.% Na, respectively. Figure 5 then shows a plot of  $\log(\Delta x)$  versus  $\log(|\epsilon|)$  according to equation (4). For  $5 \times 10^{-5} < |\epsilon| < 2 \times 10^{-2}$  we observe a critical amplitude of  $B = 224 \pm 5$  and a critical exponent  $\beta = 0.5 \pm 0.015$ . These values are seen to change at larger  $\epsilon$ .  $\beta = 0.5$  corresponds to the classical Landau value. A

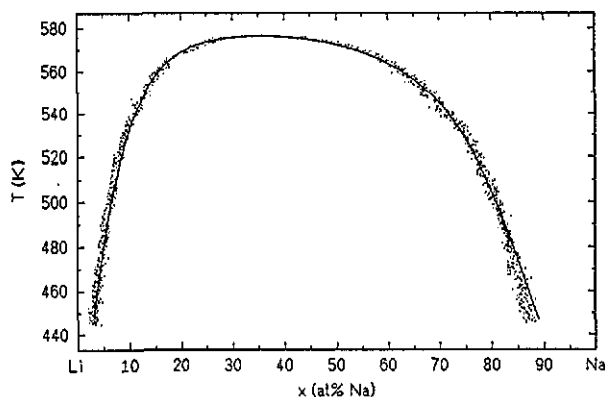


Figure 4. Binodal  $x(T)$  calculated from the individual  $\rho(T)$  points of figure 3 assuming ideal behaviour of  $V(x, T)$  according to equation (5). Full curve, values from equation (3) given by Feitsma *et al* [7].

Table 1. The critical exponents  $\alpha$  and  $\beta$ : theoretical values and our experimental data.

|          | Landau | 3D Ising          | Landau-Ginsburg-Wilson | Li/Na<br>this study |
|----------|--------|-------------------|------------------------|---------------------|
| $\alpha$ | 0      | $0.125 \pm 0.020$ | $0.110 \pm 0.005$      | 0.32                |
| $\beta$  | 0.5    | $0.312 \pm 0.002$ | $0.325 \pm 0.002$      | 0.5                 |

similar behaviour was deduced by Egelstaff and Ring [12] for Ga/Hg and Al/In alloys from the coexistence curves which they evaluated from the experimental data of Predel [13, 14]. For Ga/Pb and Ga/Tl they found  $\beta = 0.3$  and 0.35, respectively. Schürmann and Parks [15] on the other hand found for the Ga/Hg system a value for  $\beta = 0.335$  in the range  $10^{-4} < |\epsilon| < 10^{-2}$ . As mentioned above, 0.32 corresponds to the predictions of the modern theories, whereas  $\beta = 0.5$  is the value for the classical Landau behaviour.

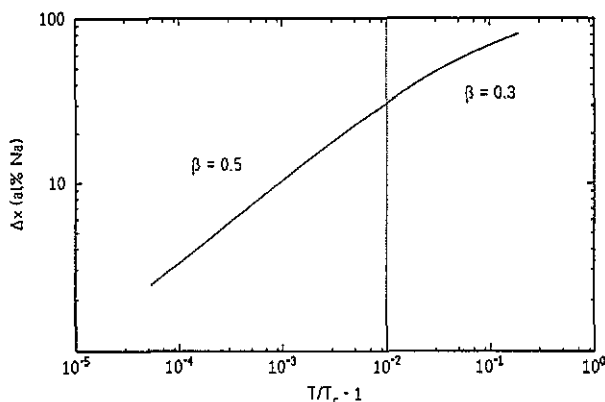


Figure 5. Plot of  $\log(\Delta x)$  obtained from a cubic spline of the points given in figure 4 versus  $\log(|\epsilon|)$ . The slope yields  $\beta$  according to equation (4).

The values for  $c_p$  versus  $T$  which we obtained at  $x_c$  are shown in figure 6. The full curve corresponds to a plot according to equation (1).  $c_p^0(T)$  was calculated according to the Neumann-Kopp rule from  $c_p(T)$  of the pure components. A least-square fit in the range  $3.9 \times 10^{-3} < \epsilon < 0.44$  yields  $A = 1.25 \pm 0.08 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T_c = 576.1 \pm 0.7 \text{ K}$  and  $\alpha = 0.32 \pm 0.07$ . The latter value agrees with the  $\alpha$  which was observed by Schürmann and Parks [1] for liquid Ga/Hg and therefore exceeds to the same significant extent the theoretical predictions.

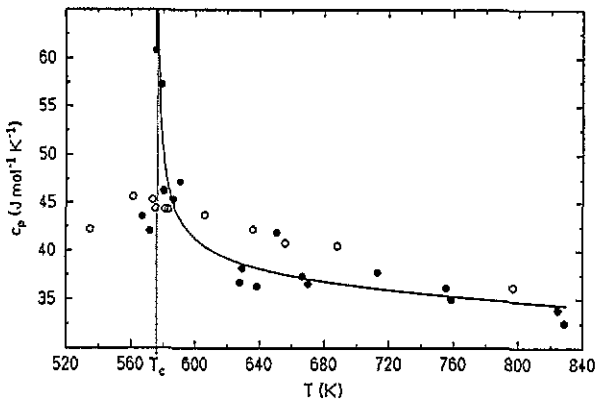


Figure 6. Full circles,  $c_p(T)$  obtained with an alloy of the critical composition  $x_c = 35$  at.% Na; full curve, fit according to equation (1); open circles,  $c_p(T)$  obtained for an alloy with 20 at.% Na.

We also investigated  $c_p$  for an alloy with 20 at.% Na. The results are given as open circles in figure 6. Here again an increase was observed when the binodal was approached from higher temperatures. A divergence of  $c_p$  is evidently observed only at the critical composition.

The theoretical predictions for the critical exponents  $\alpha$  of the heat capacity and  $\beta$  for the shape of the miscibility gap are summarized in table 1. The right-hand column contains our experimental observation for the Li/Na system.

### Acknowledgment

We are indebted to the Deutsche Forschungsgemeinschaft for financial support.

### References

- [1] Schürmann H K and Parks R D 1972 *Phys. Rev. B* **6** 348
- [2] Sengers J V 1982 *Phase Transitions: Cargèse 1980* ed M Lévy, J C Le Guillou and J Zinn-Justin (New York: Plenum) p 95
- [3] Lewis G N and Randall M 1923 *Thermodynamics and Free Energy of Chemical Substances* (New York: McGraw-Hill) p 137
- [4] Down M G, Hubberstey P and Pulham R J 1975 *J. Chem. Soc. Dalton* **14** 1490
- [5] Kanda F A, Faxon R C and Keller D Y 1968 *Phys. Chem. Liq.* **1** 61
- [6] Schürmann H K and Parks R D 1971 *Phys. Rev. Lett.* **27** 1790
- [7] Feitsma P D, Hallers J J, Werff F V D and Van Der Lugt W 1975 *Physica B* **79** 35
- [8] Ruppertsberg H and Knoll W 1977 *Z. Naturf. a* **32** 1374
- [9] Ruppertsberg H and Speicher W 1976 *Z. Naturf. a* **31** 47
- [10] Kanda F A, Faxon R C and Grant R 1968 *Phys. Chem. Liq.* **1** 49
- [11] Saar J and Ruppertsberg H 1987 *J. Phys. F: Met. Phys.* **17** 305
- [12] Egelstaff P A and Ring J W 1968 *Physics of Simple Liquids* ed H N V Temperley, J S Rowlinson and G S Rushbrooke (Amsterdam: North-Holland) p 253
- [13] Predel B 1960 *Z. Phys. Chem.* **24** 206
- [14] Predel B 1965 *Z. Metallkd.* **56** 791
- [15] Schürmann H K and Parks R D 1971 *Phys. Rev. Lett.* **26** 367