Relation between NMR Properties and Electrical Resistivity in Li-Ge, Li-Sn and Li-Pb Liquid Alloys

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Dedicated to Professor Hans-Uwe Schuster on the occasion of his 65th birthday

Recent measurements of the electrical resistivity of liquid Li-Ge alloys enable us to check relations between NMR properties and resistivity in non-metallic alloys derived by Warren in 1971. It is shown that the predicted linear relationships hold, but that the proportionality between the square root of the conductivity and the Knight shift is violated to some degree. A possible cause is the neglect of quadrupole interactions. Also, the relations only hold if the composition rather than the temperature is taken as the implicit parameter.

Key words: Liquid alloys; Electrical resistivity; Knight shift; Spin-lattice relaxation time; Molten semiconductors.

In 1971 Warren [1] derived relations between the Knight shift, K, and the Korringa enhancement factor η on the one hand and the electrical resistivity ϱ on the other hand. In the conduction regime II (diffusive motion of electrons) as defined by Mott and Davis [2] the following relations should hold:

$$K^2\varrho = \text{constant} \tag{1}$$

and

$$\sigma\eta = (e^2 d^2/3\Omega\hbar) = \sigma_0\,, \tag{2}$$

where $\sigma = 1/\varrho$, e is the electronic charge, d a jump distance and Ω the mean atomic volume. Equation (1) follows directly from the Kubo-Greenwood expression for the conductivity and from the proportionality between the Knight shift and the electronic density of states, while (2) is derived by describing the electronic conduction as a process in which the electrons jump from one atomic cell to the other. The work of Warren was given a more solid basis by Götze and Ketterle [3] using general mode coupling theory. Recently we have measured resistivities of liquid lithium-germanium alloys [4]. They prove to correspond to Mott's regime II in a considerable composition range. Combining these results with those for the Li Knight shift K [5] and spin-lattice relaxation time T_1 [6] we can check Warren's relations. Additionally we have checked (1) for Li-Pb and Li-Sn alloys.

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The resistivity measurements (see Fig. 1) show a huge peak up to approximately 1000 μΩ cm at a composition of 20 at.% Ge. A weak shoulder at this peak is found at approximately 45 at.% Ge. This shoulder is more distinct in the temperature derivative of ϱ, $d\varrho/dT$ [4]. The peak at 20 at.% Ge is attributed to the formation of an octet compound Li_4Ge [4], the shoulder to clustering phenomena similar to those found in Li-Si [8–10], but much weaker. Liquid Li-Si probably contains strongly covalently bonded Si clusters, but, descending in the fourth main group of the periodic system to Li-Pb these covalent properties are gradually lost [4]. Covalent Ge clusters of various kinds have been found in solid Li-Ge alloys [11–14].

The ^{7}Li Knight shift [5] drops sharply when germanium is added to pure lithium and has distinct minima at 20 at.% Ge and 43 at.% Ge, i.e. at approximately the compositions of the maximum and the shoulder in the resistivity. The drop is explained by electron transfer from lithium atoms to germanium atoms, so that the local electronic density, $|\psi(0)|^2_F$, at the Li nuclei is reduced. The minima are attributed to the reduction of the electronic density of states, $N(E_F)$, at the Fermi level, as expected for electrons conforming to regime II (see [15]). This decomposition in $|\psi(0)]^2_F$ and $N(E_F)$ is, however, somewhat arbitrary. The spin-lattice relaxation time [6] exhibits a similar drop as the Knight shift, but is flatter in the remaining composition range. The Korringa enhancement factor, finally, exhibits

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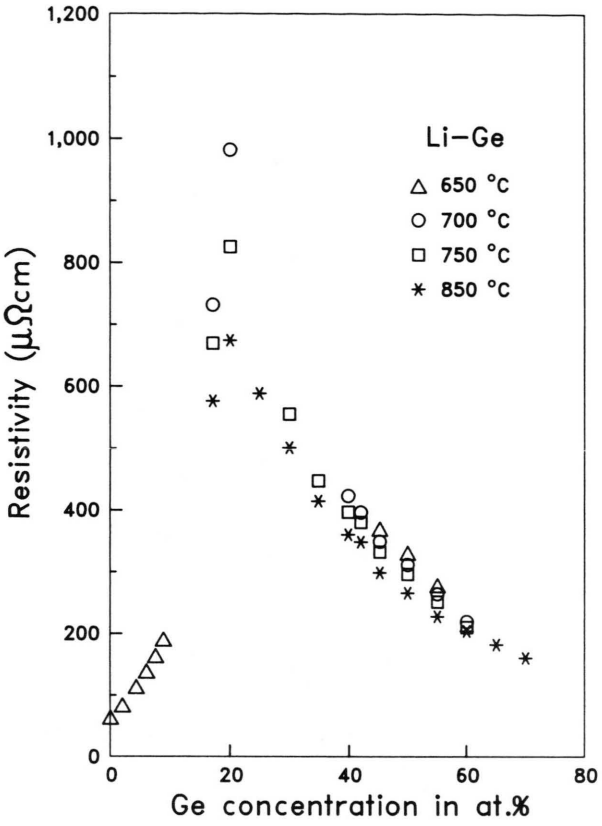

Fig. 1. The resistivity ϱ of liquid Li-Ge alloys as a function of the composition at the temperatures indicated in the figure. The data between 0 and 9 at.% Ge are adopted from [7].

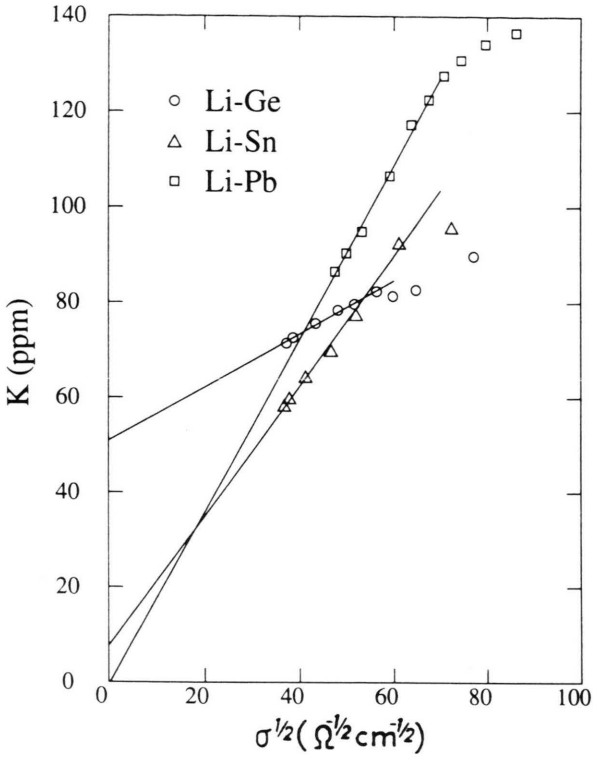

Fig. 2. The ^{7}Li Knight shift K versus the square root of the conductivity σ for liquid Li-Ge, Li-Sn, and Li-Pb alloys at temperatures close to the liquidus.

distinct peaks at germanium concentrations of 20 and 50 at.%.

The resistivities of liquid Li-Pb and Li-Sn alloys are taken from [16] and [17], respectively, and the Knight shifts from [15]. The properties of these alloy systems are amply discussed in these papers. They are in many respects analogous to those of the Li-Ge alloys. An exercise, similar to the one presented here for Li-Ge, Li-Sn and Li-Pb has been carried out previously for Li-Si [10].

In Fig. 2 the Knight shifts of ^{7}Li in liquid Li-Ge, Li-Pb and Li-Sn alloys are plotted as functions of $\sigma^{1/2}$. We see that the proportionality holds quite well in the diffusive motion regime of Li-Sn and Li-Pb, but that in the case of Li-Ge the extrapolation of the straight line does not pass through the origin. Also, it should be noted that this linear relationship was found using the composition, rather than the temperature, as the implicit parameter. Similar results have been obtained for Cs-Sb alloys [18]. For Li-Ge also a nice relationship between $\mathrm{d}\ln K/\mathrm{d}T$ and $-(1/2)\,\mathrm{d}(\ln\varrho)/\mathrm{d}T$ was found (see Figure 3). Also in this plot a maximum around 45 at.% Ge shows up.

Relation (2) has been checked in Fig. 4 for liquid Li-Ge. We see that the linear relationship between ϱ and η holds fairly well in the diffusive motion regime. The constant σ_0 is about 3200 $(\Omega\ \mathrm{cm})^{-1}$, which is close to the values of 3000 $(\Omega\ \mathrm{cm})^{-1}$ and 3400 $(\Omega\ \mathrm{cm})^{-1}$ found for the Li-Si [17] and Li-Pb [19] systems, respectively. In the metallic regime, apart from one point, η is of the order 1. For $\eta = 1$, $\sigma = \sigma_0 \approx 3200\ (\Omega\ \mathrm{cm})^{-1}$ in good agreement with the value given by Mott for the transition from regime I to regime II [2]. Remarkably, as was shown earlier [20], (2) does not hold in the diffusive motion regime for Li-Sn alloys. The experimental data conform to a relation $\sigma^2\eta = \sigma_0$ rather than to (2).

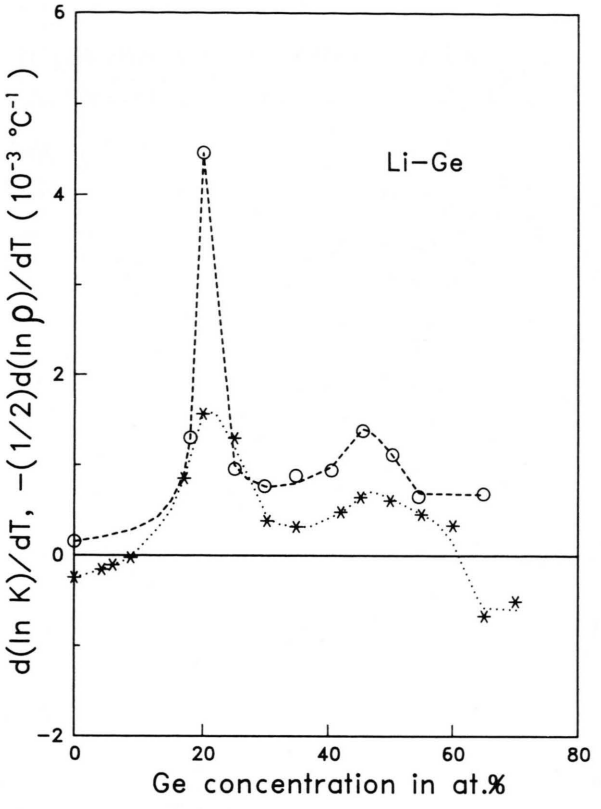

Fig. 3. d (ln K)/dT (o) compared with (1/2) d(ln ϱ)/dT (*) for liquid Li-Ge alloys at temperatures close to the liquidus.

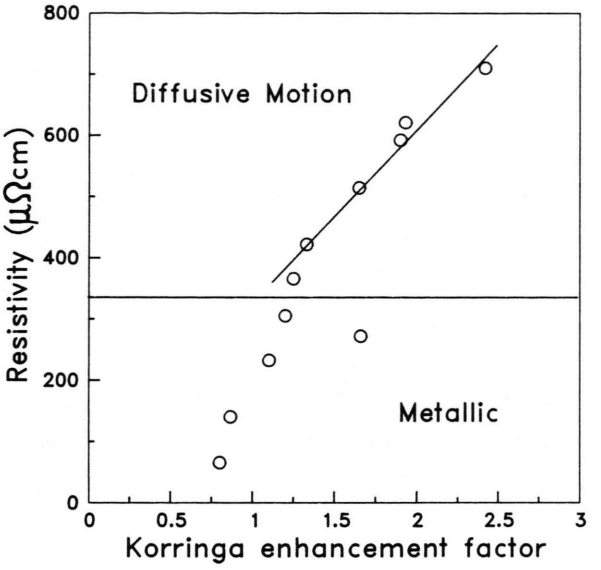

Fig. 4. Resistivity ϱ versus Korringa enhancement factor η for liquid Li-Ge alloys at 830 °C.

The data in the Figs. 2, 3, and 4 show a quite satisfactory agreement between the Warren-Götze model and experiment. It should be noted that we have left out of consideration possible quadrupole effects on the spin-lattice relaxation. Experimentally they can be distinguished only when measurements on different isotopes are carried out. It should also be noted that the Knight shifts quoted were not corrected for the chemical shift of the reference material, which was LiF in all cases.

In deriving (1), implicitly the assumption is made that $|\psi(0)|_F^2$ is constant. As mentioned above, this is probably not the case for $c_{Li} > 80\%$. These compositions were left out of consideration. For the remaining alloys the assumption is plausible within the framework of the Mott theories, but it is not rigorously proven.

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