

Knight shift of ^{23}Na and ^7Li nuclei in liquid sodium-lithium alloys

P. D. Feitsma, G. K. Slagter, and W. van der Lugt

Solid State Physics Laboratory, Materials Science Center, University of Groningen, Groningen, The Netherlands

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The Knight shifts of the sodium and lithium nuclei in liquid sodium-lithium alloys have been determined as a function of concentration at 400 °C. A linear relation between the Knight shifts and the atomic concentration has been found. The conduction-electron contact density changes by 19% for Na and by 35% for Li. Some of the theoretical implications are discussed briefly.

The Knight shifts in alkali alloys not containing lithium have been determined by Rimai and Bloembergen,¹ van der Molen *et al.*,^{2,3} and by Kaeck.⁴ A review of the results and their interpretation is given in a recent paper by van Hemmen *et al.*⁵ The experimental results can be summarized in the following rules.

(i) The Knight shift K is a linear function of the atomic concentration c .

(ii) If the indices a and b refer to the components with the smaller and larger atomic weights, respectively,

$$\frac{dK_a}{dc_b} > 0; \quad \frac{dK_b}{dc_b} > 0. \quad (1)$$

(iii)

$$\frac{1}{K_a} \frac{dK_a}{dc_b} \approx \frac{1}{K_b} \frac{dK_b}{dc_b}, \quad (2)$$

where K_a and K_b refer to the same composition. For the interpretation of rules (i)–(iii), two models have been discussed.

A. Constant P_F

According to a conjecture by Kaeck⁴ and calculations by Perdew and Wilkins,⁶ the contact density of the conduction electrons P_F is approximately independent of the composition. As in this model the spin susceptibilities χ_b of potassium, rubidium, and cesium appear to be nearly equal, the linear relation corresponding to the first rule follows by substituting

$$\Omega = c_a \Omega_a + (1 - c_a) \Omega_b \quad (3)$$

in the well-known relation

$$K = \frac{8}{3} \pi \chi_b \Omega P_F. \quad (4)$$

Here Ω is the mean atomic volume. Relation (3) applies, by definition, to ideal mixtures. For sodium alloys, the supposition of constant P_F does not lead so simply to a linear $K(c)$. Measurements in ternary alloy systems⁵ have demonstrated that P_F may be rather strongly depen-

dent on concentration in alkali alloys containing sodium.

B. Single-augmented-plane-wave (APW) model

van Hemmen *et al.*⁷ have developed a model in terms of single augmented plane waves which is based essentially on appropriate wave-function normalization. If χ_b is taken to be proportional to its free-electron value and if, again, relation (3) is applied, a linear $K(c)$ follows for all binary alkali systems not containing lithium. Indeed, the assumption of free-electron-like susceptibilities still lacks sufficient justification.

The extension of the investigations to lithium alloys is appealing from a physical point of view but entails some experimental difficulties. The conduction-electron densities of the alkali metals, although varying strongly from Cs to Li, are all considerably smaller than those of the other metals. Clearly, lithium forms an intermediate case. Therefore, it is interesting to investigate to what extent rules (i)–(iii) mentioned above are obeyed by the Na-Li alloys system, which covers a conduction-electron density range of 1:2.

A complication is that—probably as a consequence of its small core—many physical and chemical properties of pure lithium are atypical for alkali metals. The liquid Na-Li system exhibits a miscibility gap up to 303 °C.^{8–11} Lithium heavily attacks most isolating refractories and easily forms nitrides when exposed to the air. From the large size difference between sodium and lithium ions one expects a large Matthiessen resistivity for the Na-Li system, which in fact has been shown to be small compared to the other alkali systems.⁸

Fortunately, the spin susceptibilities of Na and Li are rather well known from conduction-electron-spin-resonance (CESR) experiments. Various results are collected in Table I. As the temperature dependence of χ_b is still uncertain, the extrapolation to 400 °C, at which temperature the experiments have been performed, must be

TABLE I. Spin susceptibilities of lithium and sodium.

Authors	Lithium	
	χ_p (10^{-6} cgs vol. units)	Temperature ($^{\circ}$ K)
Schumacher and Slichter (Ref. 13)	2.08	300
Ryter (Ref. 14)	2.13 ^a	4.2
Kettler <i>et al.</i> (Ref. 15)	2.09	290
Kettler <i>et al.</i> (Ref. 15)	2.18	4.2
Hecht (Ref. 16)	1.96	1.5; 77; 300
Sodium		
Schumacher and Vehse (Ref. 17)	1.13	20
Ryter (Ref. 18)	1.09	1.2

^a Value derived from Ryter's P_F and $K=0.026\%$.

guessed. We have chosen $\chi_p=2.06\times 10^{-6}$ for Li and $\chi_p=1.11\times 10^{-6}$ for Na, both in cgs volume units.

The miscibility gap and the reactivity present a number of experimental complications. These were overcome first by using LiF crucibles¹⁹ made by lathing LiF single crystals, and second by constructing a high-temperature Dewar of the type designed by Schreiber²⁰ and Clark²¹ to fit the Varian VF 16 probe head used for the NMR experiments. A fine dispersion of liquid-metal

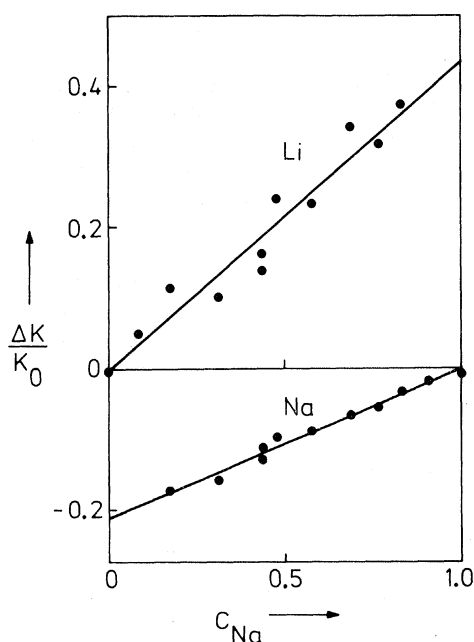


FIG. 1. Relative change $\Delta K/K_0$ of the Knight shifts of sodium and lithium nuclei as a function of the atomic concentration of sodium, c_b . Data were taken at 400° C.

particles, as required for NMR experiments, was obtained by mixing the liquid alloy with LiF powder. At higher temperatures, care had to be exercised to avoid alloy composition changes as a consequence of Watt's principle. The NMR techniques used have been described in Ref. 5.

The Knight-shift results at 400° C are given in Fig. 1, where $\Delta K/K_0=[K(c)-K_0]/K_0$ is plotted for each of the components. (K_0 is the Knight shift of the pure component at 400° C; we found $K_0=0.0257\%$ for Li and $K_0=0.1219\%$ for Na.) The slopes $K_0^{-1}dK/dc_b$ of the straight lines in Fig. 1, obtained by a least-squares fit, are 0.44 and 0.21 for lithium and sodium, respectively. The figure shows that rules (i) and (ii) mentioned above are obeyed by the Na-Li alloys. Because the Knight shift of pure lithium is much smaller than that of pure sodium, the error in $\Delta K/K_0$ is considerably larger for the lithium nuclei than it is for the sodium nuclei. Consequently, the linearity between K and c appears to be less certainly established for the lithium resonances. Yet, the deviations from the straight line are quite randomly distributed and we have no reason to assume that nonlinear terms are needed for representing the experimental data.

The third rule mentioned above [Eq. (2)] is, at the other hand, not obeyed. For example, at the sodium-rich end of the concentration range, $K^{-1}dK/dc_b=0.211$ for Li and 0.304 for Na. The relation (2) is a mathematical consequence of the single-APW model. If this relation is violated, this model is not applicable. It may also be shown that P_F is not a constant throughout the system. Indeed, $P_{F,Na}(0)/P_{F,Li}(0)=\chi_{p,Li}\Omega_{Li}P_{F,Na}(0)/\chi_{p,Li}\Omega_{Li}P_{F,Li}(0)=K_{Na}(0)/K_{Li}(0)=3.74$ (where the argument of P_F and K is c_b), whereas, in the same way, one finds $P_{F,Na}(1)/P_{F,Li}(1)=3.31$. Thus $P_{F,Na}/P_{F,Li}$ depends on c_b . Consequently, $P_{F,Na}$ and $P_{F,Li}$ cannot be simultaneously independent of concentration. Numerically, substituting known atomic volumes⁹ and susceptibilities in Eq. (4), one finds $P_{F,Na}(1)/P_{F,Na}(0)=1.19$ and $P_{F,Li}(1)/P_{F,Li}(0)=1.35$. So the conjecture of constant P_F does not hold for this alloy system. A similar conclusion was obtained for sodium in ternary alkali systems.⁵ It should also be noticed that the single-APW model requires $P_{F,Na}/P_{F,Li}$ to be constant. There is still another reason why an evaluation in terms of this model is unfeasible. The ratio of the spin susceptibilities of pure lithium and pure sodium is 1.85, whereas for free electrons it should be 1.22. The assumption of free-electron susceptibilities is of vital importance for the APW model.

So we are left with the puzzling situation that, on the one hand, the linear relation between

Knight shift and concentration still holds for the Na-Li system as well as it did for the other alkali systems, but on the other hand, as a consequence of the numerical results, we are deprived from the means of its theoretical justification in terms of the unsophisticated models previously used.

The interpretation of the results is seriously handicapped by our lack of understanding of the electronic structure of pure lithium. For solid lithium, χ_p amounts to approximately 2.6 times its free-electron value. As upon melting the Knight shift changes by only a negligible amount,²² the same value of χ_p is expected in the liquid state.²³ There exists no consensus about the origin of this high χ_p , but one is probably not far from the truth in attributing it to a combination of a large density of states (conveniently expressed by an effective mass ratio m^*/m) and a considerable enhancement by electron-electron interaction. Indeed, Ham²⁴ has calculated $m^*/m=1.66$ and, more recently, Rudge²⁵ found $m^*/m=1.65$ and $m^*/m=1.55$, depending on the type of exchange interaction applied. From the experimental results of Filby and Martin²⁶ follows a specific heat m^*/m of 2.19 which reduces to 1.82 when corrected for electron-phonon and electron-electron interaction.²⁷ For sodium, m^*/m is usually believed to be close to 1. In the alloy system, m^*/m changes more rapidly than either of the two Knight shifts. Therefore, m^*/m cannot be obtained by some simple interpolation; a reliable calculation of m^*/m is a primary precondition for a theoretical interpretation. The enhancement due to electron-electron interaction is also of the order of 1.6 for pure lithium, but in the usual approximations is a slowly varying function of Ω .²⁸ It constitutes no serious problem in explaining the Knight shift.

The sodium-lithium alloys form an ideal system, i.e., Eq. (3) applies.⁹ This enables us to calculate the free-electron susceptibility χ_{pf} . Furthermore, P_F can be expressed in the free-atom contact density P_A by $P_F = \xi P_A$, P_A being known accurately from optical pumping experiments²⁹ and atomic beam experiments.³⁰ Substituting χ_{pf} , Ω , and $P_F = \xi P_A$ into Eq. (4), we

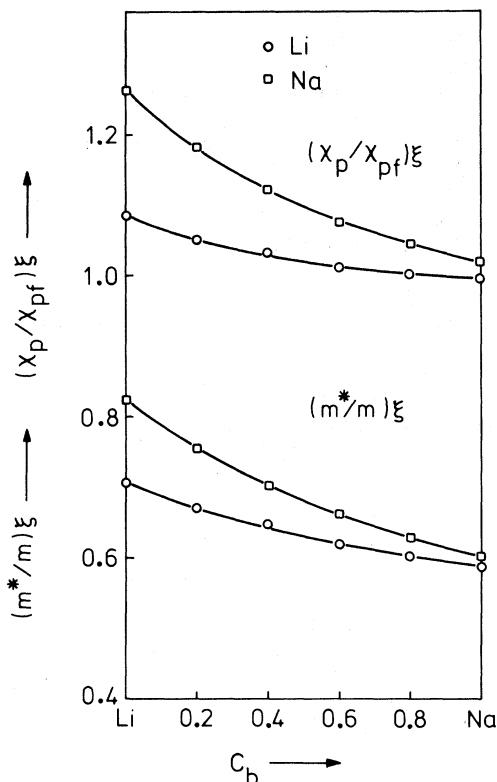


FIG. 2. $(\chi_p/\chi_{pf})\xi$ and $(m^*/m)\xi$, as derived from the measurements, plotted as a function of atomic concentration.

can express the Knight shift in the convenient quantity $\xi\chi_p/\chi_{pf}$, which is of the order of 1. Using Dupree and Geldart's results²⁸ for the electron-electron enhancement we can reduce this quantity further to $\xi m^*/m$. Both quantities are plotted in Fig. 2 as a function of concentration.

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