

ASSOCIATION IN STRONGLY INTERACTING LIQUID BINARY ALLOYS AND NUCLEAR SPIN RELAXATION

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An experimental quantity sensitive to the time development of the distance between two atoms in a liquid alloy, is the quadrupolar nuclear spin relaxation rate  $R_Q$ . The existing material for s-p-alloys shows a systematic occurrence of strong enhancements of  $R_Q$  if there is an attractive interaction among the partner elements in alloys. Using a model of associates for the alloy, it is possible to connect  $R_Q$  rather directly with the lifetime of the associate. For In-Hg<sup>3</sup> at 260 K as an example,  $10^{-11}$  sec is obtained.

In liquid A-B alloys for which thermodynamic properties indicate strong attractive interactions between unlike atoms, many properties show anomalies, and these are connected with hetero-coordination. However, neutron and X-ray scattering are so far essentially the only methods yielding direct evidence for A-B association. A possible new access<sup>1</sup> to short range order is furnished by measuring  $R_Q$ , the nuclear spin relaxation rate which is caused by fluctuating electric field gradients at a nucleus (where they interact with the probe atom nuclear quadrupole moment Q).

Considering first the measurement of  $R_Q$ , it can be performed by NMR (for data see<sup>2</sup>) or by using an angular correlation technique on nuclear isomers which are produced in the sample by a nuclear reaction (see e.g.<sup>3</sup>). This technique has been applied in liquid  $A_c B_{1-c}$  alloys of s-p-metals, with systematic variation of partner elements A,B, of concentration c and/or temperature T, and of the nuclear probe used. Metallic liquid binary alloys studied so far were: Hg-K<sup>4</sup>; In-Sb<sup>5,3,6</sup>; In-Ag, -As, -Au, -Bi, -Cd, -Cu, -Ga, -Ge, -Hg, -Tl, -Zn<sup>3</sup>; In-Pb<sup>7,8,9</sup>; In-Sn<sup>10,8</sup>; Pb-Ag, -As, -Au, Bi, -Li, -Sb, -Sn, -Tl<sup>7</sup>; Sb-Sn<sup>10</sup>; Tl-Au, -Bi, -Pb<sup>11</sup>. Considerable enhancements of  $R_Q$  over the pure liquid metal value have been observed for a number of liquid alloys, and related in<sup>1</sup> to the compound forming tendency of the alloy. This correlation has been confirmed in the alloys listed above.

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For an interpretation, we turn to the analysis of  $R_Q$ .  $R_Q$  is determined by the correlation function of the electric field gradient at the probe nucleus (efg),  $V_{zz}$ , through

$$R_Q = \text{const.} \cdot \langle V_{zz}^2 \rangle \tau \quad (1)$$

where  $\tau$  is the efg correlation time.  $V_{zz}$  is a short ranged function of the atomic distance probe-neighbour, summed over the neighbours (so that  $V_{zz} = 0$  for cubic symmetry). If in a liquid metallic alloy AB-bonding is energetically preferred over AA- and BB-bonding, then this is due to a redistribution of free conduction electrons (e.g. charge transfer), and there will be a preferential association of AB neighbours, and a longer lifetime of such associations. Although there are differences between different alloys, in general the consequences on  $\langle V_{zz}^2 \rangle$  and  $\tau$  act in the same sense, i.e. cooperate to enhance  $R_Q$ . Here we have already implicitly assumed a model of local association (order over short range in r-space) as discussed recently by Elwenspoek et al. for  $R_Q$  4,6. Such model is furnished by a description of liquid A-B alloys as a ternary mixture of free A and B atoms with AB associates (see<sup>12</sup> for details; we assume 1:1 associates only). In the free state we assume short correlation times close to those for regular alloys or pure metals<sup>13</sup>. Relatively long association will happen if B is in an associate AB, the probability for that being proportional to the concentration of AB,  $n(c,T)$ . Thus

$$R_Q(c,T) \sim \langle V_{zz}^2 \rangle_{\tau^M} \cdot (1-n) + \langle V_{zz}^2 \rangle_{\tau^A} \cdot n.$$

As to the magnitude of  $V_{zz}$  on B, we expect it to change between free A-B pairs and AB associates more or less in proportion with the change in bonding energy (through ionic or covalent admixtures to the metallic bonding). Since the same energy will enter  $\tau^A$  exponentially, see eq.(3) below, we will neglect its effect on  $V_{zz}$  at present and for the system discussed below. Finally, with  $n(0,T) = n(1,T) = 0$  and  $\tau^A \gg \tau^M$  one obtains

$$\frac{R_Q^A}{R_Q^M} \sim \frac{n(c,T) \cdot \tau^A(c,T)}{\tau^M} \quad (2)$$

Now since the spatial range of the quadrupole interaction is comparable to, most probably shorter than the nearest neighbour interaction (responsible for the bonding),  $\tau^A$  becomes an estimate of the lifetime of associations - a quantity of direct interest for any atomistic model of liquid alloys.

The model has been checked in the following way<sup>6</sup>:  $n(c,T)$  can be calculated by solving numerically the equation for  $n$  within the ternary solution model; the necessary parameters (interaction energies A-B, A-AB, B-AB, and AB bonding energy:  $W_0, W_A, W_B, W_R$  respectively) can be obtained from a fit to thermodynamic data  $\Delta H(c), \Delta S^{\text{ex}}(c), \Delta C_p^{\text{ex}}(c)$  (taken at one T). Also the relative change of  $\tau^A$  with  $c$  and  $T$  can be calculated from the same parameters by realizing that the law of mass action is also the ratio of transition probabilities for formation and decay of associates  $A+B \leftrightarrow AB$ ; then

$$\tau^A \approx v_0^{-1} \exp [(\bar{W}-W_R)/RT] \quad (3)$$

where  $\bar{W}$  is a suitable average over  $W_0, W_A$ , and  $W_B$ .  $v_0$  is unknown, maybe of order  $10^{13}$ /s. The test of the model consists in comparing the shape of the calculated curves  $n(c,T) \cdot \tau^A(c,T)$  with  $R_Q(c,T)$ , after normalization has been fixed at one point. Satisfactory agreement has been obtained for liquid In-Sb alloys where rather extensive data for  $R_Q(c,T)$  and for  $\Delta H$  etc. exist<sup>6</sup>. The model is also in agreement with the correlation of  $R_Q$  with  $\Delta H$  mentioned above<sup>1</sup>.

We demonstrate the approach by presenting in fig. 1 the data for  $R_Q(T)$  of  $\text{Hg}_{0.5}\text{In}_{0.5}$ . Two different probe nuclei, the isomers  $^{117\text{m}}\text{Sb}$  and  $^{206\text{m}}\text{Pb}$  have been used. The temperature dependence has been calculated from the  $W$  parameters (derived in turn from data in<sup>14</sup>:  $W_A = W_B = -0.7$  kcal,  $W_0 = -1.0$  kcal,  $W_R = -1.4$  kcal). The curve is seen to give a good reproduction of the temperature dependence which agrees also reasonably well between the two data sets. We use the values of fig. 1 at 260 K to derive  $\tau^A$ : For  $^{206\text{m}}\text{Pb}$  one has  $R_Q^M = 0.8 \cdot 10^3$ /sec in pure liquid Hg, and for  $^{117\text{m}}\text{Sb}$   $R_Q^M = 0.2 \cdot 10^3$ /sec in pure liquid In<sup>3</sup>; assuming that  $\tau^M \approx 0.3 \cdot 10^{-12}$  sec of<sup>15</sup> applies also for these two liquid metals, one obtains either  $1.2 \cdot 10^{-11}$  sec or  $2.4 \cdot 10^{-11}$  sec for  $\tau^A$ , respectively. We consider the factor of two disagreement as an optimistic lower estimate of the uncertainties at the present stage and summarize

$$\tau^A(c=0.5, T=260 \text{ K}) \approx 2 \cdot 10^{-11} \text{ sec} \quad (4)$$

for Hg-In. Temperature dependence can be seen from eq.(3) and fig. 1. It derives mostly from the correlation time  $\tau^A$ .

Limitations to the procedure employed here are set by rotational motion (as in Hg-K<sup>4</sup>), by uncertainties of  $V_{ZZ}$  and the type of bonding, and by the influence of the probe atom.

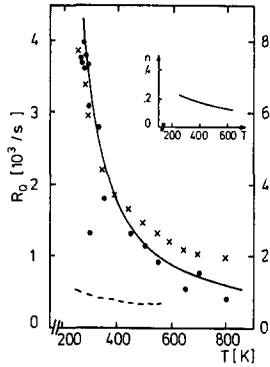


FIGURE 1 : Quadrupolar spin relaxation rates  $R_Q$  for the probes  $^{117m}\text{Sb}$  (dots, left scale) and  $^{206m}\text{Pb}$  (crosses, right scale) in liquid  $\text{In}_{0.5}\text{Hg}_{0.5}$ . Curve is  $n \cdot \tau^A$ , normalized at 500 K. Dashed curve is  $R_Q$  in pure liquid Hg ( $^{206m}\text{Pb}$ ). Inset shows concentration of associates,  $n(0.5, T)$ .

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