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Abstract. The Knight shifts of As and Ge in liquid Ge have been determined by TDPAD (time-differential perturbed angular distribution) measurements over a temperature range of 1210–1370 K, using the isomeric nuclei ^{73m}As and ^{69m}Ge as probe atoms. The Knight shifts have also been measured in liquid Ga (295–1175 K), $Ga_{0.33}Ge_{0.66}$ (1010–1210 K), $Ge_{0.66}Pb_{0.33}$ (1170–1215 K) and GaSb (975–1135 K). For both As and Ge the shifts are essentially metallic in these matrices. However, even in definitely metallic conditions for As, the shift is only about $\frac{2}{3}$ of that of Ge. Non-metallic references for the Knight shift of ^{73m}As have been established in liquid GaI_3 (515 K) and solid GaAs (1440–1510 K); for Ge reliable reference data were available.

1. Introduction

The Knight shift K in elemental and compound semiconductors above the melting point is determined by the local field B at the nucleus produced, in a first approximation, by the conduction electrons around the Fermi energy. Thus one can in principle obtain valuable information about electronic properties and the microscopic structure and bonding in solids and liquids by measuring the Knight shift. Classical semiconductors usually exhibit sharp discontinuities of the electronic properties, including the Knight shift, upon melting, when they gain metallic character. The possibility of Si existing in both the ideal covalent and a disordered metallic state has been studied recently in *a priori*-type molecular dynamics calculations (Car and Parrinello 1986, Buda *et al* 1989). While the metallic Knight shifts of molten semiconductors are known from NMR work on various III–V compounds (e.g. for InSb: Warren and Clark (1969); for GaSb: Carter *et al* (1977)), the corresponding information was lacking at that time for a prominent element: Ge. The local information on impurity (donor, acceptor) atoms (which may interact with neighbouring hostatoms to produce a metallic or a semiconducting state) which is provided by the Knight shift will be particularly interesting. It is very difficult to measure the shift, however, by conventional NMR because of limited sensitivity at low probe atom concentration. We note here that the Knight shifts in semiconducting liquid alloys have recently been discussed (Ott *et al* 1989).

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In this paper we will present experimental data on the Knight shift of As and Ge in liquid Ge and various other host melts, focusing for the latter on the case of As impurities in liquid Ge alloys. We also address the question of whether intra-atomic properties of the probe atom ('hyperfine field') can be separated from the properties of the host material ('metallic character'), i.e. from probe–host interactions. Results for the shifts of Ge and As in crystalline Ge at high temperature will be presented independently (Dürrwächter *et al* 1991).

2. Experimental details

The experiments were performed using the time-differential perturbed angular distribution (TDPAD) technique (Christiansen 1983, Schatz and Weidinger 1985) at the pulsed particle beam of the cyclotrons at KF Karlsruhe and HMI Berlin. The isomeric nuclei ^{69m}Ge ($\tau_{1/2} = 2.8(1)\mu$s, $I = 9/2^+$) and ^{73m}As ($\tau_{1/2} = 5.6(2)\mu$s, $I = 9/2^+$) were produced and aligned by ^{70}Ge(p, pn), ^{69}Ga(p, n) and ^{74}Ge(p, 2n), ^{71}Ga(α, 2n) reactions respectively. The subsequent Larmor precession of the nuclear magnetic moments in a homogeneous magnetic field ($\simeq$2–8 kG) was observed through the anisotropic γ decay of the isomeric nuclear states ($\Delta E^{As} = 361$ keV, $\Delta E^{Ge} = 398$ keV). Real-time spectra (20 μs, 1024 channels) of the γ intensities, showing the exponential decay of the isomeric level modulated by the double Larmor frequency (typically 2.5 MHz for ^{69m}Ge and 13 MHz for ^{73m}As), were recorded by a modified multichannel analyser (Brinkmann 1983). Apart from that, the experimental set-up was conventional (Dürrwächter 1989).

The samples (total weight 100–200 mg) were prepared from isotopically enriched Ge and Ga (96.8–99.7%) of 99.999% purity and from natural materials of the same or higher purity, except for Pb (99.98%). The weighed components were alloyed in evacuated sealed quartz ampoules for up to several hours to attain good homogeneity. After they had been pressed into tablets (6 mm diameter, 2 mm thickness) the samples were contained in graphite crucibles covered by thin carbon or mica foils, or, when considerable vapour pressure was to be expected, in sealed quartz ampoules with 20–60 μm Suprasil windows. As a result of careful preparation the stoichiometry deviation was less than 1%, which is sufficient for measurements in the liquid phase (metallic state). GaI$_3$ was prepared to optical purity (light yellow crystal) by evaporating I$_2$ over excess Ga 10–15 times.

During measurement the crucibles were placed inside a titanium tube, heated from the outside by a tungsten wire (field perturbation $<10^{-5}$). For temperature measurement a chromel–alumel thermoelement was placed 3 mm behind the sample inside the crucible; an accuracy of ± 5 K was determined by pyrometric calibration, temperature stability was better than ± 3 K.

3. Results

All Knight shift measurements presented were performed on ^{73m}As and ^{69m}Ge probe nuclei. A Fourier spectrum which shows the two precession frequencies of ^{73m}As and
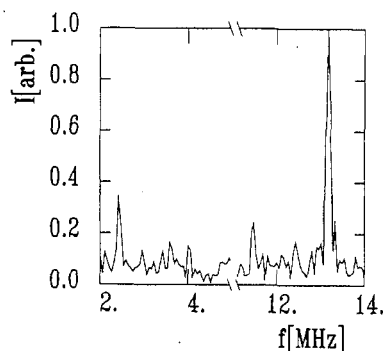
Figure 1. Fourier spectrum of a simultaneous measurement of the double Larmor frequencies of ^{69m}Ga (2.5 MHz) and ^{73m}As (13.0 MHz) in liquid Ge. The peak at 11 MHz originates from incomplete particle beam suppression during the measurement intervals.

Table 1. Knight shifts in % of As and Ge in various hosts. $\bar{T}$ is the middle of the temperature range studied (see figures 2 and 3).

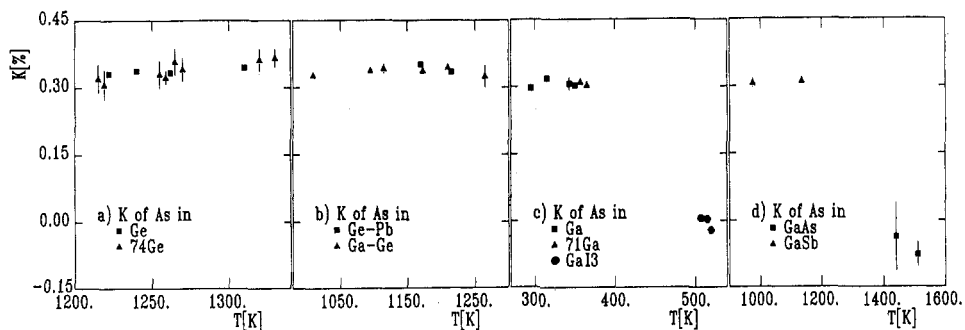| Host	^{73m}As	$\bar{T}$ (K)	^{69m}Ge	$\bar{T}$ (K)
$GaI_{3\,liq}$	0.000(5)	515		
$GaAs_{sol}$	−0.02(4)	1480		
Ge_{liq}	0.334(8)	1260	0.53(7)	1270
$Ga_{0.33}Ge_{0.66\,liq}$	0.337(7)	1150	0.53(7)	1170
$Ge_{0.66}Pb_{0.33\,liq}$	0.337(8)	1190	0.53(7)	1190
Ge_{liq}	0.305(6)	340	0.53(7)	510
$GaSb_{liq}$	0.309(17)	790	0.52(6)	725

Figure 2. Knight shifts in % of As in (*a*) liquid Ge and liquid ^{74}Ge; (*b*) liquid $Ge_{0.66}Pb_{0.33}$ and liquid $Ga_{0.33}Ge_{0.66}$; (*c*) liquid Ga, liquid ^{71}Ga and liquid GaI_3; (*d*) solid GaAs and liquid GaSb.

^{69m}Ge is presented in figure 1. The measured shifts are presented in figure 2 and figure 3 for the various matrices studied, and temperature averages are given in table 1. Under the given experimental conditions the shifts measured in the present TDPAD experiments are, directly, the Knight shifts of Ge and As in the matrices used.

Figure 2 shows results for the Knight shift of As in liquid Ge (^{74}Ge and ^{nat}Ge) and figure 3, results for Ge in liquid Ge (^{70}Ge and ^{nat}Ge). Note that the K-scales are different
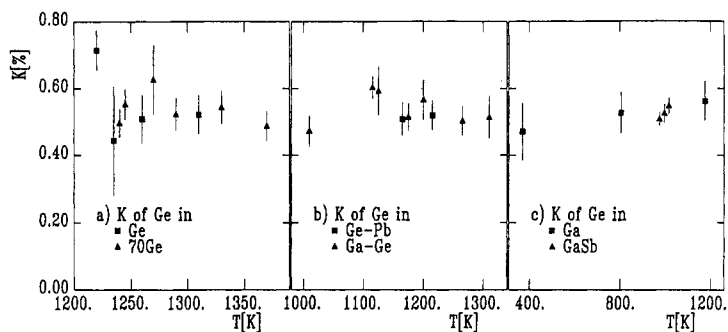
Figure 3. Knight shifts in % of Ge in (a) liquid Ge and liquid ^{70}Ge; (b) liquid $Ge_{0.66}Pb_{0.33}$ and liquid $Ga_{0.33}Ge_{0.66}$; (c) liquid ^{69}Ga and liquid GaSb.

for the two atoms. Ge and As were also measured in liquid ^{69}Ga (figure 3(c)), ^{nat}Ga and ^{71}Ga (figure 2(c)).

The precession frequencies of both As and Ge have been measured simultaneously in high-purity ^{nat}Ge, $^{70}Ge_{0.33}^{74}Ge_{0.33}Pb_{0.33}$ and $^{69}Ga_{0.33}^{70}Ge_{0.33}^{74}Ge_{0.33}$. These measurements served two purposes: first, to rule out influences on the Knight shift through the use of a different sample material (enriched isotopes compared with high-purity material of natural isotopic composition) or through the difference in probe production conditions—no difference was observed (see figures 2(a, b) and 3(a, b)); secondly the liquid alloys Ge–Pb and Ga–Ge change, i.e. reduce, the chance of As probe atoms to be in a 'bound' or associated state. Substantial reductions of the Knight shifts in other systems are discussed in terms of an association model by Ott *et al* (1989); for a review see Quitmann (1990).

As stoichiometric III–V matrices we have used GaAs and GaSb. Figure 2(d) includes data for As in liquid ^{71}GaSb and in solid ^{71}GaAs, while results for the Knight shift of Ge in liquid ^{69}GaSb are presented in figure 3(c).

As the reference point for the Knight shifts of Ge we took the (metallic) value in liquid Ga, which had been determined with respect to $Ga(NO_3)_3$ in aqueous solution (Echt *et al* 1976):

$$K(^{69}GeGa_{liq}) = 0.53(6)\%. \tag{1}$$

For As, a $^{71}GaI_3$ host was used as the reference zero point for K, since GaI_3 is an insulating salt melt at 515 °C; see figure 2(c).

4. Discussion

Let us first consider the pure liquid metallic matrices. The experimental value for the Knight shift of As impurities in liquid Ge is

$$K(AsGe_{liq}) = 0.334(8)\% \tag{2}$$

and that for Ge in liquid Ge,

$$K(GeGe_{liq}) = 0.53(7)\% \tag{3}$$

both taken at $T = 1210–1370$ K. Any temperature dependence in the liquid is limited by

the present experimental accuracy. The Knight shift of As in liquid Ga was observed earlier to be slightly temperature dependent (Ott 1989). Extrapolating the result for $T \sim 350$ K, $K(\text{AsGa}_{\text{liq}}) = 0.305(7)\%$ (figure 2(c)), to $T \sim 1150$ K, where the other metallic hosts were measured, gives a value of $K^{\text{extr}}(\text{AsGa}_{\text{liq}}) = 0.324(8)\%$, in agreement with the other metallic matrices.

Good agreement with calculated values for the metallic Knight shift of As and Ge (i.e. in liquid As and in liquid Ge respectively.) (Heighway and Seymour 1971) was found for Ge,

$$K^{\text{cal}}(\text{GeGe}_{\text{liq}}) = 0.51\%. \tag{4}$$

However, disagreement with the calculated value:

$$K^{\text{cal}}(\text{AsAs}_{\text{liq}}) = 0.53\%, \tag{5}$$

was found for the As shift, equation (2); yet the present value, i.e. that in equation (2), is essentially in agreement with another experimental value for ^{75}As in liquid As (Rigney and Blodgett 1969):

$$K(\text{AsAs}_{\text{liq}}) = 0.318(5)\%. \tag{6}$$

These authors (Rigney and Blodgett 1969) express some doubt about the metallic character of liquid As ($T = 870\,°\text{C}$, $p \sim 45$ bar vapour pressure) and suspect that the metallic shift for As might be higher. But the new data presented here for the Knight shift of As in liquid Ge, equation (2), confirm the relatively small value for the metallic shift of As. We shall come back to this point below.

We note here that a more elaborate calculation of the Knight shifts in liquid metals was carried out by Styles and Tranfield (1978), but since it does not include the elements of interest in this work we used the results of Heighway and Seymour (1971) throughout the paper.

Secondly we turn to liquid alloy matrices. For As, the Knight shift (figure 2(b)) was found to be

$$K(\text{AsGe–Pb}_{\text{liq}}) = K(\text{AsGa–Ge}_{\text{liq}}) = 0.337(7)\%. \tag{7}$$

The liquid alloys Ge–Pb and Ga–Ge had been chosen to ensure that As and Ge probe atoms were measured in a metallic melt state, and that they were both in the same matrix. Since the shifts in these melts agree with the liquid Ge values, the metallic character of both observed atoms in Ge melt is confirmed.

Turning thirdly to stoichiometric III–V compounds, we first note that for As in solid GaAs, just below the melting point, a small negative shift of $K(\text{AsGaAs}_{\text{sol}}) = -0.074(41)\%$ was found (figure 2(d)). Comparing this with the known negative chemical shift of As in GaAs ($\delta = -0.050(5)\%$; Lütgemeier 1964) our value justifies the zero-point value in GaI_3 within error.

A somewhat reduced value for the Knight shift of As was found in liquid GaSb between 975 and 1135 K, $K(\text{AsGaSb}_{\text{liq}}) = 0.309(17)\%$ (figure 2(d)), but the deviation from the value in liquid Ga remains within the error range. Apart from this case it is quite noteworthy that the shifts have very similar values for the different metallic hosts.

For Ge in liquid GaSb, $K(\text{GeGaSb}_{\text{liq}}) = 0.524(62)\%$ (figure 3(c)) was obtained which is in excellent agreement with results for liquid ^{69}Ga and the other metallic matrices.

Placing now (fourthly) the metallic Knight shifts for both Ge and As into a periodic table for the Knight shift, the present results show a typically metallic value of K for Ge

Table 2. Experimental Knight shifts K_{exp} for two rows of s–p elements; the data are taken from Carter *et al* (1977) unless stated otherwise. The factor ξ is defined in equation (8). The fraction of partial s character at the Fermi energy, $s/(s + p + d)$, is from photoelectron spectra (Indlekofer 1987), and values in parentheses from model calculations (Hafner and Jank 1990), see text.

	Cu	Zn	Ga	Ge	As	Se
K_{exp} (%)	0.26	0.34[a]	0.45	0.53[b]	0.34[b]	0.26[c]
ξ	0.95 (0.53)	0.55	0.39 (0.12)	0.28	0.12	0.06
$s/(s + p + d)$		(0.23)	0.04 (0.12)	0.03 (0.10)		
	Ag	Cd	In	Sn	Sb	Te
K_{exp} (%)	0.58	0.79	0.79	0.73	0.71	0.54[d]
ξ	0.92 (0.70)	0.64 (0.23)	0.36 (0.22)	0.23 (0.14)	0.16 (0.06)	0.09 (0.01)
$s/(s + p + d)$		(0.22)	0.06 (0.15)	0.04 (0.09)		

[a] Bucklisch and Ploumbidis (1978).
[b] This work.
[c] Maximum shift observed in liquid Se (Warren and Dupree 1980).
[d] High-temperature value from Carter *et al* (1977). in agreement with the shift found in liquid Sb–Te alloys (Hinkel and Ploumbidis 1984).

and a metallic, though clearly reduced value for As; see line 2 of table 2. Other liquid group IV and V melts display Knight shifts that also fit rather well into a smooth trend with their neighbours from groups I, II or III; for the Ag–Te row, see line 6 of table 2 (all values except for Zn, Ge and As from Carter *et al* 1977). Here the reduction occurs 'later' in the row, at Te, perhaps in accord with the general trend of the metal/non-metal borderline among p elements. As has been pointed out above, the smaller value for the Knight shift of As compared with Ge is independent of the matrix chosen. It can therefore be considered an intra-atomic, as opposed to a host or host–probe interaction effect. Qualitatively it is in accord with the increasing p character of the conduction electrons.

As a concluding remark, we want to point out a related general difficulty in the understanding of Knight shifts of p elements in liquid metals which has arisen through comparison with recent density-of-states measurements.

The conventional expression for K is

$$K \simeq K_s \qquad K_s = (8\pi/3)\Omega\chi_P\langle|\Psi(0)|^2\rangle_{E_F} = (8\pi/3)\Omega\chi_P|\Psi_{at}(0)|^2\xi \qquad (8)$$

where Ω is the atomic volume, χ_P the Pauli spinsusceptibility and $\langle|\Psi(0)|^2\rangle_{E_F}$ the probability density of conduction electrons near the Fermi edge at the nucleus. Thus one expects the major contribution to come from those conduction electron states at $E = E_F$, which have atomic s character (at least for the lighter elements). $|\Psi_{at}(0)|^2$ is the electron probability density at the nucleus of the free atom and the factor $\xi = \langle|\Psi(0)|^2\rangle_{E_F}/|\Psi_{at}(0)|^2$ is introduced to account for any difference in the hyperfine coupling between the free atom and the metal; see for example Carter *et al* (1977). Obvious contributions which cause ξ to deviate from unity are: (i) the partial s character at E_F, in short $s/(s + p \ldots) \leqslant 1$ and (ii) the change (compression) of the Ψ_s function between the atom and the melt. However, hybridization and core-polarization effects have to be considered as well. Systematic analyses for a number of s–p metals (Carter *et al* 1977) found ξ roughly between 0.8 and 0.1, decreasing with increasing number of electrons in each row of the periodic table.

To obtain approximate values for Ge and As we used the experimental Knight shifts together with atomic $|\Psi_s(0)|^2$ from the most recent calculation (Koh and Miller 1985) and values for χ_P and Ω from Heighway and Seymour (1971). The results for ξ, listed in table 2, reproduce the general trend of the earlier values (Carter *et al* (1977); in parentheses in table 2) although they are systematically larger.

A difficulty arises, however, when one compares our studies with the series of recent photoelectron spectroscopy studies of valence bands of liquid s–p metals by Indlekofer and Oelhafen (1988; Indlekofer *et al* 1988). As to the atomic l character these authors found progressively more p and less s character at E_F as one proceeds from group III to V metals. For some liquid metals, the curves presented by Indlekofer and Oelhafen include a separation into contributions to the valence band density of states from s and p electrons. This separation has been made by comparison of spectra taken at different excitation energies, using the calculated energy dependencies of the corresponding atomic photo-ionization cross sections. Values for the fraction of s character, s/(s + p + d), are presented in table 2 (from figure 28 and figure 35 in Indlekofer 1987). They are seen to be rather small, ranging from $\simeq0.06$ in liquid In to $\simeq0.03$ in liquid Ge. Very recent calculations of partial densities of states of liquid metals (Hafner and Jank 1990) give somewhat larger values, between $\simeq0.23$ in liquid Zn and $\simeq0.09$ in liquid Sn (Hafner and Jank 1990; numbers in brackets in table 2, lines 4 and 8).

The general trends of both ξ and s/(s + p + d) with the periodic number suggest that one should consider the ratio s/(s + p + d) as the dominating part in ξ. Then agreement is found only for the set of smaller ξ-values from Carter *et al* (1977) and for the larger numbers for s/(s + p + d) from Hafner and Jank (1990). The ξ-values calculated for our own work, on the other hand, exceed the experimental s/(s + p + d) values from Indlekofer (1987) by a factor of 6 or 10. Thus it appears that the Knight shift in the first-order *ansatz* of equation (8) and the photoelectron results cannot yet be reconciled, at least not at the admittedly simple level of discussion sketched here.

As far as the Knight shift theory is concerned, contributions from core polarization and from the electron orbital momentum, which are considered to be negligible or to cancel out in the formulation of equation (8), may be more substantial than assumed so far. In a recent theoretical approach of Ebert *et al* (1986) the orbital contributions to the Knight shift of transition metals (V, Cr, Nb and Mo) were calculated using a Green function method. They found a large Van Vleck term, mainly from the d electrons, dominating the Knight shift and giving it a positive sign; however, the p electron contribution to K_{vv} also turned out to be non-negligible (15–30% of the total Knight shift). A similar calculation of K in liquid s–p metals might therefore be worthwhile.

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