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Thermoelectric power of liquid Li-Na alloys

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Measurements of the thermoelectric power of liquid Li-Na alloys have been performed throughout the entire concentration range and at temperatures up to 400 °C. The results are in good agreement with calculations within the diffraction model. In the alloy with critical composition (65 at. % Li), critical effects have been observed in a temperature range up to several degrees above the phase-separation temperature.

INTRODUCTION

The thermopower measurements presented in this paper form part of a systematic investigation of the electronic properties of liquid Li-Na alloys. In an earlier paper[1] measurements of the electrical resistivity have been presented and discussed. The results could be explained reasonably well within the diffraction model. Also Knight shift measurements have been performed[2]; both the ^{7}Li and the ^{23}Na Knight shifts show a linear dependence on concentration. From a thermodynamical point of view the system Li-Na is rather exceptional, as it is the only alloy of lithium with an alkali metal exhibiting miscibility for all concentrations at atmospheric pressure[3,4] albeit not below 307 °C. Neutron-diffraction measurements in an alloy of nearly the critical composition showed that the atoms in the liquid have a preference for like nearest neighbors up to at least 150 °C above the critical temperature T_c,[5] whereas close to T_c critical opalescence has been observed.[6] Resistivity measurements demonstrated that the increase of the concentration fluctuations close to T_c also influences the electronic properties. A strong increase of the temperature derivative of the electrical resistivity is observed when the temperature approaches T_c.[7]

EXPERIMENTAL

For straightforward measurements of the thermopower of a liquid metal, the liquid has to be contained in a sample holder of nonconducting, inert material. LiF was chosen as container material, as it is an insulator which is virtually insoluble in both liquid Li(Ref. 8) and in liquid Na(Ref. 9) below 600 °C. The cell used for the measurements is sketched in Fig. 1. It consists of a tube of LiF, supplied with three calibrated Copper-Constantan thermocouples, and a stainless-steel wire used as fluid-level indicator. The commercially obtained thermocouples are sheeted with a wall of stainless steel (AISI 316). The LiF tube was made by drilling a hole through the entire length of a monocrystalline rod of LiF. By means of springs, the top end of the tube is connected to a stainless-steel manipulation rod. By pressing the manipulation rod, the LiF cell can be lowered into a crucible containing the metal to be investigated. The cell is immersed just as deep as necessary to achieve electrical contact between the indicator wire and the thermocouples. Crucible and cell are heated by means of an electronically controlled furnace. The furnace is supplied with auxiliary coils to establish the desired temperature gradient across the sample. Because Li and Na mix relatively slowly above the consolute temperature[5] and no facilities were available to stir the sample, the alloys were held at about 370 °C for a sufficiently long period before the cell was pressed into the liquid. A period of 72 h appeared in all cases to be long enough to ensure reproducible results.

The measurements were based upon the "small-ΔT" method described in Ref. 10. The thermovoltages were measured against copper. For the absolute thermopower S_{Cu} of copper we adopted[11] $S_{\mathrm{Cu}}(t) = 1.54 + 0.00545t \pm 0.15$ μV/°C, valid for $20 < t < 500$ °C.

The samples were prepared from commercially obtained Li and Na with nominal purities of 99.98 and 99.93 at%, respectively. Sample preparation and measurements occurred in a high-purity helium atmosphere (oxygen and nitrogen content less than 5 ppm).

RESULTS

The results of our measurements in pure liquid Li are shown in Fig. 2 and can be expressed by

$$S_{\mathrm{Li}}(t) = (16.16 + 0.0438t - 0.466\times10^{-4}t^2)\ \mu\text{V}/°\text{C},$$

where t denotes the temperature in °C ($220 < t < 420$ °C). The results agree within the errors with previous measurements by Kendall,[12] but the measured values of S_{Li} are somewhat higher than those reported by Ioannides *et al.*[13]

The measured thermopower of pure Na is shown in Fig. 3; the result can be expressed by:

$$S_{Na}(t) = -4.95 - 0.02647t \ \mu V/°C ,$$

valid for $120 < t < 400$ °C. The measurements provided agreement within 0.5 μV/°C with previous measurements.[10, 12, 14]

In Fig. 4 the thermopower S of liquid Li-Na at 310°C and 400 °C is shown as a function of concentration. The total error in S is estimated to be ± 0.4 μV/°C. S was found to depend almost

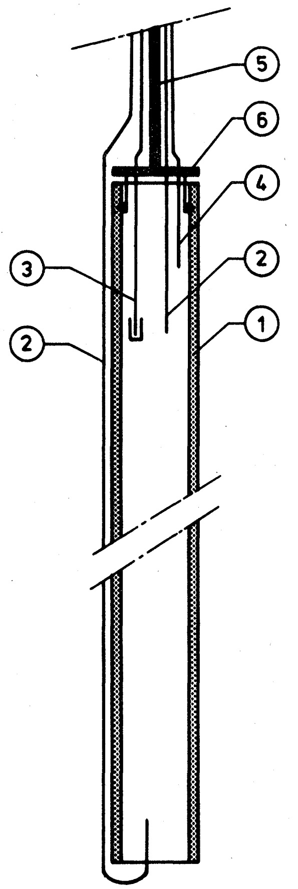

FIG. 1. Cell for thermopower measurements. 1: LiF tube (length 140 mm, diameter 10 mm). 2: Copper-Constantan thermocouple, sheeted with stainless steel, with grounded hot junction. 3: see 2, but insulated hot junction. 4: indication wire for fluid level. 5: manipulation rod. 6: stainless-steel disk with alumina feedthroughs for thermocouples.

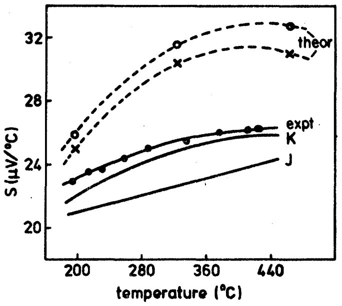

FIG. 2. Thermopower S of pure liquid Li versus temperature. expt: present experimental result. K: from Ref. 12, typical error ±1 μV/°C. J: from Ref. 13, typical error ±2 μV/°C. theor: calculated, using experimentally obtained structure factors, ---O--- Hartree screening, ---×--- Toigo-Woodruff screening.

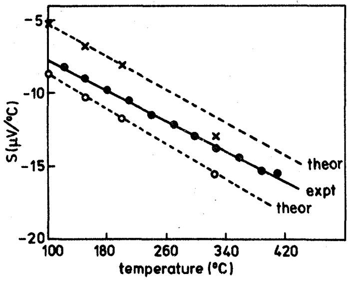

FIG. 3. Thermopower S of pure liquid Na versus temperature. expt: present experimental result. The differences between the line drawn and the results presented in Refs. 10, 12, and 14 are indistinguishable at this scale. theor: calculated using experimentally obtained structure factors; ---O--- Hartree screening, ---×--- Toigo-Woodruff screening.

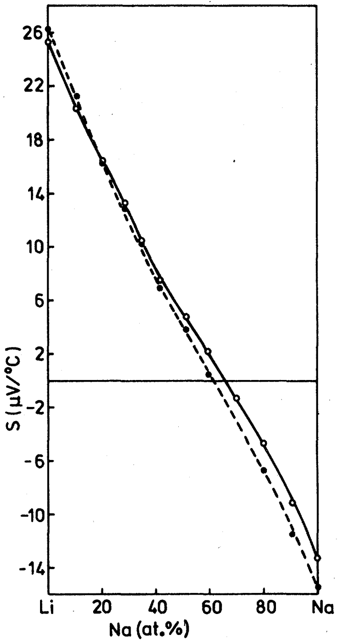

FIG. 4. Thermopower S of liquid Li-Na alloys as a function of Na concentration. —O—, 310 °C; ---●---, 400 °C.

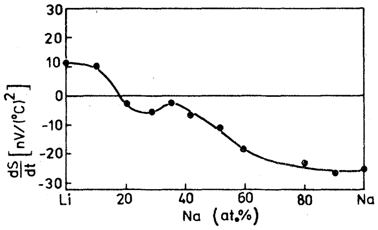

FIG. 5. Temperature derivative, dS/dt, of the thermopower of liquid Li-Na alloys at 355 °C vs Na concentration.

linearly on the temperature for all concentrations. The temperature derivative of the thermopower, dS/dt, at 355 °C is shown in Fig. 5. The error in the dS/dt is typically ±1.0 nV/(°C)^2. In the alloy with critical composition (65.3 at.% Li), the temperature was lowered in steps of 0.5 °C close to T_c in order to observe possible critical effects. A sudden increase of S starting approximately 3 °C above T_c was found (Fig. 6).

DISCUSSION

In this section the experimentally obtained results will be compared with the results of calculations within the diffraction model. Within this model the thermopower is related to the form factors $w_q(k_F)$ and the Bhatia-Thornton partial structure factors[15] $S_{NN}(q)$, $S_{NC}(q)$, and $S_{CC}(q)$ by the following formulas:

$$S = \frac{\pi^2 k_B^2 T}{3eE_F}\,(3 - 2s - \tfrac{1}{2}r)\,, \tag{1}$$

where

$$s = \frac{F(2k_F, k_F)}{\langle F(q, k_F)\rangle} \text{ and } r = \frac{\langle k_F[\partial F(q, K_F)/\partial K]_{K=k_F}\rangle}{\langle F(q, k_F)\rangle} \tag{2}$$

with

$$F(q, k_f) = (\bar{w})^2 S_{NN}(q) + 2\bar{w}\,\Delta w\, S_{NC}(q) + (\Delta w)^2 S_{CC}(q), \tag{3}$$

$$\langle F(q, k_F)\rangle = \int_0^1 F(q, k_F)\; 4\left(\frac{q}{2k_K}\right)^3 d\left(\frac{q}{2k_F}\right), \tag{4}$$

$$\bar{w} = c_{\mathrm{Li}}\, w_q^{\mathrm{Li}}(k_F) + c_{\mathrm{Na}}\, w_q^{\mathrm{Na}}(k_F)\,, \tag{5}$$

and

$$\Delta w = w_q^{\mathrm{Li}}(k_F) - w_q^{\mathrm{Na}}(k_F). \tag{6}$$

The form factors were calculated from slightly modified Shaw-model potentials[16]; electron-electron interactions were included by using Toigo-Woodruff screening.

For pure metals the $S_{NC}(q)$ and $S_{CC}(q)$ vanish. Experimentally obtained values of the $S_{NN}(q)$ of pure liquid Li (Ref. 5), at 197 °C, 322 °C, and 452 °C have been used to calculate the thermopower of Li as a function of temperature. The result, shown in Fig. 2, is in reasonable agreement with the experimental values.

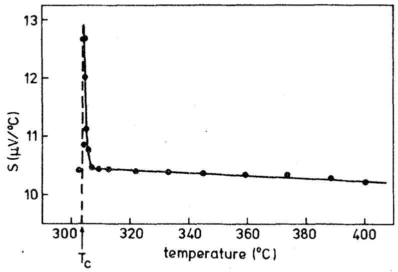

FIG. 6. Thermopower S of a Li-Na alloy with the critical composition, 65.3 at. % Li, as a function of temperature.

The thermopower of pure liquid Na was calculated for several temperatures, using experimentally obtained structure factors from Huijben *et al.*[17] (100 and 150 °C), Greenfield *et al.*[18] (200 °C), and Waseda *et al.*[19] (325 °C). The results are plotted in Fig. 3. Except for the thermopower calculated for 325 °C, the results are in good agreement with the experiment. The poorer agreement at 325 °C is probably due to the inaccurate way in which the structure factor at this temperature is tabulated in Ref. 19.

Next we will consider the measurements in the alloys. The form factors $w_q^{\mathrm{Li}}(k_F)$, and $w_q^{\mathrm{Na}}(k_F)$ happen to be nearly equal for a common k_F. Referring to Eq. (3) this implies that both the thermopower and the electrical resistivity $[\propto \langle F(q, k_F)\rangle]$ are nearly independent of $S_{CC}(q)$ and are determined mainly by the term in Eq. (3) containing $S_{NN}(q)$. Experimental data on the $S_{NN}(q)$ of liquid Li-Na are not available [the neutron-diffraction measurements reported in Ref. 5 provided information mainly on the $S_{CC}(q)$]. Therefore we had to rely upon the solutions of the Percus-Yevick equation for a binary mixture of hard spheres. Values for the hard-sphere diameter σ and the packing fraction η were determined by fitting the height and position of the first peak of the hard-sphere structure factor to the experimental structure factors of the pure components. At 310 °C we obtained $\sigma = 2.80$ Å, $\eta = 0.462$ for Li and $\sigma = 3.35$ Å, $\eta = 0.421$ for Na. The calculated thermopower is in good agreement with experiment (Fig. 7) and proves to be rather insensitive to the choice of the hard-sphere parameters. This is illustrated (Fig. 7) by the result of a calculation using (random) hard spheres parameters from Ref. 1: $\sigma = 2.70$ Å, $\eta = 0.404$ for Li and $\sigma = 3.26$ Å, $\eta = 0.397$ for Na. Also, exchange and correlation

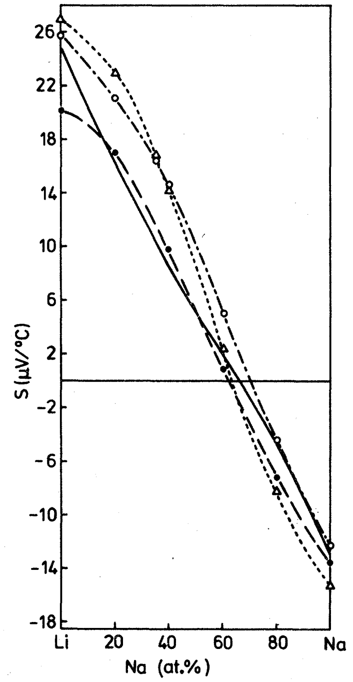

FIG. 7. Thermopower S of liquid Li-Na at 310 °C as a function of Na concentration. —, experimental; ---○---, Toigo-Woodruff screening; ---△---, Hartree screening; —●—, Toigo-Woodruff screening, random hard sphere structure factor parameters from Ref. 1.

effects in the electron gas have a minor influence on the result.

Finally we will discuss the critical effects observed in alloys containing approximately 65 at.% Li. Neutron-diffraction measurements in a 61-at.% Li alloy[5] provided the $S_{CC}(q)$ for several temperatures close to T_c. For small q, $q < 0.5$ Å^{-1}, $S_{CC}(q)$ increases strongly when the temperature approaches T_c, and is in good agreement with the Ornstein-Zernike prediction:

$$S_{CC}^{OZ}(q) = S_{CC}(0)/(1+q^2\xi^2)\,, \tag{7}$$

where ξ denotes the correlation length for concentration fluctuations. According to Ruppersberg *et al.*[5] the anomalous behavior of $d\rho/dt$ close to T_c might be entirely due to the temperature dependence of the $S_{CC}(q)$ for $q \simeq 2k_f$: $q^3(dS_{CC}^{OZ}/dt)$ shows almost exactly the behavior of the $d\rho/dt$ (Fig. 7 in Ref. 5). We used the function $q^3(dS_{CC}^{OZ}/dt)$, with values for the critical exponents from Ref. 6, to calculate the S_{CC} part of $d\rho/dt$ close to T_c. The aforementioned form factors for Li and Na were used. The calculated $d\rho/dt$, shown in Fig. 8, is in only qualitative agreement with the results of Schürmann and Parks.[7] In the same way, adopting once more for $S_{CC}(q)$ the Ornstein-Zernike prediction [Eq. (7)] and for $S_{NN}(q)$ and $S_{NC}(q)$ the hard-sphere approximation, we calculated the temperature derivative of the thermopower, dS/dt, close to T_c. A similarly bad agreement was obtained. In spite of the large increase of the $S_{CC}(q)$ for small q, the calculated $d\rho/dt$ and dS/dt are very small, due to the fact that $\Delta w \simeq 0$ in the term containing $S_{CC}(q)$ in Eq. (3).

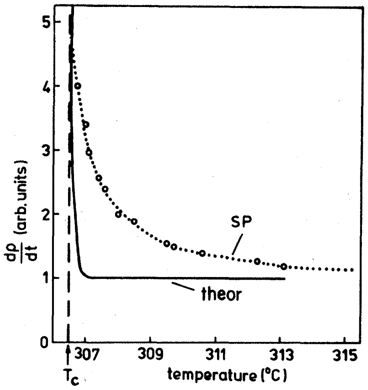

FIG. 8. Temperature derivative, $d\rho/dt$, of the electrical resistivity of a Li-Na alloy with the critical composition. —, calculated; ···○···, expt. from Schürmann and Parks (Ref. 7).

Of much more influence on ρ and S is the $S_{NN}(q)$. Possibly the expected broadening of the first peak of the $S_{NN}(q)$, due to the development of small "droplets" with different composition close to T_c (Fig. 9 in Ref. 5) can account for the observed critical effects in the electrical resistivity and thermoelectric power. Furthermore, we note that at temperatures up to approximately 2 °C above T_c the correlation length for concentration fluctuations, ξ, exceeds the estimated mean free path of the electrons.[5] This implies that the assumption of a homogeneous electron gas is not fulfilled in this temperature range.

CONCLUSIONS

The measured thermopower of pure liquid Li and pure liquid Na can be explained fairly well within the diffraction model, using experimentally obtained structure factors. Also, the thermopower of liquid Li-Na alloys calculated within this model, using random hard-sphere structure factors, is in good agreement with the experimentally obtained results. In an alloy containing 65 at.% Li, close to T_c critical behavior of the electrical resistivity and thermopower has been observed. These effects can not be explained in a straightforward fashion in terms of the diffraction model. This might be due to the observed large concentration fluctuations close to T_c, which invalidate the assumption of a homogeneous electron gas.

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