Electrical Resistivity and Phase Separation in Dilute Liquid Alloys of Sodium in Selenium

C. van der Marel and W. van der Lugt
Solid State Physics Laboratory, University of Groningen, The Netherlands

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The electrical resistivities of liquid selenium and seleniumrich Na-Se alloys have been measured. The results of dilute alloys are interpreted in terms of percolation theory. A previously determined phasediagram was found to be incomplete.

The electrical resistivity of pure liquid selenium has been measured by many investigators [1–7]; yet only a few of them describe the way in which their samples were prepared. Abdullaev et al. [3] and later Gobrecht et al. [4] and Koningsberger [5] have found that small amounts of oxygen have an enormous influence on the electrical resistivity of the liquid. Furthermore it was found [3, 5] that the resistivity of deoxidized selenium is a smooth function of temperature at the melting point T_m, whereas the resistivity of ordinary selenium of high metallic purity exhibits a jump of about three orders of magnitude at T_m. Koningsberger [5] performed both ESR and resistivity measurements on deoxidized as well as ordinary liquid selenium. Only from samples exhibiting a negligible jump in resistivity at T_m, reproducible ESR results were obtained. This confirmed the result of Abdullaev et al. [3] that the jump in the resistivity at T_m is a measure of the oxygen content of the material.

The deoxidation method we used is based upon the method described by Koningsberger [5]. A layer of about 20 grammes of selenium shot ($\varnothing \simeq 3$ mm; Alfa Ventron; met. imp. < 10 ppm) is placed in a carefully cleaned quartz vessel. The vessel is brought into a stainless steel tube, which through a liquid nitrogen trap is connected with a high vacuum diffusion pump. The tube is heated slowly (30 K/hr) under high vacuum (5×10^{-7} Torr) up to a temperature of about 160 °C and kept at that temperature for about four hours. Thereafter, the tube is filled with helium, disconnected from the vacuum system and opened in a high purity, helium filled glove box (oxygen < 1 ppm; water < 1 ppm). To test the deoxidation method, a measurement of the change of the resistivity at the melting point has been performed. A change by a factor of two was found, in agreement with the results of both Koningsberger [5] and Abdullaev et al. [3] in their best deoxidized samples.

Sodium metal of high purity was obtained from Merck A.G.; details on purity and handling are reported by Feitsma et al. [8].

Due to the high energy of mixing of sodium and selenium it was found to be impracticable to prepare the alloys by melting liquid Na and Se together. Instead, the alloys were prepared by dissolving the solid compound Na_2Se in liquid selenium. The compound Na_2Se was prepared from stoichiometric amounts of Na and Se in a sealed, helium filled quartz tube (Figure 1). The selenium side of the tube was heated to 180 °C, the sodium side to 150 °C. Selenium vapour moves to the colder end of the tube, where it reacts with the molten sodium. It took about 72 hours to transform all the Na and Se into about 4 grammes of Na_2Se. By means of X-ray diffraction we checked the purity of the obtained white powder; it was found to contain more than 95% Na_2Se and some Na_2Se_2.

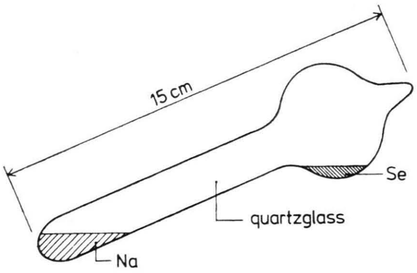

Fig. 1. Sealed tube for the preparation of Na_2Se.

The conductivity measurements have been performed by means of the well known four point method. According to Lundkvist and Sillen [9], quartz is the appropriate container material for

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Reprint requests to Dr. W. van der Lugt, Solid State Physics Laboratory, 1 Melkweg, 9718 EP Groningen, The Netherlands.

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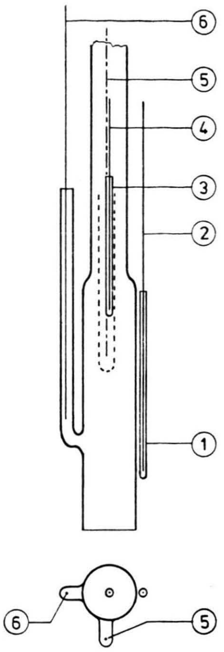

Fig. 2. Side- and bottom-view of the quartz cell used for the resistivity measurements. ② and ④ denote calibrated chromel-alumel thermocouples (stainless steel wall), provided with platinum sockings (① and ③). ⑤ and ⑥: platinum wire (∅ = 0.2 mm).

measurements on selenium at high temperatures. The quartz cell used (Fig. 2) is connected above with a stainless steel plunger, which fits vacuum-tight an outer tube. In the glove box a platinum crucible is filled with the alloy and put at the bottom of the outer tube. The stainless steel plunger with the quartz cell is pressed into the outer tube, until the quartz cell touches the solid alloy. Next the apparatus is placed in an electronically stabilized furnace and heated; when the alloy is molten the quartz cell is pressed into the liquid alloy (because of the large increase of volume at T_m — about 17% [10] — melting of Se in the quartz cell would ruin it). To test the homogeneity of the liquid, the plunger is moved up, then down; if the same value for the resistivity is measured when the quartz cell is back in its lowest position, the alloy is assumed to be homogeneous. The temperature is measured by means of two chromel-alumel thermocouples, provided with platinum sockings. An electrical current is led from the upper thermocouple through the liquid to the platinum crucible; the voltage between the two Pt leads (∅ = 0.2 mm), hanging freely in the capillaries, is measured. It is easy to show that the accurate position of the electrodes is of no importance, provided they are not close to the bottom of the capillaries. The cell was calibrated with caesium [11].

The results of our measurements are shown in Figure 3. All the experimental points fit well to the curves drawn, and the experimental uncertainties (3% in the resistivity and 3 °C in the temperature) are within the widths of the lines drawn. Only the measurements in pure selenium are less accurate due to the aforesaid influence of oxygen and other impurities. The discrepancies between several independent measurements of the resistivity of pure deoxidized selenium are found to be about 50%. For $T < 420$ °C the resistivity of pure selenium exhibits simply activated behaviour, in agreement with Abdullaev et al. [3], Gobrecht et al. [4] and Koningsberger et al. [5], and can be described by $\sigma = \sigma_0 \exp(-E/kT)$ with

$$\sigma_0 = 0.08 \pm 0.04\ (\Omega\,\mathrm{cm})^{-1}\,,$$
$$E = 0.47 \pm 0.05\ \mathrm{eV}\,.$$

At higher temperatures the activation energy increases due to the increasing influence of intrinsic conduction compared with the defect conduction prevailing at lower temperatures.

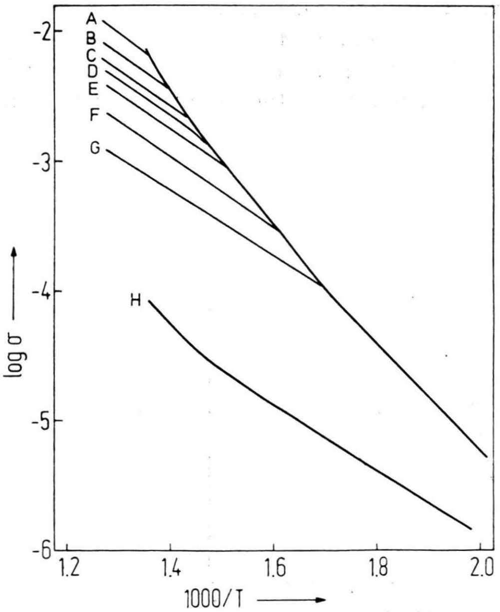

Fig. 3. Measured values of $^{10}\log \sigma$ vs. $1000/T$; A to H corresponds to 0.80, 0.60, 0.51, 0.40, 0.30, 0.20, 0.10 and 0.00 at. % of Na, respectively.

At high temperatures the resistivity of the alloys exhibits simply activated behaviour. When the temperature decreases, at some value a kink is observed in the $^{10}\log \sigma$ vs. $1000/T$ plot (Figure 3). It is assumed that below that temperature phase separation occurs: a sodium-rich phase with lower density separates off on top of the alloy, whereas in the cell the sodium concentration decreases. This assumption finds support in our observations in the glove box: when cooling a liquid Na-Se alloy, below some temperature grey drops are observed, floating on top of the black selenium rich alloy. Figure 4 gives a plot of the measured immiscibility region, not mentioned by Mathewson [12]. We note that, as platinum is attacked by selenium at temperatures higher than 480 °C, the available concentration range was restricted to $0.0 < c_{\mathrm{Na}} < 1.0$ at.%.

The conductivity in the dilute alloys can be assumed to consist of two parts: defect conduction as in pure selenium, which we assume to be unaffected by small amounts of sodium, and hopping conduction by carriers associated with the sodium atoms. The sodium 3s electrons may be thought to be excited to low mobility states near the band edge [13] or to be tunneling between states near the Fermi energy. With our results we cannot distinguish between the two mechanisms and we shall rather refer to a hopping mechanism covering both possibilities. To obtain the conductivity due to hopping alone, the pure selenium conductivity has to be subtracted from the results as drawn in Figure 3. Only for $c_{\mathrm{Na}} < 0.3$ at.% the correction is found to be significant. The resulting $^{10}\log \sigma$ vs. $1000/T$ curves are all straight lines; the points could be nicely fitted by $\sigma(x, T) = \sigma_0(x) \exp(-E(x)/kT)$. E is found to be nearly independent of the sodium concentration x: $E(x) \simeq 0.55 \pm 0.02$ eV $(x \neq 0)$. To obtain theoretically the variation of hopping conductivity with impurity density, we consider the model which has successfully been used by Pettit and Camp [14] for the explanation of the behaviour of the conductivity of dilute Se-Tl alloys. The model is based upon the critical path analysis introduced by Ambegaokar, Halperin and Langer [15] (AHL). According to AHL the system may be replaced by a three dimensional network, in which every pair of impurities is connected through a conductance G_{ij}. The rate for a carrier to hop from one site i to a site j at a distance d_{ij} is given by [16]

$$\Gamma_{ij} = \Gamma_0 \exp\{-(2d_{ij}/\xi) - (\Delta/kT)\},$$

where ξ is the radius of the orbit of the valence electron localized at the impurity and Δ is some activation energy. It is easy to show [15] that the conductance G_{ij} is related to Γ_{ij} according to $G_{ij} = e^2 \Gamma_{ij}/kT$. The essential step in the critical path analysis is the assumption that the conductivity, σ, of the system is proportional to the critical percolation conductance G_c:

$$G_c = \frac{e^2}{kT} \Gamma_0 \exp\{-(4r_c/\xi) - (\Delta/kT)\},$$

where r_c is determined as follows: Around all impurities a sphere with radius r (r small) is drawn. A value $r = r_c$ can be found for which a path exists through overlapping spheres across the whole system, whereas for $r < r_c$ no such path exists. This threedimensional percolation problem has numerically been solved by Seager and Pike [17]

$$r_c = 0.7\, r_s,$$

where $r_s = (3/4\pi n)^{1/3}$ and n is the number density of impurities. Combining the above equations we find:

$$\sigma = C \exp\{-(2.8\, r_s/\xi) - (\Delta/kT)\}.$$

From this equation a linear relation between the experimental $\ln \sigma_0$ and r_s is expected; in Fig. 5 the experimental values of $\ln \sigma_0$ are plotted against r_s. For small impurity concentrations the points lie on a straight line, and from the slope we find $\xi = (19 \pm 3)$ a.u. For $r_s < 22$ a.u. the points deviate

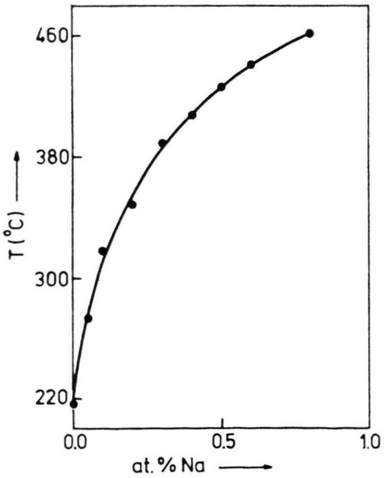

Fig. 4. Liquidus line as determined from our resistivity measurements.

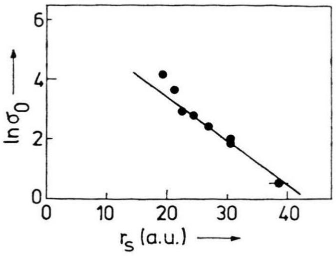

Fig. 5. The behaviour of ln σ_0 vs. r_s; r_s is half of the sodium atom spacing.

from the straight line, in rough agreement with Ref. [17]. This deviation may be expected, because the approximation $\sigma \sim G_c$ is incorrect for concentrations where many parallel conductances $\simeq G_c$ exist [15]. Stated otherwise, the assumption of independent carriers at the impurities is invalidated when the localized valence electron wavefunctions at the impurities start to overlap [16], i.e. when $r_s \lesssim \xi$.

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