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Nuclear magnetic resonance studies of liquid metal alloys

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Abstract. The Knight shift K and quadrupolar relaxation rate R_q in liquid metallic systems, in which effects of bonding become increasingly prominent, are surveyed. In Rb, a theoretical calculation of R_q , including mode-coupling theory for the liquid, and the r -dependent Sternheimer factor, predicted closely the recent experimental redetermination. In Ge, and in Cu–Ge and similar nearly free-electron systems, the quantitative analysis of K still poses problems, while qualitatively $K(x)$ displays clearly a correspondence to the resistivity maximum. In metallic alloys with compound forming tendency, models based on an association ($A + B \rightleftharpoons AB$) connect K and R_q quantitatively with the heat of mixing, but the microscopic foundation of the association *ansatz* is uncertain.

1. Introduction

An understanding of liquid metals and alloys is important from very diverse points of view, such as phase diagrams, heat and other transport, crystallization and glass formation, and electrons in disordered matrices. NMR results have contributed to many of these questions. An extremely useful collection of the existing material has been presented in 1976 by Carter *et al* [1]. An update of references to later work will appear [2]. General references to NMR and related techniques are [3] and [4]. The present survey will concentrate on the Knight shift K and quadrupolar relaxation rate† R_q . Techniques which use unstable nuclear states (β -NMR or TDPAD, see [4]) are especially important where NMR is difficult or impossible (low sensitivity; very low concentration; no quadrupolar interaction because $I < 1$).

2. Pure liquid metals

Liquid alkalis are considered as the simplest and best understood metallic liquids. The dynamic quadrupolar perturbation of the nuclear spin, i.e. $R_q = (1/T_1)_q$, is determined by an ionic and an electronic ingredient, namely by the relative motion of near neighbours

† Isotopic separation or an estimate of the magnetic relaxation rate R_m allows one to derive R_q from the observed total rate $R = R_q + R_m$. The precise expression for R_q differs for NMR and TDPAD [4].

i , and by the electrostatic field gradient V_{zz} at the NMR nucleus, induced by the momentary presence of all neighbours i :

$$R_q \sim Q^2 \int \left\langle \sum_i V_{zz}^{(i)}(t=0) \sum_j V_{zz}^{(j)}(t) \right\rangle dt \quad (1)$$

or in abbreviated form $R_q \sim Q^2 \langle V_{zz}^2 \rangle \tau$. After several early attempts (see [5] and references therein) a new series of calculations for Rb followed in the 1980s [6, 7]. Among these, the work of Bosse *et al* [6] for Rb treated in detail the EFG contribution of the conduction electrons including an r -dependent Sternheimer correction, while the dynamics of the ion cores was calculated by mode-coupling theory. A redetermination of R_q for liquid Rb was done shortly after that by Dupree and Rogers [8]: $R_q = 99(22) \text{ s}^{-1}$, in satisfactory agreement with the calculation in [6] which gives $R_q = 60 \text{ s}^{-1}$ (in [7], $R_q = 24.4 \text{ s}^{-1}$). Quite good agreement has also been achieved for the temperature dependence in Ga [9], but precise calculations are still lacking for most liquid metals.

The Knight shift K originates primarily from a spin polarization of the conduction electrons (at the Fermi energy ε_F) which is transferred to the nucleus (by the finite s -electron density $|\psi(0)|^2$ at the nucleus)

$$K \approx K_s = (8\pi/3)\chi_P\Omega\langle|\psi(0)|^2\rangle_F. \quad (2)$$

Here χ_P is the Pauli spin susceptibility ($\sim N(\varepsilon_F)$) and Ω an atomic normalizing volume. K thus combines local with average conduction electron properties. K has been measured only recently for a rather interesting elemental liquid metal: Ge. Dürrwächter *et al* [10] found at 1210–1370 K that $K(\text{Ge}) = 0.53(7)\%$, while the value predicted by Heighway and Seymour [11] from a systematic study was 0.51%. The excellent agreement is, however, somewhat surprising for the following reasons:

(i) There is no agreement for As, where $K = 0.31\text{--}0.33\%$ (in metallic conditions [1, 10]) while [11] predicted 0.53%. The usefulness of the immediate explanation by the 'increasing p character' is reduced by (ii).

(ii) Recent density-of-states measurements by photoelectron spectroscopy [12] indicate a rather high p character at ε_F (and for some electron volts below) already in liquid Ge, Sn and Pb. Then the usual direct term for K and K_s (equation (2)) becomes too small to sustain the agreement with experiment (see [10]). The resolution of this discrepancy may come from (iii).

(iii) The Van Vleck contribution to K can be very considerable, e.g. in d elements [13]. It remains to be seen whether this effect, and perhaps further corrections, may re-establish a proportionality of K with $N(\varepsilon_F)$ as is implied in (2), and *grosso modo* observed experimentally.

3. Binary alloys

In liquid alloys $A_{1-x}B_x$ of $A \equiv \text{Cu, Ag, Au}$ with $B \equiv$ polyvalent p metals from group IIIA, IVA, VA, a nearly free-electron (NFE) description will be appropriate; see the description [14] of electrical resistivity $\rho(x)$ by the Faber–Ziman *ansatz*. Using an average electron–ion pseudopotential $v(q)$, one has $\rho \sim \int_0^{2k_F} q^3 |v(q)|^2 S(q) dq$; $S(q)$ is the average structure factor of the liquid alloy. The resistivity achieves a maximum versus x when $2k_F \sim [((1-x)Z_a + xZ_b)/\Omega]^{1/3}$ matches q_p , the peak of $S(q)$; this tends

to happen at about 1.8 electrons/atom [15]. There are concomitant effects in the enthalpy $\Delta H(x)$ of mixing [16], magnetic susceptibility χ and Knight shift [17].

These expectations are nicely confirmed by a measurement of K for ^{63}Cu in $(\text{Ag}_{0.5}\text{Cu}_{0.5})_{1-x}\text{Ge}_x$ [18]; for χ , see [19], for ρ see [20] and for ΔH see [21]. It is interesting to note that δK for Cu seems to be independent of the Cu-to-Ag ratio [18] whereas $|\Delta H|$ is largest in Cu–Ge [21]; this is probably due to a d-state contribution to ΔH [18]. A comparable case is $K(x)$ and $\rho(x)$ in Cs–Na, where probably excited Cs d states influence ρ , but not K [22, 23].

A rough estimate of the bond energies can be obtained using δK . Let the average energy gain by the conduction electrons at ε_F , due to their (pseudopotential) interaction with the liquid structure, be $\delta\varepsilon_s$. The Knight shift depression $\delta K/K$ implies a reduction in the density of states: $\delta N(\varepsilon_F)_K = N(\varepsilon_F) \delta K/K$. Since this is caused by the energetic downshift of states by $\delta\varepsilon_s$, the total energy gain, assumed to be the main part of the observed ΔH , will be

$$\Delta H \approx \frac{1}{2} \delta N(\varepsilon_F) \delta\varepsilon_s^2. \quad (3)$$

Using the values for $(\text{Cu}_{0.5}\text{Ag}_{0.5})_{0.75}\text{Ge}_{0.25}$, $\Delta H = -6 \text{ kJ mol}^{-1}$ [21]; $\delta K/K_{\text{FE}} = -0.2$ [18]; one arrives at $\delta\varepsilon_s \approx 1 \text{ eV}$. This fits reasonably with the magnitude of the shift $\delta\varepsilon_w$, as expected from the width δq_s of the $S(q)$ curve: $\delta\varepsilon_w \approx \delta q_s (\delta\varepsilon/dq)_{\text{FE}} = 2\varepsilon_F \delta q_s/q_P$.

The above-mentioned effects of bonding (and equivalently scattering) correspond to the Brillouin-zone effects well established e.g. in the Cu–Zn alloys. The application of the NFE model is supported by the *symmetric* shape of the deviation of $K(x)$ from the (free-electron) interpolation; by essentially identical $\delta K/K$ for both nuclei of the alloy [18], and by the occurrence of eutectics or weakly bound intermetallics with wide solubility in the solid state. In contrast, the model of association (see below) predicts an asymmetry in $K(x)$ and sharp stoichiometries. In terms of the above integral expression for ρ , the NFE effects stem mainly from $S_{nn}(q)$, while the association model focuses on the concentration fluctuation structure factor $S_{cc}(q)$ (see [24]) together with their corresponding interactions v_{nn} or v_{cc} .

As the last group of systems, liquid alloys with strong bonding and compound-forming tendency will be considered. When the interaction in a series becomes stronger, the broad resistivity maximum $\rho(x)$ grows into a sharp high peak at the stoichiometry x_s (see, e.g., the review in [23]). However, already at moderate increases in ρ_{max} , where the NFE model seemingly still produces good agreement, K starts to behave in a characteristic way. In $\text{Li}_{1-x}\text{In}_x$, $\rho(x)$ increases ‘only’ by a factor of 4 [25], while K for both ^7Li and ^{115}In decrease by about $\delta K/K = 0.5$ from their pure metal values towards $x_s = 0.25$. However, both K -values *stay low* on their respective minority sides, in contrast to, for example, Cu–Ge, Cu–Al [18]. The same shape has been found in virtually all the Li–(III, IV, V) systems, Cs–Au, Cs–Sb on the alkali, Cu–Te on Cu and Te, Sn–Te on Te.

This concentration dependence suggests the use of a chemical equilibrium *ansatz* of the type well accepted for thermodynamics of liquid alloys [24, 26]; schematically



Here A and B denote the state of the two constituent atoms as ‘free’ metallic like, while AB (generally $A_\mu B_\nu$) denotes a ‘bound’ associated state (bimodal distribution of states). The respective concentrations of these three species are obtained from the law of mass action and interaction parameters (energy, entropy of formation of AB, interactions A–AB, etc). For a general discussion of Li alloys along this line see [27]. The connection between $K(x)$ and $\Delta H(x)$ can be made quantitative by fitting the said parameters to

$\Delta H(x)$, as was done by Ott *et al* [28] for the cases mentioned in the literature (Te alloys and Cs alloys). Alternative concepts have been developed in [29]. Both the usefulness and the abstract nature of the *ansatz* (4) induce new questions:

(i) What are the structures, lifetime, bond character, etc, defining the associate (ionic, as for Li–Pb [30]; Zintl ions for (K, Rb, Cs)–IV [31]; Jahn–Teller distortions in less strongly bound alloys [32])?

(ii) Can the bimodal distribution underlying equation (4) be demonstrated experimentally?

It has been pointed out earlier by Warren [33] that the large increase in R_q found in some liquid alloys is most probably caused by an increase in the decay time of the correlation function, i.e. in τ in equation (1). A systematic study of R_q in liquid In alloys and other systems had revealed that there are in fact large temperature-dependent increases in R_q in many metallic alloys (compared with the pure liquid metals), and that they correlate systematically with the A–B interaction strength ($R_q \sim |\Delta H|$) [34]. A quantitative analysis of the R_q data existing (some 20 metallic alloys with intermediate bonding), based on equation (4) and a few simple assumptions, was undertaken in [32]. Basically, τ in equation (1) was derived from the *dynamic* equilibrium behind equation (4). The rate $1/\tau_d$ of the back reaction $AB \rightarrow A + B$ and the rate $1/\tau_e$ of the exchange reaction $A' + AB \rightarrow A + A'B$ are both determined by the equilibrium (4), i.e. they are fixed by the known ΔH , ΔG via the interaction parameters. Then $1/\tau = 1/\tau_d + 1/\tau_e$. A rather satisfactory description of R_q for the cases considered was achieved in [32]. In a few cases, observed $R_q(x)$ data were used to predict $\Delta H(x)$, namely for Ba–Cd, Ba–Sn and Na–Sb. Again, there remain questions such as the following:

(i) comparison of neutron scattering $S_{ab}(q, \omega)$ and transport properties with the association model, and with R_q ;

(ii) discussion of those cases, where disagreements occur (see sections 5 and 6 in [32]); check of the rates R_q where they were ‘predicted’ (i.e. from ΔH) in [32]: **Au–Ga**, **Hg–In**, **Hg–K**, **In–Na**;

(iii) connection with the cases of small R_q increases [35], and with those of liquid semiconductors [33].

By fitting in the last-mentioned missing links, it would then appear possible to describe in a coherent picture NMR properties and ΔH , χ , σ , etc, for a wide range from pure simple liquid metals to liquid semiconductors.

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