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LETTER TO THE EDITOR

On the minimum size of metallic clusters in a liquid semiconductor system

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Abstract. Use is made of the fact that the NMR Knight shift K can be used as a local, i.e. atomic scale, indicator of whether the electronic state of the atom is metallic or non-metallic. We have measured K for the probe atom Bi in the liquid semiconductor system Tl–Te, and find that K_{Bi} drops in a narrower range around Tl₂Te than either K_{Te} or the susceptibility. Adopting the quasichemical model for the analysis, it is concluded for this system that a Bi atom needs only a very small number of metallic neighbours (either Tl or Te) in order to show the metallic value of K .

It is generally assumed that liquid semiconductors develop when suitable liquid metals A, B are mixed, because there is strong bonding in a stoichiometric ratio



Even if the bonding energy is large compared to $k_{\text{B}}T$, reaction (1) leaves behind a surplus of component A or B at all number fractions or concentrations $x_{\text{A}} = x$, except if the composition is exactly at $x_{\text{s}} = \mu/(\mu + \nu)$. Let us look at this situation on a microscopic scale, where each atom is surrounded by ‘a few’ nearest neighbours only, typically about 10 in the liquid state. Consider one particular atom which happens to be unbound at present. One may then ask: what is the minimum number of surplus component atoms among the NN of the given atom which allows such a ‘cluster’ to appear as a true metallic state? It appears obvious to us that a finite number of surplus atoms (i.e. atoms not engaged in any of the bonded A_μB_ν species) have to be nearest neighbours in order to form a metallic state locally.

A suitable atomic scale detector is the Knight shift K

$$K = 8\pi/3\chi_{\text{P}}\Omega\langle|\psi(0)|^2\rangle_{\text{F}} \quad (2)$$

where χ_{P} is the Pauli susceptibility, and Ω the atomic volume. The quantity $\langle|\psi(0)|^2\rangle_{\text{F}}$, the density at the nucleus of electrons with energy at the Fermi level, locally samples the metallic character of the electronic state. Corrections to the Knight shift formula (2) [1–3] will be assumed not to change this specific sensitivity which is localised in r space via ψ , and is selective in energy (ε_{F}) via the prescription $\langle|\psi(0)|^2\rangle_{\text{F}}$. The fact that in all liquid semiconductors there is a strong decrease of the Knight shift [4], and in particular, that there is asymmetry of K around the stoichiometry [5–7], support this assumption. Experimentally the Knight shifts observed on the two atoms of a binary alloy which becomes semiconducting do *not* follow the same trend, as a function of concentration; rather each of them has a higher K on its majority, and a lower K on its minority side.

Examples are metal–tellurium alloys (Cu–Te [8], Sn–Te [5], Cs–Au [6]). This behaviour appears natural if one assumes that each atom, A or B, in the liquid alloy A–B can be in two distinct states as indicated by (1), with a fast dynamic equilibrium between them. Note that (1) is often and successfully used to describe energetic effects in liquid alloys (see e.g. [9, 10]). The two states can be expected to have different hyperfine interactions; these are then ‘atomic scale detectors’ of whether the atom is in the right hand side, or left hand side state of (1). On this assumption it was possible to explain the Knight shifts [5, 6] and quadrupolar relaxations [11] in liquid alloys with A–B bonding.

We have studied the Knight shift K in a liquid semiconductor system which displays a clear dip in conductivity at its stoichiometry, namely Tl_2Te . Some data for K on Tl [12] and Te [13] have been reported before. We have measured K on an atom of a third element, Bi, which was chosen as a ‘spectator’ because it has the property to form *metallic* alloys, not liquid semiconductors, with either of the liquid components Tl or Te. The metallic behaviour of Bi–Te and Bi–Tl alloys is known from earlier studies of their Knight shifts [14, 15]. This peculiarity of the atom studied makes it a metallic partner for whichever component appears as the metallic surplus. Because of its weak interaction with either Tl or Te, isolated Bi atoms may be considered as spectators imbedded in a Tl–Te surrounding, the behaviour of which is the matrix behaviour (see (3)).

The Knight shift was measured using the TDPAD technique. The Bi concentration is extremely low ($<10^{-8}$); for details see e.g. [16, 17]. Figure 1 shows the results for K in liquid $\text{Tl}_x\text{Te}_{1-x}$ as a function of x , at a temperature 740 K, i.e. above the melting point of the compounds (Tl_2Te : 698 K; Tl_5Te_3 : 728 K) and above the Tl– Tl_2Te liquid demixing limit [18]. It is seen that the Knight shift assumes a very low, essentially non-metallic value at the matrix stoichiometry Tl_2Te , $x = 0.666$, and that this dip is rather narrow in concentration. The temperature dependence and relaxation rate were also measured, and will be reported elsewhere [19].

We note here that the shape of the curve $K(x)$ in liquid semiconductors is very different for different systems. The minimum is, for example, rather broad in $\text{Ga}_x\text{Te}_{1-x}$ and $\text{In}_x\text{Te}_{1-x}$ for K_{Ga} , K_{In} , respectively, and for K_{Te} [12, 20]. It is also broad or, more precisely asymmetric for K_{Cu} in $\text{Cu}_x\text{Te}_{1-x}$ [8]. The asymmetry becomes the most prominent feature in systems like Sn–Te, Cs–Au and Cs–Sb (these cases are discussed in recent papers [5–7]). We take the narrow and rather symmetric shape of the minimum of K_{Bi} in $\text{Tl}_x\text{Te}_{1-x}$ as a signal of the metallic interaction of the Bi atom with both Tl or Te atoms when these are surplus and in a metallic state.

As to the present case of the Bi Knight shift in $\text{Tl}_x\text{Te}_{1-x}$, it does not follow that of Te, nor the susceptibility $\chi(x)$. This is demonstrated in figure 1 where the normalised curves for χ , K_{Tl} and K_{Te} in liquid $\text{Tl}_x\text{Te}_{1-x}$ are shown (data from [12, 13, 21] respectively).

The point of view adapted for the analysis of the sharp dip of K_{Bi} in Tl–Te is based on the quasichemical model for the thermodynamics of liquid alloys which we have previously applied to nuclear spin relaxation in metallic liquid alloys [19] and to the Knight shift [5–7]. It starts from the assumed reaction (1). The quasichemical model has seen significant developments since its introduction to metallic alloys [22], see e.g. [9–11, 23]. It will be used here in a simplified version which is a good approximation when the gain in free enthalpy involved in (1) is large (large compared to an average metallic interaction A–A, B–B, and between the probe and either A or B). The reaction is assumed to have proceeded to the right hand side, (almost) to the full extent possible at the given concentration. If M_A and M_B are the mole numbers of A and B respectively

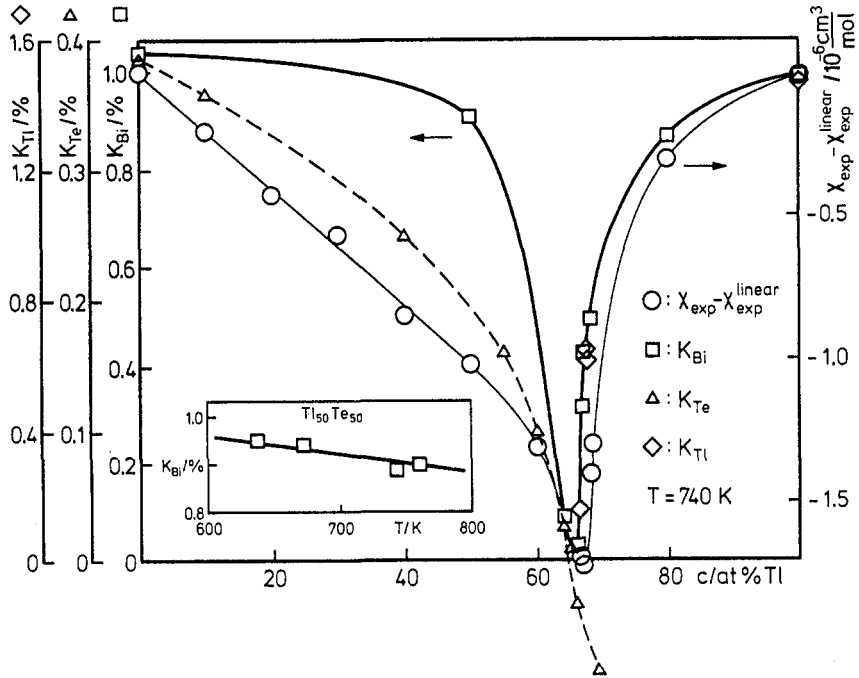


Figure 1. For the liquid semiconductor alloy Tl_xTe_{1-x} we show \circ : the magnetic susceptibility χ_{exp} at 740 K from [21], normalised by forming $\bar{\chi} = \chi_{exp} - \chi_{exp}^{linear} = \chi_{exp} - (x_{Te}\chi_{Te} + x_{Tl}\chi_{Tl})$; \triangle : the Knight shift K_{Te} at 740 K from [13]; \diamond : K_{Tl} at 740 K from [12]; \square : K_{Bi} at 740 K (this work, the point at $x_{Tl} = 0.8$ was taken at 1040 K). The inset presents the temperature dependence of K_{Bi} at $x = 0.5$.

in the ingot, $x = x_A = M_A / (M_A + M_B)$ and $x_s = \mu / (\mu + \nu)$, then the concentrations \bar{n}_1 of free A or \bar{n}_2 of B, and \bar{n}_3 of the aggregates $A_\mu B_\nu$ are

$$\bar{n}_1 = \alpha x \quad \bar{n}_2 = 1 - \left[1 + \frac{\nu}{\mu} (1 - \alpha) \right] x \quad \bar{n}_3 = [(1 - \alpha) / \mu] x \quad x \leq x_s \tag{3}$$

$$\bar{n}_1 = 1 - \left[1 + \frac{\mu}{\nu} (1 - \alpha) \right] (1 - x) \quad \bar{n}_2 = \alpha (1 - x) \quad \bar{n}_3 = \frac{(1 - \alpha)}{\nu} (1 - x) \quad x \geq x_s$$

where α is the degree of dissociation of the aggregate $A_\mu B_\nu$. Note that we choose the normalisation $\bar{n}_1 + \bar{n}_2 + (\mu + \nu)\bar{n}_3 = 1$ i.e. to the total number of atoms. If the volumes of A and B happen to be equal, and additive in $A_\mu B_\nu$, then $\bar{n}_1, \bar{n}_2, \bar{n}_3$ are the volume fractions of free A, free B and aggregates $A_\mu B_\nu$, respectively.

A probe atom which does not have an interaction with either A or B or $A_\mu B_\nu$, comparably strong to the A–B interaction will then microscopically ‘sample’ its neighbourhood and find a larger or smaller number of metallic, i.e. free, neighbours (\bar{n}_1, \bar{n}_2). That Bi will not be bound to any sizable degree can be inferred from the absence of any binary strongly bound compounds in the Bi–Tl as well as the Bi–Te system [18, 24]. To our knowledge the possible existence of ternary compounds is a small effect in liquid alloys, even at the correct stoichiometric composition of the ternary (see the analogous

case in In-Sb-Te [25]). The said 'sampling' then comprises both the important factors in (2), namely χ_F as well as $\langle |\psi(0)|^2 \rangle_F$.

Equations (3) give the average concentrations of free, metallic neighbours \bar{n}_1 , \bar{n}_2 . We assume a fixed number of nearest neighbours N , and a statistical distribution of free and bound atoms among these. (Thus we neglect medium range order, or interactions $A-A_\mu B_\nu$, $B-A_\mu B_\nu$, $A_\mu B_\nu-A_\mu B_\nu$.) Then the probability distribution of the number N_m of free A and B in the first shell around the probe atom, for a given average $\bar{N}_m = N(\bar{n}_1 + \bar{n}_2)$, is

$$P(N_m) = (N/N_m)(\bar{N}_m/N)^{N_m}(1 - \bar{N}_m/N)^{N-N_m} \quad (4)$$

using the binomial distribution. One obtains with $\alpha = 0$: $\bar{N}_m = N\bar{n}_2$ for $x \leq x_s$, $\bar{N}_m = N\bar{n}_1$ for $x \geq x_s$. Here N_m is the number of metallic neighbours (0, 1, 2, . . . N). In the present example of a Bi probe atom in liquid Tl_xTe_{1-x} , where the stoichiometry is at $x_s = \frac{2}{3}$, we have considered $N = 10$ (see Gay *et al* [26]). The exchange of atoms in the nearest neighbour shell is very fast, and we need not consider this process in determining the Knight shift. It will also be assumed that the sensitivity of the measurement of K does not depend on the value of K .

We can now determine the number of additional metallic nearest neighbour atoms required by a Bi atom in order to show a metallic Knight shift. If this number is N_0 then the Bi Knight shift will be metallic with a probability

$$P = \sum_{N_0}^N P(N_m). \quad (5)$$

Whenever there are too few metallic neighbours, i.e. less than N_0 , then $K = 0$.

One may assume that the Knight shift determined by the metallic surrounding of Bi shows a linear dependence on the concentration. This appears justified in view of the comparatively small variations of K_{Bi} in the liquid Tl-Bi [15] and Te-Bi [14] systems: K_A , i.e. K for Bi in pure liquid Tl, has been measured as $K_A = 1.0\%$ [15], and K_B can be extrapolated from the liquid Bi-Te system [14] as $K_B = 1.065\%$. Then one arrives at

$$K = P[xK_A + (1-x)K_B]. \quad (6)$$

In figure 2 we present curves calculated for the case of Bi in liquid Tl_xTe_{1-x} alloys. Curves for $N_0 = 1, 2, \dots, 10$ are drawn in figure 2. It is seen that for Bi at 740 K the number of neighbour atoms over and beyond the one Bi atom is

$$N_0 = 1 \dots 2 \quad (7)$$

on both the Te and the Tl rich side. The necessary minimum cluster size is $1 + N_0$ (the 1 is for the Bi). Our results, (7) thus indicate a small number like 2 or 3 in condensed matter at high temperature. It may be compared to the minimum cluster sizes for isolated metallic clusters where, e.g., the number is about 10 for Na clusters *in vacuo* [27].

The wider shapes calculated in figure 2 for larger N_0 may well apply to systems other than the one of interest here. A discussion of the similar case of an As impurity in liquid Ga_xTe_{1-x} will be given elsewhere [28].

In conclusion we stress again that the use of an atomic probe which is very sensitive to the local metallic character, namely the Knight shift, and a straightforward application of the quasichemical model, suggest that one can identify very small regions in liquid semiconductors as displaying a metallic nature.

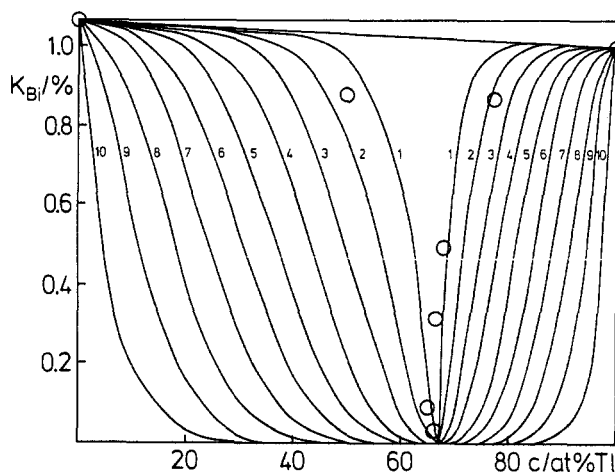


Figure 2. Knight shift of very dilute Bi atoms, K_{Bi} , in liquid $\text{Ti}_x\text{Te}_{1-x}$ (open circles). The curves are predictions for K_{Bi} as explained in the text. They correspond to the assumption that $N_0 = 1 \dots 10$ 'free' atoms (left hand side of (1)) have to be nearest neighbours of a Bi atom in order to make Bi display a metallic value for K .

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