Dependence of Electrotransport on Composition in Simple Liquid Binary Alloys

S. J. LARSSON, A. LODDING, T. PERSSON,
and C. ROXBERGH

Physics Department, Chalmers University of Technology

(Z. Naturforsch. 28, 314—315 [1973];
received 2 December 1972)

To Professor A. Klemm on his sixtieth birthday

The phenomenon of electrotransport in a binary liquid alloy with perfectly miscible components is representable in terms of measurable resistivity and diffusivity parameters. The formulae are compared with experimental data from measurements of electrotransport in liquid Na-K. The predicted magnitudes as well as signs of the relative mobilities are satisfactorily borne out by the experiments.

The interest at this Institute in liquid metal electrotransport dates back to the early 1950-s, and is a consequence of Professor A. KLEMM's stay at Gothenburg as Visiting Professor. His introduction of the concept of electron wind to explain the "Haefner-effect" has greatly stimulated the research in the field, and contributed to start the systematic investigation of which the present paper is a part.

In a recent study of electrotransport in liquid Na-K alloys¹ an attempt was made to express, for any li-

quid metal binary with perfectly miscible components and in terms of a few wellknown or measurable parameters, the temperature and composition dependence of the effective charge number Z_{A-B}^* . This entity is defined by

$$v_{A-B} = (D_i/kT) \cdot Z_{A-B}^* E e, \quad \dots (1)$$

where v_{A-B} is the relative migration velocity of the two alloying components A and B in the field E , and D_i their inter-diffusion coefficient.

The relation arrived at [cf. ¹ Eq. (16)] can be written as

$$\begin{aligned} -\bar{\rho} Z_{A-B}^* = & [(1-2c_A)\rho_A^* + \frac{1}{2}\Delta\rho_D^*] \\ & + \frac{D_A^* - D_B^*}{D_A^*} [c_A^2\rho_A^* + \frac{1}{2}\rho_D^* - \bar{\rho}]. \end{aligned} \quad (2)$$

In the experiments on the Na-K system, the last term is only between 2% and 15% of the whole. Here $D_{A,B}^*$ are the respective tracer diffusion coefficients for $c_{A,B} = 0$, $c_{A,B}$ denoting the respective mole fractions. $\bar{\rho}$ is the alloy resistivity; ρ_A^* is the resistivity increment on mixing B as impurity in pure A, or vice versa (see Ref.²); $\frac{1}{2}\rho_D^*$ denotes the "defect resistivity" of mobile species, obtainable from studies of isotope electrotransport³; and $\frac{1}{2}\Delta\rho_D^*$ is the difference in this entity between A and B.

Fig. 1. The concentration dependence of relative effective charge numbers of electrotransport in liquid Na-K alloys at 100° and 250° C. Full curves: from Eq. 2 with $\rho_A^* = 1.35$, $\Delta\rho_D^* = 0.25$, $\rho_{DK}^* = 0.6$. Broken curves: interpolated experimental. Empty circles: Ref. ¹; Full circles: Ref. ⁶; Diamonds: Ref. ⁷; Crosses: Reference ⁸.

In Ref.¹ it was shown that the temperature dependence of Z_{A-B}^* , as measured for liquid Na-K at low Na concentrations, agreed very well with the above formulae, when the parameters $\varrho_0^* \simeq 1.35$ and $\frac{1}{2}\Delta\varrho_D^* \simeq 0.25$ (in $\mu\Omega \text{ cm}/\%$ def.) were substituted. This ϱ_0^* value is in good agreement with resistivity measurements^{2, 4, 5}. The difference in $\frac{1}{2}\Delta\varrho_D^*$ is at least qualitatively plausible: from Haeffner-effect measurements³ one has inferred $\frac{1}{2}\Delta\varrho_D^* = 0.6 \pm 0.4 \mu\Omega \text{ cm}/\%$ for potassium, while the (so far unmeasured) corresponding term for sodium may be assessed to lie between 0 and 1.2.

The purpose of this communication is to show that also the concentration dependence of Z_{A-B}^* , as observed in several investigations of Na-K^{1, 6-8}, is reasonably represented by the above equations, adopting the above given values of the parameters ϱ_0^* and $\Delta\varrho_D^*$.

The plots based on Eq. (2) are shown for two temperatures in Figure 1. For their construction the resistivity data were taken from Refs.^{4, 5} and the diffusivity data from Reference⁹.

The figure also shows all hitherto obtained experimental data for Z_{Na-K}^* at 100° and 250 °C. According to Ref.¹, the points represented by filled circles⁶

probably lie much too low, due to experimental shortcomings; the crosses⁸ are thought to be of the right order of magnitude but might be on the low side due to convection effects.

It is seen that the theoretical curves agree excellently with the low Na results, measured in Ref.¹, and qualitatively also with those obtained at various compositions in References^{7, 8}. As regards the cross-over from negative to positive Z_{Na-K}^* , our equations predict it to lie at about 60 % Na and somewhat temperature dependent, which is in very good agreement with experiments⁶⁻⁸. This sign reversal of electrotransport in liquid binary alloys has been treated by phase-shift approach theory^{8, 10, 11} which, however, expects a cross-over in Na-K at about 32 % Na, rather than the experimentally observed 60 %. The formalism of Ref.¹ is seen to lead to the essentially correct prediction, but only as a consequence of $\Delta\varrho_D^*$ being positive, which is theoretically not a priori obvious and has not yet been proved experimentally; new Haeffner-effect measurements on the Na-K system are now in preparation.

This work has been supported by the Swedish Natural Science Research Council and the W. & M. Lundgren Science Fund.

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