

# NMR STUDIES OF LIQUID METALS AND ALLOYS

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## ABSTRACT

Nuclear magnetic resonance studies of liquid metals and alloys have shared with the corresponding studies of solid metals the main objective of understanding the behaviour of conduction electrons in the neighbourhood of the Fermi surface, but a significant number of experiments have also been directed to a study of atomic order and atomic motions. In the first category the relative simplicity of liquids as compared with solids has encouraged attempts to explain Knight shift and relaxation data by rather simple treatments based on nearly free electron ideas. In pure liquid metals Knight shifts, and to a lesser extent their temperature coefficients and the Korringa constants, are semi-quantitatively understood in this way, although the situation in alloy systems is often not so clear. Recently progress has been made in understanding conduction electron behaviour in liquid semiconductors, where a breakdown of the Korringa relation has been interpreted as due to partial localization of the electrons. Data are becoming available on the occurrence of local magnetic moments in dilute liquid alloys containing transition metals.

In the second category of experiments come the direct measurement of self-diffusion coefficients through the effect on spin-echoes of diffusion in a field gradient, and electric quadrupolar relaxation brought about by atomic motions which sometimes in alloys dominates all other spin-lattice relaxation mechanisms and which in principle is capable of providing information on atomic short-range order and dynamics.

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## 1. INTRODUCTION

Nuclear magnetic resonance has been observed in about twenty liquid metals. For obvious experimental reasons these are mainly the metals with lower melting points (up to about 1100°C); for the same reasons transition metals are almost entirely absent from the list. However, measurements up to ~1300°C have recently been made, and the list continues to grow.

There are a number of reasons why experimenters may choose to use liquid rather than solid metals.

First, there is the practical advantage that in the liquid state a number of interactions are motionally averaged out, including inhomogeneous and anisotropic Knight shifts, dipolar and indirect interactions between nuclei, and electric quadrupole interactions. While these effects are, in principle at least, a source of a wealth of detailed information in the solid state, their

effects on a resonance in the solid can be so severe as to make the resonance unobservable from some or all nuclei. A second practical advantage lies in the fact that many metals which are immiscible in the solid state, or almost so, are miscible in the melt, so that greatly extended ranges of alloy compositions may be investigated.

A second reason for studying liquid metals is the expectation of greater simplicity of interpretation of the data than for the solids, since it is well known that for many properties a nearly free electron (NFE) model is often adequate. Although it is now becoming increasingly evident that many simple solid metals (those for which there is no d band too close to the Fermi level) are also nearly free-electron-like, this is not always so, and in some metals we may wish to rely on melting for the removal of complicating features of the electronic band structure. It is to the interpretation of the n.m.r. data in terms of a NFE model that this paper is mainly addressed.

Third, we may of course be interested in specific features of the liquid state such as the investigation of short-range atomic order and thermal motions of the atoms, or the possibility of pseudogaps and conduction electron localization in liquid semiconductors. These subjects are briefly discussed.

## 2. KNIGHT SHIFTS IN PURE METALS

The first question that should be asked is how far we understand quantitatively the Knight shift in pure liquid metals. Experimental values of the shift at the melting point, its temperature dependence and the change on melting (taken mainly from Heighway and Seymour<sup>1</sup>) are shown in *Tables 1-3*. We are concerned with the isotropic shift and we believe (ignoring transition metals for the moment) that the bulk of the shift comes from the direct Fermi contact interaction in the well-known way

$$K = (8\pi/3)\Omega P_F \chi_p \quad (1)$$

where  $\Omega$  is the atomic volume;  $P_F = |\Psi(0)|_F^2$  is the probability density at the

*Table 1.* Experimental Knight shifts in liquid metals at their melting points compared with theoretical values obtained from a single OPW model

	$\gamma^2$	$K(\%)$			$\gamma^2$	$K(\%)$	
		Theory	Expt			Theory	Expt
Li	66	0.09	0.026	Rb	994	0.82	0.662
				Ag	679	0.74	0.575
Na	176	0.15	0.116	Cd	668	0.77	0.795
Al	148	0.18	0.162	In	642	0.79	0.786
				Sn	623	0.75	0.73
				Sb	600	0.72	0.72
K	490	0.41	0.265	Te	585	0.70	0.38
Cu	438	0.52	0.264				
Ga	412	0.53	0.449	Cs	1620	1.63	1.44
As	386	0.52	0.32	Hg	1240	1.45	2.42
				Tl	1170	1.31	1.48
				Pb	1130	1.34	1.49
				Bi	1100	1.32	1.41

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 Table 2. Temperature coefficients of Knight shifts in liquid metals ( $\times 10^{-5} \text{ deg}^{-1} \text{ C}$ )

	$\frac{1}{\chi_p} \frac{d\chi_p}{dT}$ (free electron)	$\frac{1}{\Omega P_F} \frac{d\Omega P_F}{dT}$ (zero-order)	$\frac{1}{K} \frac{dK}{dT}$ (incl. first-order)	$\frac{1}{K} \frac{dK}{dT}$ (expt)
Lj	-4	-1		0
Na	-7	-1	+ 26(a), + 22(b)	+ 16
Al	-3	0		+ 1
K	-8	-3	+ 38(a)	+ 11
Cu	-3	-1		+ 5
Ga	-3	0	- 17(c)	- 6
Rb	-9	-4	+ 27(a)	+ 17
Ag	-3	-1	+ 7(c)	+ 5
Cd	-3	-1	+ 2(c), 0(d)	+ 2
In	-3	0	- 6(c), - 7(d)	- 8
Sn	-2	0	- 6(c), + 1(d)	- 2
Sb	-3	+ 4		+ 2
Te	-3	+ 1		+ 200
Cs	- 10	- 9		- 31
Hg	- 5	- 2		- 15
Pb	- 3	0	- 9(c)	- 6
Bi	- 3	0	- 6(c)	- 9

(a) Perdew and Wilkins<sup>2</sup>.

(b) Ritter and Gardner<sup>3</sup>.

(c) Ford and Styles<sup>4</sup> and Styles (private communication).

(d) Halder<sup>5</sup>.

 Table 3. Changes of mass susceptibility<sup>(a)</sup> and Knight shift on melting

	$\frac{\chi_L - \chi_S}{\chi_L - \chi_i}$ (%)	$\frac{K_L - K_S}{K_L}$ (%)		$\frac{\chi_L - \chi_S}{\chi_L - \chi_i}$ (%)	$\frac{K_L - K_S}{K_L}$ (%)
Li	1	- 1	Al	- 18	- 2
Na	2	2	Ga	160	66
K	1	2	In	5	- 4
Rb	- 1	1	Tl	40	0
Cs	0	- 2	Sn	- 35	- 3
Mn	-	- 4(b)	Pb	44	0
Cu	- 8	5	Bi	780	190
Ag	- 17	5	Te	270	100
Cd	21	24			
Hg	- 80	0			

(a) Taken from Dupree and Seymour<sup>6</sup>, except Cu, Ag from Dupree and Ford<sup>7</sup>.

(b)  $K_L - K_S$  is positive,  $K_L$  negative.

nucleus for conduction electrons averaged over the Fermi surface; and  $\chi_p$  is the conduction electron spin volume susceptibility. There may in addition be a non-negligible core polarization term whose magnitude has been estimated theoretically for a number of metals; it is found to be between five and twenty per cent of the total shift for the alkalis, for instance<sup>8</sup>. In principle it is possible to go some way towards disentangling the two effects from the Korringa relation (see below), but in practice it is not possible to do this unambiguously. In the following we shall not deal in detail with the core

polarization shift, but it will be necessary to bear its existence in mind when comparing equation 1 with experiment.

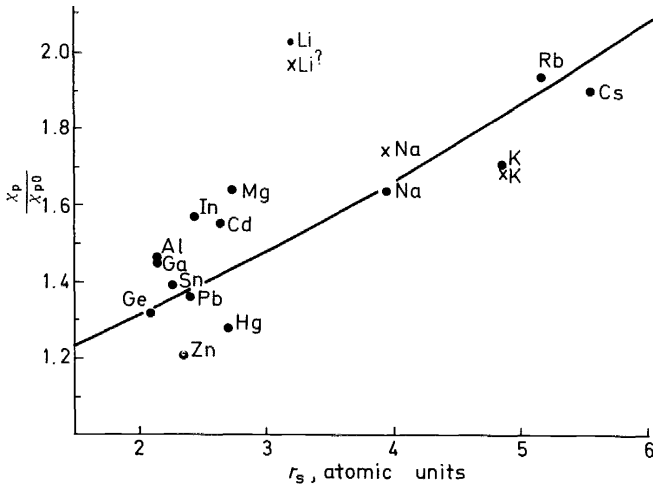
(a) *Conduction electron spin susceptibility*

In view of the difficulty of measuring  $\chi_p$  directly (a quantity of considerable interest because of its relation to the electron density of states at the Fermi level), the possibility of deducing this quantity from measured Knight shifts and equation 1 is attractive. However, at the present time  $\Omega P_F$  cannot normally be calculated with sufficient confidence to make this possible, and instead  $\chi_p$  must be regarded as input information in trying to understand values of  $K$ .

Apart from a very few cases where  $\chi_p$  has been measured experimentally through conduction electron spin resonance (Li: Enderby *et al.*<sup>9</sup>; Na: Devine and Dupree<sup>10</sup>), either an attempt must be made to extract it from the total susceptibility or a theoretical value must be used. It has recently been shown that a plausible set of  $\chi_p$  values can be obtained from measured total susceptibilities by allowing for core diamagnetism and conduction electron diamagnetism in a consistent manner for the alkalis and many B group metals of different valencies<sup>6</sup>. One finds that  $\chi_p$  is consistently larger than would be predicted for free non-interacting electrons, viz.

$$\chi_{p0} = \mu_B^2 N(E_F) \quad (2)$$

where  $\mu_B$  is the Bohr magneton and  $N(E_F)$  the density of states at the Fermi level per unit volume, for both directions of spin together. Recent theoretical calculations for free electrons (Hamann and Overhauser<sup>11</sup>; Dupree and Geldart<sup>12</sup>) agree in attributing this enhancement to the effect of electron-electron interactions (*Figure 1*). There remains the question of the effect of



*Figure 1.* Experimental and theoretical enhancements of  $\chi_p$  for liquid metals due to electron-electron interactions as a function of electron sphere radius  $r_s$ . Experimental values are deduced from total susceptibilities (●) or e.s.r. (×). The full curve represents the theoretical results of Dupree and Geldart<sup>12</sup>, from whose paper this figure is adapted. The results of Hamann and Overhauser<sup>11</sup> (1966) are very similar

the atomic potential on the conduction electron density of states and, hence, on  $\chi_p$ . This is usually represented by introducing an effective electron mass  $m^*$ . Detailed computations have been carried out for several liquid metals to second order in a pseudopotential, and in general it is found that  $m^*$  is close to the free electron mass  $m$  (for a survey see Faber<sup>13</sup>). Typically, calculated  $m^*/m$  values lie in the range 0.9 to 1.0, with, however, a scatter between the results of different authors for the same metal which may be as much as 0.1. According to Jena and Halder<sup>14</sup>, for six alkali and group B metals  $m^*/m$  becomes closer to unity as temperature is increased above the melting point. A clear exception is Li, for which  $m^*/m$  has been estimated<sup>15</sup> as 1.24. This value has been used in *Figure 1*; the evidence of that diagram points to a considerably higher value  $\sim 1.55$ , and indeed other calculations have given results<sup>16</sup> as high as 1.52. The overall situation is that (apart from Li) one can have reasonable confidence in  $\chi_p$  values deduced from equation 2 using  $m^* = m$  and including the (substantial) theoretical electron-electron enhancement of *Figure 1*.

(b) *The electron contact density factor  $\Omega P_F$*

In view of the nearly free electron nature of liquid metals, it is appropriate to attempt the calculation of  $\Omega P_F$  from the starting point of plane waves. Of course if  $\Psi(\mathbf{r})$  were merely a plane wave  $\exp(i\mathbf{k} \cdot \mathbf{r})$ ,  $\Omega P_F$  would be unity and this would lead to far too small values of  $K$ . Although electrons may be representable by the superposition of a few plane waves in the regions between the ion cores, one must represent in some way the oscillations and radial nodes within the core regions and, hence, the pile-up of electron density near the nucleus. Perhaps the best way would be to use the augmented plane wave method, but no doubt because of its much greater simplicity the less exact orthogonal plane wave (OPW) method has usually been used instead.

The best that one could hope for would be that a single OPW would give a good estimate of  $\Omega P_F$ . We therefore begin by writing the wave function of an electron at the Fermi surface as

$$\Psi_{\mathbf{k}}(\mathbf{r}) = C[\exp(i\mathbf{k} \cdot \mathbf{r}) - \sum_{i,n} \{ \int d^3\mathbf{r}' \Psi_{in}^*(\mathbf{r}') \exp(i\mathbf{k} \cdot \mathbf{r}') \} \Psi_{in}(\mathbf{r})] \quad (3)$$

where  $k = k_F$ ;  $C$  is a normalization factor;  $\Psi_{in}(\mathbf{r})$  is a core state wave function; and the summation extends over occupied core states  $n$  of all ions  $i$ . For a spherical Fermi surface  $\Omega P_F$  is then readily obtained<sup>17</sup>. If as a simplifying approximation  $\exp(i\mathbf{k}_F \cdot \mathbf{r})$  is taken to be constant over the region of an ion core,  $\exp(i\mathbf{k}_F \cdot \mathbf{r})$  factors out and the result is particularly simple

$$\Omega P_F = \gamma^2 / \beta \quad (4)$$

where  $\gamma$  is an orthogonalization factor given by

$$\gamma = 1 - \sum_n \Psi_n(0) \int \Psi_n^*(\mathbf{r}) d^3\mathbf{r} \quad (5)$$

and  $\beta$  is a normalization factor

$$\beta = 1 - \Omega^{-1} \sum_n \left| \int \Psi_n(\mathbf{r}) d^3\mathbf{r} \right|^2 \quad (6)$$

These functions depend only on the core state wave functions and the atomic

volume; there is no structure dependence and the result does not therefore distinguish between solid and liquid except in so far as their densities differ. The quantity  $\gamma$  is dominated by the contribution from the outermost core shell, and it is  $\gamma$  which gives rise to the rapid increase of  $K$  through the Periodic Table as the maximum core principal quantum number increases; by contrast,  $\beta$  is a little less than unity and roughly constant for all metals. The results of calculations of  $K$  using equation 4 show good enough general agreement with experiment<sup>1</sup> to encourage proceeding with refinements.

At the expense of a little additional complexity, one can allow for the variation of  $\exp(i\mathbf{k}_F \cdot \mathbf{r})$  over the core volume; this has the effect of reducing calculated values of  $\Omega P_F$  by between five and fifteen per cent below those given by equation 4. It also introduces an explicit dependence of  $K$  on the Fermi wave vector, which may be important for changes of  $K$  in alloys<sup>18</sup>. Table 1 shows values of  $\gamma^2$  calculated using atomic wave functions tabulated by Herman and Skillman<sup>19</sup> for those liquid metals in which Knight shifts have been measured. Different choices of core wave functions naturally produce different values for  $\gamma^2$  with a spread of perhaps 10–20 per cent; for instance, the values obtained by Mahanti *et al.*<sup>20</sup> for alkali metals for core functions given by Clementi<sup>21</sup> differ from those in Table 1 by about ten per cent. Also shown are the resulting  $K$  values;  $k_F$  has been calculated for a free electron gas of density deduced from the valency and density of the liquid metal at its melting point, the variation of  $\exp(i\mathbf{k} \cdot \mathbf{r})$  over the cores has been allowed for and  $\chi_p$  has been calculated as described above. The marked increase from row to row of the Periodic Table is reproduced, and the absolute magnitudes of  $K$  are mainly in reasonable agreement with experiment. Where there are large discrepancies, one can usually plead special causes: the lack of p states in the Li core makes an OPW procedure unreliable; for Cu and probably Hg the presence of a d band near the Fermi level could make the general approach untenable; and in Te (Figure 2)  $K$  increases rapidly with increasing temperature (extrapolating to about 0.6 per cent near the boiling point), in keeping with a trend towards free electron behaviour at high enough temperatures<sup>23</sup>.

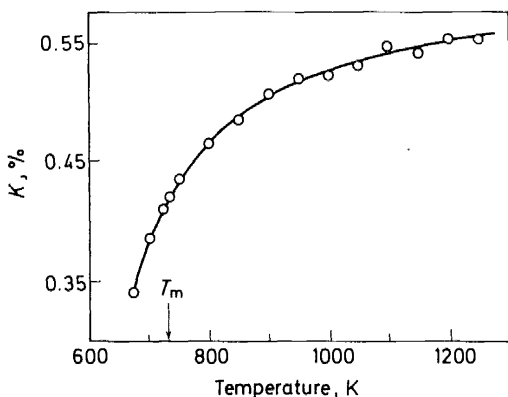


Figure 2. Knight shift of  $^{125}\text{Te}$  in liquid and supercooled tellurium as a function of temperature<sup>22</sup>.  $T_m$  indicates the melting point

As a next step, one can allow for the effects of scattering by the ion cores on the wave functions between the cores. It is well known that this scattering is often rather small and may be dealt with by a perturbation treatment, allocating to each ion a weak pseudopotential. The pseudo wave function  $\varphi(\mathbf{r})$  so obtained is then to be orthogonalized to the core as before. The form of the correction to  $\Omega P_F$ , to first order in the pseudopotential, was derived by Faber<sup>24</sup>, Lackmann-Cyrot<sup>25</sup> and Watabe *et al.*<sup>26</sup>. These authors assumed, explicitly or implicitly, that  $\varphi(\mathbf{r})$  is a sufficiently slowly varying function of  $\mathbf{r}$  to be regarded as constant over the core. This results in a proportionality between the true and pseudo contact densities, and equation 4 is replaced by

$$\Omega P_F = \frac{\gamma^2}{\beta} \left[ 1 + 2Z \int_0^\infty d \left( \frac{q}{2k_F} \right) a(q) \frac{u(q)}{u(0)} \frac{q}{2k_F} \ln \left| \frac{q + 2k_F}{q - 2k_F} \right| \right] \quad (7)$$

Here  $Z$  is the valency,  $a(q)$  the liquid structure factor and  $u(q)$  the Fourier transform of the pseudopotential of a single ion. It has been assumed that  $u(\mathbf{r})$  is spherically symmetrical and is a local potential. (The quantitative effects of the non-locality which must, in general, be present can be appreciable—see Ritter and Gardner<sup>3</sup>, for example—but as we shall see in some cases the effect may not be too important.) Figure 3 displays the general way in which the functions occurring in the integral depend upon wave vector  $q$ .

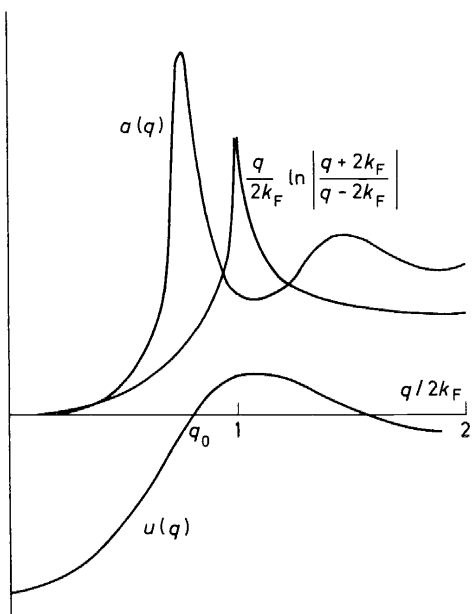


Figure 3. Schematic wavenumber dependence of terms involved in the first-order correction to the contact density  $\Omega P_F$  according to equation 7,  $a(q)$  is the liquid structure factor and  $u(q)$  the pseudopotential form factor

Clearly rather accurate pseudopotential form factors and liquid structure factors are needed even beyond  $2k_F$ , possibly beyond present capabilities.

However, it seems clear that, whatever the uncertainties, the correction term in equation 7 is not always small compared with unity, so that it cannot be regarded as satisfactory (indeed Heighway and Seymour<sup>1</sup> found values as large as  $-1.5$  for In and Sn and  $-2.5$  for Pb).

The root of the trouble seems to lie in the approximation of almost constant  $\varphi(\mathbf{r})$  over the volume of an ion core. (As discussed by Faber (ref. 13; Section 4.11), it may also be appropriate when using some forms of pseudopotential to substitute  $\{a(q) - 1\}$  for  $a(q)$  at large  $q$ ; in view of the discrimination against large  $q$  contributions in the following, this complication need not worry us.) While, as we have said, such an approximation introduces an error no worse than about  $-10$  per cent for a plane wave of wavenumber  $k_F$ ,  $\varphi(\mathbf{r})$  contains plane wave components extending to much higher wavenumbers and the decrease of the orthogonalization factor with increasing wavenumber must therefore be taken into account; each component of  $\varphi(\mathbf{r})$  is to be separately orthogonalized. This is the reasoning of Perdew and Wilkins<sup>2,27</sup>, who obtain, instead of equation 7

$$\Omega P_F = \frac{\gamma^2(k_F)}{\beta'} \left[ 1 + 2Z \int_0^\infty d\left(\frac{q}{2k_F}\right) a(q) \frac{u(q)}{u(0)} \int \frac{d\hat{q}}{2\pi} \frac{\gamma(k_F + q)}{\gamma(k_F)} \frac{E(q)}{E(k_F) - E(k_F + q)} \right] \quad (8)$$

where  $E(k)$  is the free electron energy and the pseudopotential has again been assumed to be local. The essence of this equation is that the orthogonalization factor  $\gamma$  of equation 4 is replaced by

$$\gamma(k) = 1 - \sum_n \Psi_n(0) \int \Psi_n^*(\mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}) d^3\mathbf{r} \quad (9)$$

If the wavenumber dependence of  $\gamma$  were removed, the angular integral in equation 8 would reduce to the logarithmic term in equation 7.  $\beta'$  is a slightly modified form of the normalization factor  $\beta$  in equation 6. The use of equation 8 now leaves the first-order term smaller than unity in those cases where it has been computed, although still sometimes not sufficiently so that we can be confident in ignoring higher-order terms. Perdew and Wilkins<sup>2</sup>, using the Ashcroft<sup>28</sup> empty-core potential and the hard sphere structure factors of Ashcroft and Langreth<sup>29</sup>, find that the first-order term reduces the single OPW result for  $K$  by about 30 per cent of itself for Na and 36 per cent for K (bringing results closer to experiment), and less than one per cent for Rb. Ritter and Gardner<sup>3</sup> find a reduction of seven per cent for Na using a Shaw optimized pseudopotential and a full non-local calculation. Ford and Styles<sup>4</sup> find reductions of about 15 per cent for In and Sn and 30 per cent for Pb, which, however, do nothing to improve agreement with experiment. In view of the nature of the functions which have to be multiplied within the integrals, the results must be expected to be rather sensitive to the details of the form factors and structure factors used, and it may be that it will not prove possible to obtain very precise absolute values for  $K$ . On the other hand, the decrease of the orthogonalization factor at large wavenumbers lessens the effect of non-locality of the pseudopotential. Fortunately also, as emphasized by Perdew and Wilkins<sup>2</sup> and by Ritter and Gardner<sup>3</sup>, among others, this situation does not necessarily mean that fractional changes of  $K$



with temperature (and possibly changes upon alloying also) cannot be usefully discussed in terms of equation 8, and we now turn to the temperature dependence of the shift and its change on melting. The reader who wishes to follow further refinements in the calculation of absolute values of  $K$ , including core polarization and relativistic effects, is referred to the papers of Das and co-workers; in particular, Mahanti *et al.*<sup>20</sup> discuss the alkali metals, and although the calculations refer to the solid state, much of the work is relevant to the liquids also.

(c) *Temperature coefficient and change of shift on melting*

In almost all liquid metals  $K$  is only slightly temperature dependent (Table 2, column 4, and Figures 4 and 5), even in cases such as Ga and Cd where that in the solid is violently temperature dependent.

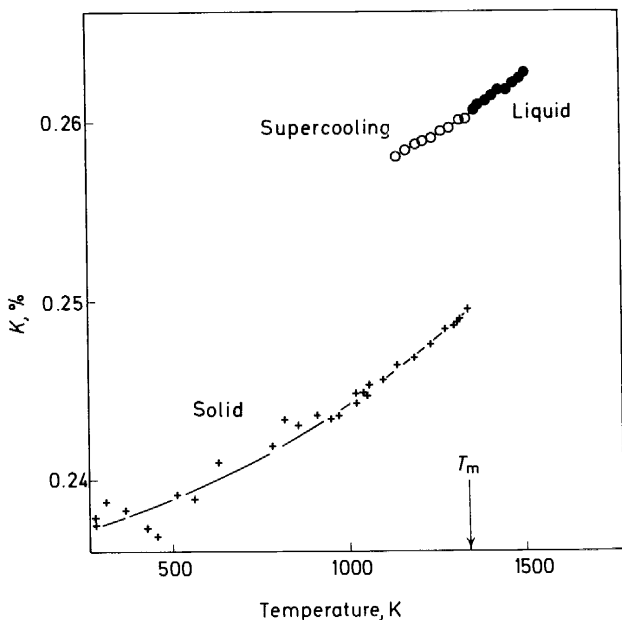


Figure 4. Knight shift of  $^{63}\text{Cu}$  in liquid and solid copper<sup>30</sup>

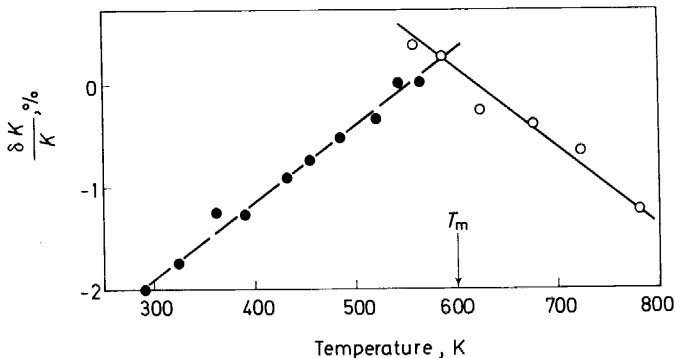


Figure 5. Knight shift of  $^{207}\text{Pb}$  in liquid and solid lead<sup>31</sup>

For simple metals  $K$  can be expected to change with temperature on account of the change of  $\chi_p$  and  $\Omega P_F$

$$\frac{1}{K} \frac{dK}{dT} = \frac{1}{\chi_p} \frac{d\chi_p}{dT} + \frac{1}{\Omega P_F} \frac{d\Omega P_F}{dT} \quad (10)$$

For free electrons  $\chi_p$  changes with temperature through the volume expansion (the explicit temperature dependence is negligible), which affects both  $N(E_F)$  and the electron-electron enhancement (*Figure 1*), and the resulting temperature coefficient is of order  $-3 \times 10^{-5} \text{ deg}^{-1} \text{C}$ . For several metals, including Cd, In, Sn and Pb, the observed coefficient of the total susceptibility is consistent with such behaviour, while for others (Sb, Hg, Bi) the observed coefficient is larger, which suggests a modest increase of  $m^*/m$  towards unity<sup>6</sup>. Jena and Halder<sup>14</sup> find theoretically a temperature-dependent  $m^*$  in Na, K, Ga, In and Sn, for which, however, there seems to be no room in the measured total susceptibilities in the cases of In and Sn. In *Table 2* (column 1) we have used free interacting electron values, and recognize that in some cases the values may be in error by a few times  $10^{-5} \text{ deg}^{-1} \text{C}$ .

Even to zero order in the pseudopotential volume expansion will also affect  $\Omega P_F$  through  $\Omega$  itself and through  $k_F$  ( $\propto \Omega^{-\frac{1}{3}}$ ). The effect, is, however, small (column 2 of *Table 2*). Much more important is the temperature dependence (column 3) arising from the first-order pseudopotential correction of equation 8. This arises in part from orthogonalization changes due to changing  $k_F$ , and in part from the flattening and broadening of the first peak of  $a(q)$ . For alkali metals, at least, the latter is the main effect, and indeed (Ritter and Gardner<sup>3</sup>) consideration of the general form of any  $u(q)$  near the peak of  $a(q)$ , i.e. just above  $2k_F$  for monovalent metals, shows that for them one should expect a positive temperature coefficient. This is found for Na, K and Rb, but the large negative coefficient for Cs is surprising and unexplained. For polyvalent metals the coefficients are normally negative; probably this is a systematic effect of larger  $k_F$  values which change the positions of the peak in  $a(q)$  relative to  $u(q/2k_F)$ .

Thus, for simple metals, much of the temperature coefficient of  $K$  comes from the first-order pseudopotential correction to  $\Omega P_F$ , even though it may contribute rather little to the magnitude of the shift itself; one expects and finds a systematic valence dependence. Of course there are exceptions. It has already been commented that the large positive coefficient for Te (*Figure 2*) is due to an increasing metallic character (increasing  $N(E_F)$ ), as evidenced by increasing paramagnetism and decreasing Hall coefficient. In liquid Cu (and in the solid also)  $K$  is believed to be influenced importantly by s-d hybridization<sup>30</sup>, both  $m^*$  and  $P_F$  being affected; temperature dependences of both quantities arise from the volume dependence of the hybridization. Finally, in the case of Mn (Warren<sup>32</sup>), the one liquid transition metal so far investigated,  $K$  is  $-0.82$  per cent at the melting point and becomes rapidly more negative at higher temperatures. As has been done for many solid transition metals, comparison of the temperature dependences of the shift and susceptibility can be used to separate orbital and spin contributions to them (assuming that the latter provides the temperature dependence in a narrow d band); for liquid Mn the d spin susceptibility contributes 75 per cent of the whole.

The change of  $K$  on melting is very small for many metals (*Table 3*). This interesting fact has received much attention, as it seemed to indicate that solid state band effects might carry over to the liquid, or that there might be substantial, but mutually cancelling, changes in  $\chi_p$  and  $P_F$ . It now seems established, however, that the explanation of Ziman<sup>33</sup> that neither quantity changes greatly because many solid metals, like the liquids, are NFE-like, is substantially correct; even if  $m^*/m$  is not exactly unity, at least it is not very structure-sensitive. In such metals one is left with the residual problem of trying to interpret the fractional changes in  $K$  of a few per cent that do occur. One may calculate  $\chi_p$  changes from changes in volume and in  $m^*$  where calculations of the latter are available. Alternatively, some idea of  $\chi_p$  changes may be had (*Table 3*) from the quantity  $(\chi_L - \chi_S)/(\chi_L - \chi_i)$ , where  $\chi_{L,S}$  are total mass susceptibilities and  $\chi_i$  the ion core contribution; this measures the fractional change in the conduction electron (spin plus orbital) part. As for  $\Omega P_F$  changes, equation 8 may be used for solid metals as well as liquids, although structure factors  $a(q)$  for solids near the melting point are not as well known as for liquids. In a calculation using  $\chi_p$  derived from a calculated density of states and a solid state structure factor in which multiphonon contributions were neglected, Ritter and Gardner<sup>3</sup> overestimated the change in  $K$  for Na by a factor of three; using an Einstein model for  $a(q)$ , Perdew and Wilkins<sup>2</sup> found better agreement for Na, K and Rb. Where there are small changes in  $K$  but nevertheless large changes in  $\chi$ , as in Hg, Al, Ti, Sn and Pb, the susceptibility changes must presumably be attributed to the conduction electron diamagnetism rather than to  $\chi_p$ ; quantitative explanations are lacking even for the 'NFE solids' Al, Sn and Pb.

Where changes in  $K$  and  $\chi$  are both large (Cd, Ga, Bi, Te), there are known to be large band structure effects in the solid which disappear in the liquid. The case of Cd has been particularly thoroughly studied<sup>34,35</sup>; the calculated increases of 27 per cent and 8 per cent in  $\chi_p$  and  $\Omega P_F$  (expressed here as percentages of the solid values) account nicely for the change in  $K$  and (rather less well) for the susceptibility change. For Cu the volume dependence of the s-d hybridization to which the temperature dependence of  $K$  has been attributed seems also to be responsible for the change on melting; both effects are found to depend in the same way on volume, so that the hybridization, although volume-dependent, is not appreciably structure-dependent. The same type of dependence on volume occurs also in Ag<sup>36</sup>.

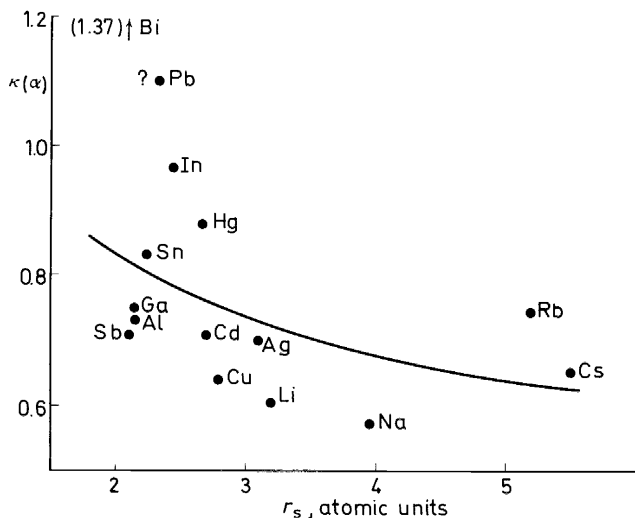
#### (d) *The Korringa relation*

If  $K$  and the spin-lattice relaxation rate  $T_1^{-1}$  are both due only to the direct contact interaction, the relation between them is expected to be

$$K^2 T_1 T = \frac{\hbar \gamma_e^2}{4\pi k_B \gamma_n^2} \cdot \frac{1}{\kappa(\alpha)} \quad (11)$$

where  $\gamma_e$  and  $\gamma_n$  are electron and nuclear gyromagnetic ratios, respectively. The factor  $\kappa(\alpha)$  allows for the different enhancements of  $K^2$  and  $T_1^{-1}$  by the electron-electron interaction (measured by  $\alpha$ ); it is less than unity and not (usually) appreciably temperature-dependent (see, for instance, Bhattacharyya *et al.*<sup>37</sup>; Narath and Weaver<sup>38</sup>; Shaw and Warren<sup>39</sup>: discussions are mainly directed at alkali metals). It is more difficult to calculate the enhancement

of  $T_1^{-1}$  (which requires a knowledge of the frequency- and wavenumber-dependent electron spin susceptibility  $\chi_p(q, \omega)$ ) than that of  $K$ ; there are several calculations in the literature for free electrons involving different approximations. The curve in *Figure 6* shows the results of a calculation by Dupree and Geldart<sup>40</sup> which approximates  $\chi''(q, \omega_0)$  by  $\chi''(q, 0)$ , where the double prime represents the imaginary part and  $\omega_0$  is the resonance frequency. The experimental results, with a few exceptions, cluster near enough to the curve to suggest that equation 11 contains most of the physics of the situation. (Data for *solid* alkali metals at low temperatures, which are probably more accurate than the liquid data, fit the curve rather better.)



*Figure 6.* Experimental reciprocal Korringa enhancement factors  $\kappa(\alpha)$  as a function of electron sphere radius  $r_s$ . The curve is a theoretical result for the effect of electron-electron interactions (Dupree and Geldart<sup>40</sup>)

A complicating circumstance is the possibility of contributions to  $K$  or  $T_1^{-1}$  by other than the direct contact interaction. In Ga, Sb, Hg and Bi there is an electric quadrupolar contribution to the relaxation rate, and this has been subtracted before compiling values of  $\kappa(\alpha)$ . However, core polarization effects can contribute to both  $K$  and  $T_1^{-1}$ , and this has not been allowed for

*Table 4.* Experimental reciprocal Korringa enhancement  $\kappa(\alpha)$  in liquid metals<sup>(a)</sup>

Li	Na	Al	Cu	Ga	Rb
0.61	0.57	0.73	0.64	0.74	0.74
Ag	Cd	In	Sn	Sb	Tc
0.70	0.71	0.97	0.84	0.71	1.4
Cs	Hg	Pb	Bi		
0.65	0.88	~ 1.1	1.37		

<sup>(a)</sup> Taken mainly from Dupree and Seymour<sup>6</sup> and updated. Cs from Tranfield (private communication).

in Table 4. Core polarization by the s part of the conduction electron wavefunction does not affect equation 11, but the p part, while contributing a small positive or negative part to  $K$ , makes a relatively much smaller change in  $T_1^{-1}$ ; denoting the contributions to  $K$  by  $K(\text{cp},s)$  and  $K(\text{cp},p)$ , respectively, we would have

$$(T_1 T)^{-1} \propto [K(\text{direct}) + K(\text{cp}, s)]^2 + \frac{1}{3}[K(\text{cp}, p)]^2 \quad (12)$$

Allowance for  $K(\text{cp}, p)$  calculated by Mahanti *et al.*<sup>20</sup> for Na, Rb, Cs (positive in each case) would increase the  $\kappa(\alpha)$  values in Table 4 and Figure 6 by about 2 per cent, 5 per cent and 6 per cent, respectively, which does not alter the general conclusion of the preceding paragraph. Figure 6 may indicate substantial negative  $K(\text{cp}, p)$  parts in Bi and In (the relaxation data for Pb are poorer), an unwelcome conclusion in view of our earlier discussion unless counteracted by a roughly equal positive  $K(\text{cp}, s)$ .

Exceptionally for Cu,  $\kappa(\alpha)$  changes strongly with temperature and this has been attributed by El-Hanany and Zamir<sup>30</sup> to the effect of the volume dependence of  $m^*$  on  $\alpha$  (but see Dupree and Ford<sup>7</sup>). In liquid Mn the observation that  $T_1 T = \text{constant}$  indicates relaxation by itinerant electrons, and the magnitude of  $T_1$  is consistent with core polarization relaxation (possibly with some orbital relaxation) produced by the d electrons; the small change of  $T_1$  at the melting point suggests little change in the d band characteristics on melting.

### 3. KNIGHT SHIFTS IN ALLOYS

It is not possible here to review all the data on n.m.r. in liquid alloys (mostly measurements of  $K$ ), or the many attempts to explain the observations. As a broad generalization, one often finds that the shifts for both constituents of a binary alloy change roughly linearly with atomic concentration, and in approximately parallel fashions (though there are many exceptions). Fractional changes  $\Delta K/K$  across the composition range are typically 5–20 per cent except for alkali metal alloys, where  $\Delta K/K$  is more often 20–50 per cent or even more; they are not very temperature-dependent (except for transition metal solutes; see below).

To interpret results for alloys of 'simple' metals one should allow first for changes in  $\chi_p$ ; these arise from  $N(E_F)$  changes depending on average valency and atomic volumes, and electron-electron enhancement changes depending on  $r_s$ . Second,  $\Omega P_F$  changes need to be calculated from an extension of equation 8 (Perdew and Wilkins<sup>2</sup>), which includes solute and solvent pseudopotential form factors and partial structure factors in a straightforward manner in place of the simple product  $a(q)u(q)$ . Where there are large solute-solvent valency differences or volume changes, one must expect changes in  $k_F$  to affect the orthogonalization factor  $\gamma(k_F)$ , and the pseudopotentials themselves may be energy-dependent. A few calculations have attempted to take most of these factors into account; for instance, Perdew and Wilkins give a successful account of shifts in several alkali-alkali alloy systems in this way. They find variations of less than ten per cent in  $P_F$  in systems where  $\Omega$  changes by over 100 per cent. This feature of relative insensitivity of  $P_F$  to  $\Omega$  in alkali-alkali alloys also emerges from the single OPW calcula-

tions of van Hemmen *et al.*<sup>41</sup>. In most other systems volume changes are much smaller and do not dominate the behaviour of  $K$ .

Most other calculations which have been reported have been based on equation 7 directly (i.e. with no allowance for the  $k$  dependence of  $\gamma$ ), or alternatively have used a partial wave analysis (following Blandin *et al.*<sup>42</sup>) which is now recognized to be equivalent to using equation 7. Authors have not always allowed for changes in  $\chi_p$ . In general, with either method of calculation, only modest success is achieved, differences between theory and experiment of factors of two or more in  $\Delta K/K$  being common. This is equally true of systems such as In-Ga, In-Tl, Sn-Pb and Sb-Bi in which there are no valency differences and only small volume changes and which should therefore behave rather simply<sup>43,44</sup>, and systems with solute-solvent valency differences. In treating the second type of system the partial wave method has usually been employed with phase shifts deduced in a variety of ways. Rigney and Flynn<sup>45</sup> were able to explain the broad pattern of solvent shifts in a range of alloys as a function of solvent valency and solute-solvent valency differences, by choosing  $s$  and  $p$  phase shifts so as to reflect the idea that no atomic cell should contain the equivalent of more than two  $s$  electrons, so that further screening of higher valency solutes must be accomplished by  $p$  wave shifts. Figure 7 shows as an example experimental<sup>31</sup> and predicted rates of change of solvent shift  $K(\text{Pb})$  with solute concentration  $c$  in liquid lead alloys for solutes of different valencies. Quantitative agreement

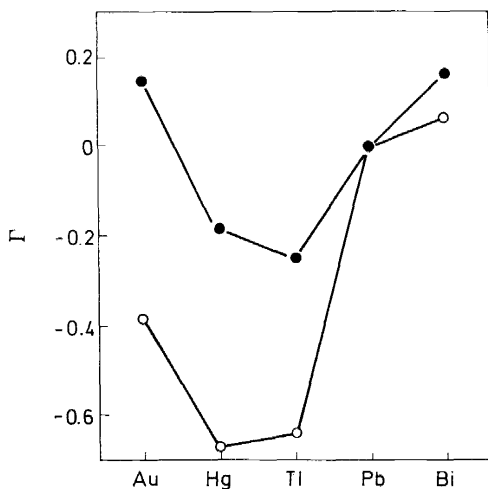


Figure 7. Experimental (●) and theoretical (○) concentration coefficients of the  $^{207}\text{Pb}$  Knight shift  $\Gamma\{[1/K(\text{Pb})]dK(\text{Pb})/dc\}$  in liquid lead alloys as a function of solute valency

could not be expected, since the analysis does not include a treatment of the relation between  $\varphi(0)$  and  $\Psi(0)$  in circumstances where  $k_F$  changes considerably; the value of the model lies rather in the simplicity of the physical picture it provides.

In the case of transition metal or rare earth atom solutes there is liable to exist, in addition to the distortion of electron charge density around a solute

atom that we have considered so far, an oscillatory conduction electron spin density. This can produce changes in solvent Knight shift an order of magnitude bigger than that due to charge density distortion. Solvent shifts can thus be used to investigate the formation and properties of local moments in metals. (The use of liquid metals eases solubility problems.) If a local moment exists, as for Mn in Cu<sup>46</sup>, a temperature-dependent solvent shift appears accompanying a Curie-Weiss susceptibility. If there is no local moment but only an impurity band paramagnetism, as for Mn in Al<sup>47</sup>, a nearly temperature-independent susceptibility and solvent shift appear. The transition between these two cases has been studied through the <sup>27</sup>Al shift in Al<sub>x</sub>Cu<sub>1-x</sub>(Mn) alloys by Odle *et al.*<sup>48</sup>. The effect at solvent sites may be through an exchange coupling between impurity spins and conduction electrons (positive  $J_{sd}$ ) or by hybridization of impurity and conduction electron wave functions (negative effective  $J_{sd}$ ). In principle, though not necessarily in practice, the two mechanisms can be distinguished by the sign of the solvent shift.

Recently attention has turned to the n.m.r. of the magnetic impurity itself. Walstedt and Warren<sup>49</sup> have measured  $K$  and  $T_1$  for <sup>55</sup>Mn in liquid Al<sub>x</sub>Cu<sub>1-x</sub> and are able to separate the d spin and orbital impurity susceptibilities. Such a division enables the intra-atomic interactions to be determined<sup>50</sup>. They also observe a contribution to  $T_1^{-1}$  (<sup>55</sup>Mn) at Cu-rich compositions which they attribute to local moment spin-lattice fluctuations, and from which  $J_{sd}$  can be deduced. Of course, more extensive n.m.r. studies have been carried out on 'magnetic' impurities in solid metals (see, for instance, Narath<sup>51</sup>).

#### 4. NMR IN LIQUID SEMICONDUCTORS

Although quantitative agreement is lacking, general behaviour of alloys discussed in Section 3 is usually understandable on NFE lines. However, this does not extend to liquid semiconductors, that is alloys (often containing Se or Te) in which the conductivity drops in the neighbourhood of particular compositions from a normal metallic value of  $\approx 3000 \text{ ohm}^{-1} \text{ cm}^{-1}$  to values as low as  $200 \text{ ohm}^{-1} \text{ cm}^{-1}$ ; near these compositions the temperature coefficient of conductivity is positive. On a model proposed by Mott<sup>52</sup> the Fermi level at such a composition lies in a region of low  $N(E)$  (a pseudogap), the electron states in the pseudogap become progressively more localized as the gap deepens, and the conductivity goes over from a free path to a hopping process. The predictions for n.m.r. are threefold: a small  $N(E_F)$  means a reduced  $K$ ; while approaching the hopping regime, the conductivity should be proportional to  $N(E_F)^2$  and, hence, to  $K^2$ ; and the Korringa relation should fail owing to the partial localization, which should increase the correlation time  $\tau$  of the electron motion above the itinerant value  $\sim 10^{-15}$  s, making  $\omega_0\tau$  closer to unity and increasing the efficiency of the relaxation process<sup>53</sup>. Some or all of these features have been observed in liquid In-Te, Ga-Te (Warren<sup>53, 54</sup>), Tl-Te (Brown *et al.*<sup>55</sup>), Cu-Te, Ga-Se-Te (Warren<sup>56</sup>) and Se-Te (Seymour and Brown<sup>57</sup>), and the data are generally consistent with the pseudogap model. The relaxation rate may be enhanced more than

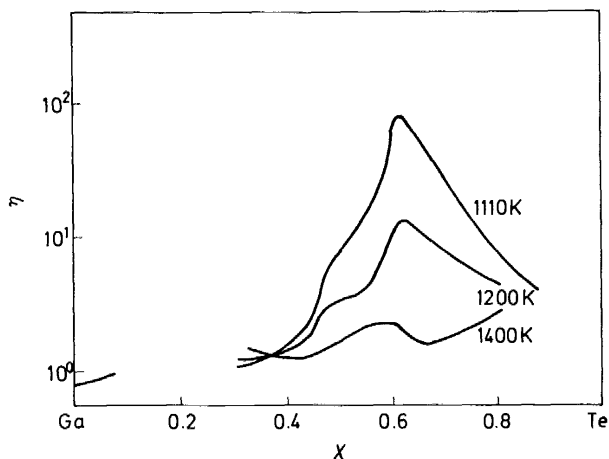


Figure 8. Enhancement  $\eta$  of the magnetic spin-lattice relaxation rate of  $^{69,71}\text{Ga}$  in liquid  $\text{Ga}_{1-x}\text{Te}_x$  alloys. The maximum enhancement occurs at  $\text{Ga}_2\text{Te}_3$ . A miscibility gap occurs near  $x = 0.2$ . (A selection of data from Warren<sup>54</sup>; experimental points are omitted)

100-fold above the Korringa value. Figure 8 shows the effect in Ga-Te and indicates the filling of the pseudogap for  $\text{Ga}_2\text{Te}_3$  as temperature is increased. Thus, in these materials n.m.r. is sensitive to the detailed dynamic behaviour of the electrons and provides information on electron transport processes. In the extreme of yet lower conductivities, as in liquid Se<sup>57</sup>,  $T_1$  is governed by interaction with localized electrons in a fashion analogous to relaxation by paramagnetic impurity ions in aqueous solution.

## 5. QUADRUPOLEAR RELAXATION IN LIQUID METALS AND ALLOYS

In most liquid metals it has been possible to explain spin-lattice relaxation rates as due to the contact interaction with conduction electrons. But for a few nuclei with  $I > \frac{1}{2}$  there is an additional relaxation rate  $T_{1Q}^{-1}$  involving coupling of the nuclear electric quadrupole moment  $Q$  with the fluctuating electric field gradient produced by thermal motion of the ions. The effect can be identified with certainty when there is a pair of isotopes with differing ratios of magnetic moments and of electric quadrupole moments ( $^{69,71}\text{Ga}$ ,  $^{121,123}\text{Sb}$ ,  $^{199,201}\text{Hg}$ ); it is also believed to occur for In and Bi. The quadrupolar rate is most marked near the melting point and in the supercooled state. It is also found to be larger in liquid alloys than in the metals themselves,  $T_{1Q}^{-1}$  being a roughly parabolic function of composition. As an example Figure 9 shows  $T_{1Q}^{-1}$  for  $^{69}\text{Ga}$  in liquid gallium over a wide temperature range<sup>58</sup>. Other data may be found in Claridge *et al.*<sup>59</sup>, Cartledge *et al.*<sup>60</sup> and Warren<sup>54</sup> and in the references to earlier work contained therein.

Interest in the effect stems mainly from the fact that  $T_{1Q}$  is sensitive to the



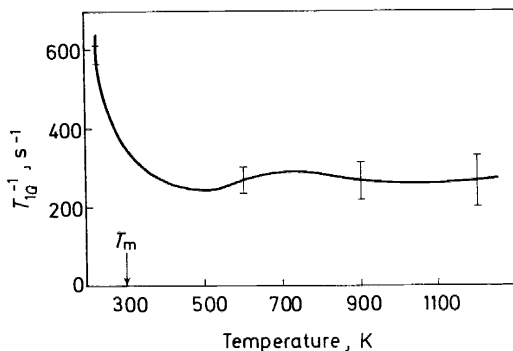


Figure 9.  $^{69}\text{Ga}$  quadrupolar relaxation rate in liquid and supercooled gallium (Kerlin<sup>58</sup>)

microscopic arrangement and dynamics of the ions. An approximate relation for  $T_{1Q}$  is

$$\frac{1}{T_{1Q}} = \frac{3(2I + 3)}{40I^2(2I - 1)} \cdot \frac{e^4 Q^2 \bar{q}^2}{\hbar^2} \cdot \tau_i \quad (13)$$

where  $\bar{q}^2$  is the mean square field gradient at a nucleus and is assumed to be characterized by an autocorrelation function which decays exponentially with time constant  $\tau_i$  ( $\omega_0 \tau_i \ll 1$ ). One might expect  $\tau_i$  to vary inversely as the self-diffusion coefficient  $D$ ; if so,  $\tau_i$  would supply the majority of the temperature dependence of  $T_{1Q}$ , which should therefore become longer at higher temperatures. This is qualitatively correct, but the relationship with the diffusion coefficient is not as simple as these crude considerations suggest.

A theoretical treatment of the coupling to the diffusional motion has been given by Sholl<sup>61</sup> for liquid metals and later extended to alloys by him<sup>59</sup> and by Jolly and Titman<sup>62</sup>. An important feature of the theory is the appearance in it of the ionic three-body correlation function, which makes the phenomenon potentially valuable for obtaining information about this elusive quantity. Unfortunately, it is deeply buried in the formulation, and it remains to be seen whether information about it can in practice be extracted. With some approximations Sholl's result for a metal is

$$1/T_{1Q} = (C/D)(I_1 + I_2) \quad (14)$$

and for species A in concentration  $c$  in an AB alloy

$$1/T_{1Q} = (C/D) \{ cI_1 + (1 - c)a^2I_1 + c^2I_2 + (1 - c)^2a^2I_2 + 2c(1 - c)aI_2 \} \quad (15)$$

where  $a$  is the ratio of field gradients produced by B and A ions;  $D$  is assumed the same for A and B; and  $C$  absorbs the constant terms.  $I_1$  is an integral which alone describes a nucleus interacting separately with the field gradients produced by other ions;  $I_2$ , containing the three-body correlation function describing the angular distribution of ions round the nucleus in question,

partially cancels  $I_1$  reflecting the partial cancellation of the individual gradients. Equation 15 shows the observed parabolic dependence for  $I_2 \sim -0.9 I_1$ . The large effect in alloys comes from the fluctuations in gradient when near-neighbour ions move away and are replaced by dissimilar ions.

Some evidence exists<sup>58, 60, 63</sup> from  $T_{1\rho}$  values for solid and liquid at the melting point and from persistence of substantial quadrupolar relaxation to very high temperatures where diffusional motion would be too rapid to be effective, that coupling to vibrational modes of ionic motion is also involved. (It is possible, however, that the persistence to high temperature comes from an increasing  $q^2$  partially counteracting the decrease of  $\tau_i$ .) In order to put the theory on a sounder footing (and to accommodate both types of motion), present theoretical efforts (Sholl, to be published; Warren, private communication) are directed towards formulation of the theory in terms of time-dependent pair distribution functions which may be obtained from neutron scattering experiments or from molecular dynamics computations.

Finally, while considering the question of molecular motions, it should be mentioned that the bulk diffusion coefficient of liquid Li has been measured by Murday and Cotts<sup>64</sup> by a quite different application of n.m.r., but the method is unlikely to be applicable to many other liquid metals because of their shorter  $T_1$ s.

## 6. CONCLUSION

A very large amount of the n.m.r. data for liquid metals is explicable in terms of a NFE model. To obtain exact agreement with experimental Knight shifts is, however, beyond present capabilities, because although we have a formulation which is probably capable in principle of doing so, structure factors and pseudopotential form factors are not known with sufficient accuracy, and the possibility of other contributions to the observed shifts is an added complication. Temperature coefficients of shifts are qualitatively understood, and their insensitivity to melting; general features of their changes in alloys are understood but quantitatively good calculations are seldom possible. The Korringa relation shows up the rôle of electron-electron interactions, in the evaluation of which much progress has been made. NMR of solvent and solute nuclei is useful in the investigation of local moments in dilute alloys and can yield values for interatomic and intratomic exchange energies. A beginning has been made on the study of liquid transition metals. Nuclear magnetic resonance—and anomalous Korringa products, in particular—have thrown light on the microscopic dynamics of conduction electrons in liquid semiconductors. Finally, the study of quadrupolar relaxation may prove equally fruitful in the investigation of the microscopic dynamics of the ions.

## ACKNOWLEDGEMENTS

It is a pleasure to acknowledge many helpful discussions with my colleagues Drs R. Dupree, C. A. Sholl and G. A. Styles.

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