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## Electrical resistivity and ${}^7\text{Li}$ Knight shift of liquid Li–Si alloys

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**Abstract.** The electrical resistivity  $\rho$  and the  ${}^7\text{Li}$  Knight shift  $K$  of liquid Li–Si alloys have been measured for Li concentrations between 0 and 50 at. % Si. From 0 to 20 at. % Si both the electrical conductivity and the Knight shift decrease strongly. Above 20 at. % Si,  $\rho$  levels off at approximately  $650 \mu\Omega \text{ cm}$  and also  $K$  remains nearly constant at approximately 25% of the pure-Li Knight shift. When the results are combined with available  $T_1$  data, the Korringa enhancement  $\eta$  is calculated. The approximate relation between  $\rho$  and  $\eta$  proposed by Warren for the diffusive motion regime holds very well. An interpretation on the atomic level is proposed by assuming that in the alloys with more than 20 at. % Si the Si atoms form just the number of covalent bonds necessary to keep  $E_F$  at a minimum in the density of states.

### 1. Introduction and discussion of the solid alloys

The investigation of the liquid Li–Si system forms part of a systematic study of liquid alkali-group IVb alloys. For a review the reader is referred to a paper by van der Lugt and Geertsma (1987).

For the experimentalist the Li–Si system is attractive as it is suitable for investigation by a variety of techniques.  ${}^7\text{Li}$  is an excellent nucleus for NMR. Van der Marel *et al* (1984) have already determined the spin–lattice relaxation time  $T_1$  by the  $\beta$ -NMR method. Furthermore,  $\text{Li}_{0.653}\text{Si}_{0.347}$  is a ‘zero alloy’ for neutron diffraction. A structural investigation using this technique is carried out in parallel to the present study of electronic properties.

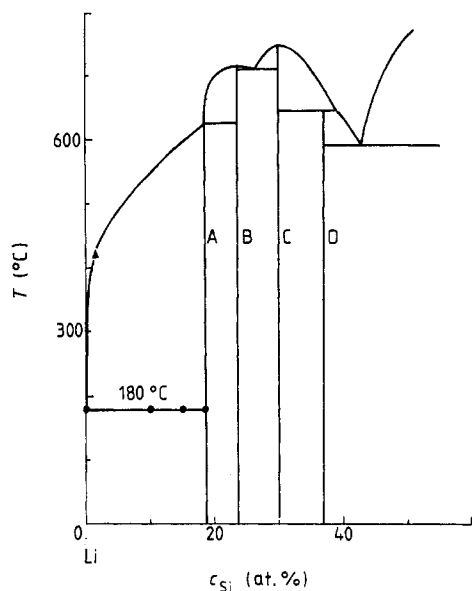
From a technological point of view, solid Li–Si alloys are potentially suitable for use in dry cells because of the high diffusivity of Li ions (Wen and Huggins 1981).

In previous studies of alkali-group IVb alloys the possible formation of ‘Zintl ions’ in the liquid has been an important point of discussion. In a theoretical study of the stability of such ions, Geertsma *et al* (1984) proposed a ‘phase diagram’ indicating the occurrence of metallic clustering, semiconducting clustering and non-clustering compounds, the term clustering here applying to a restricted class of polyanions. According to this scheme, Li–Si does not form  $(\text{Si}_4)^{4-}$  ions, as a consequence of the smallness of the Li atoms.

Indeed, tetrahedra are absent in the crystal structures of the solid Li–Si compounds (Axel *et al* 1966, Frank *et al* 1975, Von Schnering *et al* 1980a, b).

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**Figure 1.** The Li-Si phase diagram (from Van der Marel *et al* 1985): A,  $\text{Li}_{22}\text{Si}_5$ ; B,  $\text{Li}_{13}\text{Si}_4$ ; C,  $\text{Li}_{14}\text{Si}_6$ ; D  $\text{Li}_{12}\text{Si}_7$ .

The Li-Si phase diagram (Sharma and Seefurth 1976, Wen and Huggins 1981, Van der Marel *et al* 1985, figure 1) shows four intermediate phases, with nominal compositions  $\text{Li}_{22}\text{Si}_5$ ,  $\text{Li}_{13}\text{Si}_4$ ,  $\text{Li}_{14}\text{Si}_6$  and  $\text{Li}_{12}\text{Si}_7$ . As seen in figure 1, these compounds are all in the composition range between 18 and 38 at. % Si. The crystal structures show a rich variety of polyanions. As is to be expected, the number of Si-Si bonds that characterises a polyanion increases with decreasing Li content.  $\text{Li}_{12}\text{Si}_7$  has the most intricate structure found so far; the unit cell has 152 atoms and contains as 'Zintl ions' both five-membered  $\text{Si}_5$  rings and three-pointed  $\text{Si}_4$  stars. The electronic structure of  $\text{Li}_{12}\text{Si}_7$  has been studied by Böhm *et al* (1985); covalent Si-Si bonding appears crucial to structural stability.

Anion-anion bonding alone, however, is not sufficient to explain the experimental facts in Li-Si compounds. As an example, consider the  $\text{Li}_7\text{Si}_3$  compound, in which the Si ions occur in pairs (dumb-bells). If the electronic structure of  $\text{Li}_7\text{Si}_3$  were related to the term scheme of a Si-Si pair in the same way as the electronic structure of  $\text{NaSn}$  derives from the term scheme of the tetrahedron (Van der Lugt and Geertsma 1987), the Fermi level would be in the band, formed out of the anti-bonding  $\pi_g$  states of the pair, and  $\text{Li}_7\text{Si}_3$  would be metallic. In reality,  $\text{Li}_7\text{Si}_3$  is a semiconductor with a very small band gap of 0.08 eV (von Schnering *et al* 1980b). Similar considerations hold for  $\text{Li}_{13}\text{Si}_4$  and  $\text{Li}_{12}\text{Si}_7$ ; the electronic properties are not consistent with the Zintl model in its simplest form (ionic bonding between  $\text{Li}^+$  and  $\text{Si}_n^{(n-)}$ , and covalency only between anions).

It follows that the bonding character of  $\text{Li}_{13}\text{Si}_4$ ,  $\text{Li}_7\text{Si}_3$  and  $\text{Li}_{12}\text{Si}_7$  cannot be explained in the same simple way as in the case of equiatomic  $\beta$ -NaSn and analogous compounds. In particular, the electron states below  $E_F$  are not governed by the anion potentials as exclusively as in, for example, KPb. At present, the problem of bonding in these solid Li-Si compounds is being tackled in a series of papers from the Max Planck Institute, Stuttgart (Böhm *et al* 1984 and 1985, Nesper *et al* 1986, Ramirez *et al* 1986).

As to the expected behaviour of liquid alloys, we may compare Li-Si with Li-Pb. The latter shows an indication of salt-like behaviour near the composition  $\text{Li}_4\text{Pb}$ .

Replacing Pb by Si enlarges the electronegativity difference, while the anion size becomes smaller, favouring covalent bonding. At higher Si concentrations, we are therefore prepared to find covalent bonds between Si ions to form polyanions as in the crystal structures of the solid compounds.

## 2. Experiments

Owing to the high melting temperature of Si, the measurements had to be restricted to alloys with less than 50 at% Si.

Resistivity measurements on liquid Li–Si alloy are very experimentally difficult. In part, the problems are due to the extreme aggressiveness of liquid Li and Li vapour at the measurement temperature, in particular towards insulating ceramics such as  $\text{Al}_2\text{O}_3$  or BN. This precluded constructing an insulating measuring cell. Rather we used the metal tube method (van der Marel *et al* 1982), but here the situation is complicated by the corrosivity of Si towards refractory metals (Van der Marel *et al* 1985). For the measuring tube, we tried both Ta and W but were left with W as the only practicable choice, as the resistivity of our Ta tube appeared to be irreproducible in the temperature range pertaining to our experiments.

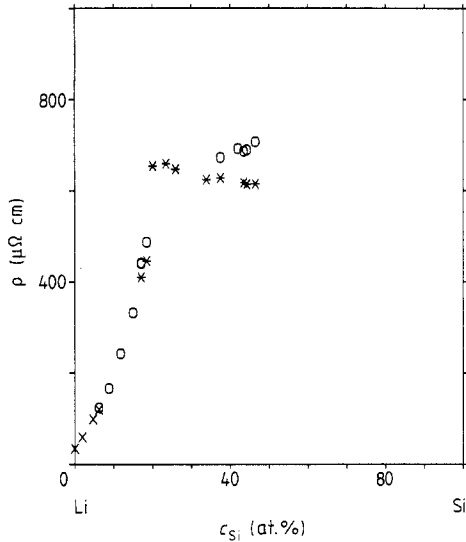
For the Knight shift measurements we used a Varian VF16 wide-line spectrometer provided with a furnace which is capable of heating the sample to 800 °C without damaging the inside of the probe holder (which tolerates no higher than 60 °C). The construction is derived essentially from that of Styles and Sheffield (1976) and was gradually improved (Van der Marel *et al* 1980). Essential for the present design is the use of a coaxial heater element resulting in an almost homogeneous magnetic field.

Samples were dispersed in fine LiF powder; together with the LiF crucible, this powder provided the reference signal. The metal signal was obtained from particles between 200 and 300  $\mu\text{m}$  in size. We did not succeed in making a dispersion for Li-rich samples, as such samples are too soft to be filed or crushed. The high liquidus temperatures prohibited us from making a dispersion by directly stirring LiF powder into the liquid. Thus, measurements were restricted to a composition range of  $0.18 < c_{\text{Si}} < 0.50$ .

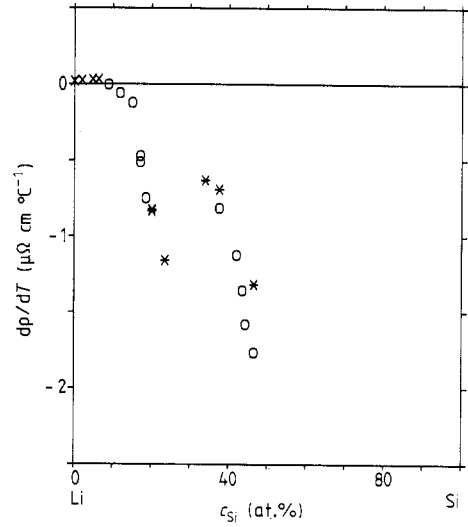
## 3. Results

Figure 2 shows the measured resistivity  $\rho$  and figure 3 its temperature derivative  $d\rho/dT$ . In contrast with the usual behaviour of  $\rho$  in compound-forming systems, there is no sharp maximum in the  $\rho$  against composition curve, but rather a plateau between  $c_{\text{Si}} = 20$  at.% and  $c_{\text{Si}} = 45$  at.%. In this concentration range, resistivity values around 650  $\mu\Omega\text{ cm}$  are reached, characteristic of Mott's 'regime of diffusive motion'. The temperature derivative  $d\rho/dT$  is strongly negative in this region, and has minima near 20 and 43 at.% Si.

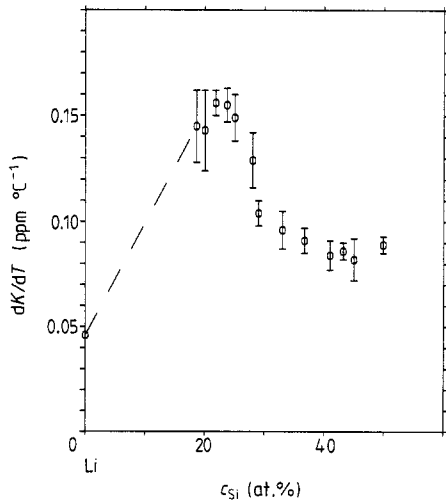
In figure 4 the  $^7\text{Li}$  Knight shift is displayed and in figure 5 its temperature derivative. The NMR measurements mirror the resistivity results; the  $^7\text{Li}$  Knight shift decreases to roughly one third of its value for pure Li between  $c_{\text{Si}} = 0$  and  $c_{\text{Si}} = 20$  at.%. Subsequently,  $K$  exhibits a further slight monotonous decrease up to  $c_{\text{Si}} = 50$  at.%. In  $dK/dT$ , the peak at 20 at.% Si is the most remarkable feature.



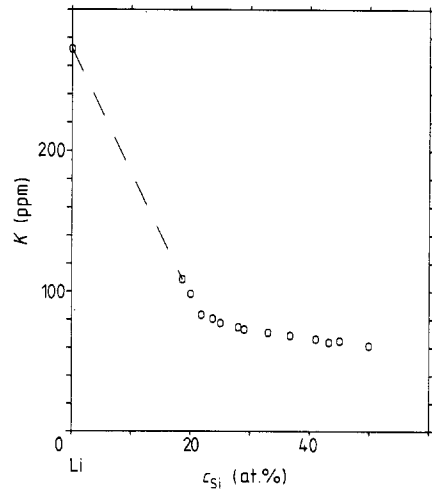
**Figure 2.** Resistivity  $\rho$  of liquid Li-Si alloys as a function of composition, interpolated for temperatures of 500 °C (x), 700 °C (O) and 760 °C (\*).



**Figure 3.** Temperature derivative  $dp/dT$  of the resistivity of liquid Li-Si alloys as a function of composition, interpolated for temperatures of 500 °C (x), 700 °C (O) and 760 °C (\*).



**Figure 4.** The Knight shift  $K$  of liquid Li-Si alloys at a temperature of 727 °C, plotted as a function of composition. The experimental error is smaller than the size of the data symbols.



**Figure 5.** The temperature derivative  $dK/dT$  of the Knight shift plotted as a function of the composition.

## 4. Discussion

### 4.1. Relations between resistivity and NMR data

The theoretical interpretation is clearly outside the scope of the diffraction model. Instead, we try to understand the results as being a consequence of a lowered density of

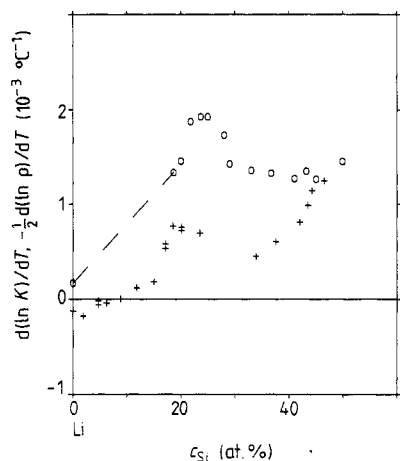


Figure 6.  $d(\ln K)/dT$  (O) compared with  $-\frac{1}{2} d(\ln \rho)/dT$  (+).

electron states at the Fermi level. For the resistivity, we have a proportionality (Mott and Davis 1979)

$$\rho = \rho_0 g^{-2} \quad (1)$$

where  $g$  is the Mott  $g$ -factor:  $g = N(E_F)/N_{\text{free}}(E_F)$ ;  $\rho_0$  is almost independent of temperature and concentration.

The  $^7\text{Li}$  Knight shift is approximately proportional to the contact density at the Li nucleus, in so far as it is provided by states at the Fermi energy. The decrease in  $K$  is thus the combined effect of reduction in  $N(E_F)$  and depletion of the Li  $s$  band. In an effort to separate the two, we compare the logarithmic temperature derivatives of  $\rho$  and  $K$  (figure 6). If  $K$  depends on  $N(E_F)$  only, we would have

$$d(\ln K)/dT = -\frac{1}{2} d(\ln \rho)/dT. \quad (2)$$

In figure 6  $d(\ln K)/dT$  and  $\frac{1}{2}d(\ln \rho)/dT$  are critically compared. It should be noted that the error in  $d \ln K/dT$  is estimated to be of the order of 20%, and that in  $d(\ln \rho)/dT$  significantly smaller. As (2) apparently does not hold, charge transfer must play an important role. Formulated more precisely, the ratio of Li  $1s$  to Si  $6p$  partial density at the Fermi level is shown to be temperature dependent for  $c_{\text{Si}} < 40$  at.%. The peak in  $dK/dT$  at 20 at.% Si must be explained chiefly by an increase in Li contact density with rising temperature. Around  $c_{\text{Si}} = 45$  at.%, both sides of (2) are nearly equal; here,  $dK/dT$  does reflect the increase in the total density of states at  $E_F$  with rising temperature.

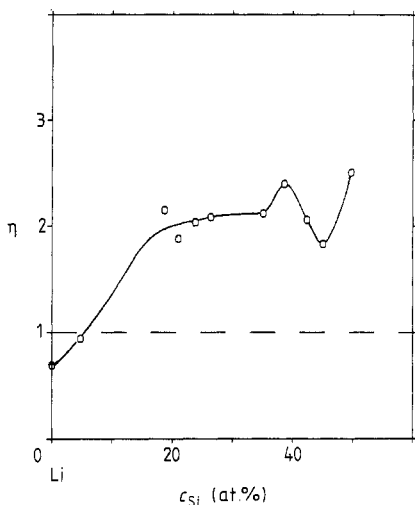
Recent  $T_1$  measurements by the Grenoble  $\beta$ -NMR group (Van der Marel *et al* 1984) enable us to calculate the Korringa enhancement  $\eta = (K^2 T_1 T)_{\text{Korr}}/K^2 T_1 T$ . In figure 7,  $\eta$  is plotted as a function of concentration, for a temperature of 727 °C. In the diffusive motion regime, we have an approximate relation (Warren 1971)

$$\sigma\eta = \sigma_0 = \text{constant} \quad (3)$$

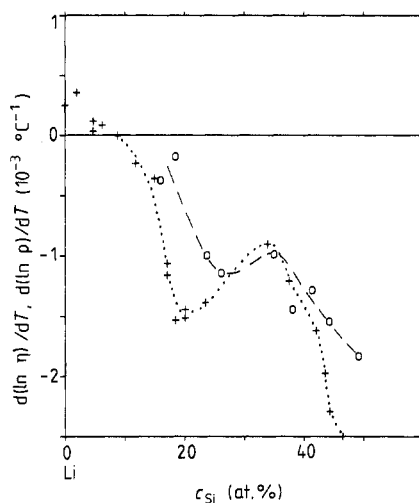
or

$$d(\ln \rho)/dT = d(\ln \eta)/dT. \quad (4)$$

We compare the temperature dependences of the  $\sigma$  and  $\eta$ , rather than  $\sigma$  and  $\eta$  themselves. The latter would not be very informative, as both quantities do not change much



**Figure 7.** The Korrunga enhancement  $\eta$  for liquid Li-Si alloys at 727 °C.



**Figure 8.** Comparison of  $d(\ln \eta)/dT$  (○) with  $d(\ln \rho)/dT$  (+).

with composition in the region of interest (the constant  $\sigma_0$  in equation (4) is  $3000 \Omega^{-1} \text{cm}^{-1}$ ). Equation (4) is confirmed in figure 8. It is found to hold with satisfactory accuracy.

#### 4.2. Atomic and electronic structure

The comparison between  $\rho$ ,  $T_1$  and  $K$  has been helpful in showing the consistency of the experimental data on the Li-Si liquid alloys system. To go beyond this and to discuss the physical origin of the plateau in  $\rho$  and  $K$  between 20 and 45 at.% Si, we have to construct a model for the atomic and electronic structures. Polyanionic clusters occur in the solid phases of most alkali-group IV compounds. More particularly the persistence in the liquid phase of tetrahedral polyanions has been advocated as an explanation for the anomalous resistivities of alkali-Pb and alkali-Sn alloys (Van der Marel *et al* 1982, Meijer *et al* 1986, Van der Lugt and Geertsma 1987) and the behaviour of the Knight shift in liquid Na-Sn (Van der Marel *et al* 1983). Model calculations (Geertsma *et al* 1984) showed the feasibility of this explanation; it was found that cluster formation is favoured by a large ratio of anion-to-cation diameter. For Li-Si, the calculations predicted that  $\text{Si}_4$  tetrahedra could not be stable. The small size of the Si ion, however, indicates a tendency towards covalent bonding. As with the alkali-Pb alloys, we look at the crystal structures of the solid compounds for guidance. The various Zintl ions ( $\text{Si}_2$  pairs,  $\text{Si}_4$  stars and  $\text{Si}_5$  rings) that have been observed in the crystals certainly should be considered for inclusion in a model of the atomic structure of the liquid. Clearly, we are somewhat embarrassed by this rich choice; without further information, it is not possible to decide which Zintl ions to include in the model, and in what proportions.

The high-resistivity plateau can, in principle, be explained without such detailed knowledge. If indeed covalent bonding is dominating, it is energetically favourable if  $E_F$  is in a gap, i.e. in a deep minimum of the density of states between bonding and anti-bonding states. By making the plausible assumption that for each alloy composition the polyanions form precisely the number of covalent bonds needed to keep the Fermi

level in this minimum the Knight shift and resistivity results are, at least qualitatively, understood.

This interpretation would then be corroborated by the results of recent measurements of the thermopower of liquid Na-Sn. In the tin-rich alloys this quantity turns out to be unexpectedly small, a non-event that can be explained by making the same assumption about  $E_F$ . These results and their interpretation will be communicated in a separate paper.

### Acknowledgments

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