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^{209}Bi NMR IN MOLTEN Bi-BiBr₃ MIXTURES

R. Dupree and J.A. Gardner*

Physics Department, University of Warwick, Coventry CV4 7AL, England.

Abstract.- The ^{209}Bi shift and relaxation have been measured in several Bi-BiBr₃ mixtures. The behaviour is very different from that observed in Bi-BiI₃ mixtures. The ^{209}Bi shift decreases strongly as BiBr₃ is added to Bi and the relaxation rate increases rapidly. The NMR data give strong evidence for the formation of short-lived BiBr₃ "molecules" in the metal rich mixtures.

Introduction

Metal-molten salt systems are one of the classes of liquid which undergo a metal-nonmetal transition as the concentration of metal is varied. Although the electrical conductivity has been measured in a number of these systems, there have only been a few investigations using techniques such as NMR and ESR capable of giving microscopic information about these mixtures⁽¹⁻³⁾. Earlier we reported NMR investigations of the Bi-BiI₃ system⁽¹⁾. The results were anomalous in that the ^{209}Bi NMR shifts observed appeared to have metallic values even when the conductivity was non metallic (i.e. $\sim 1(\Omega \text{ cm})^{-1}$). Although an explanation in terms of concentration fluctuations to a metallic environment in the Bi-BiI₃ mixtures would fit the data, the thermodynamic evidence suggested that this was unlikely. We therefore decided to investigate the related Bi-BiBr₃ system to see whether this behaved in a similar fashion. The electrical conductivity⁽⁴⁾ of Bi-BiBr₃ mixtures is virtually identical to that of Bi-BiI₃ and the magnetic susceptibility⁽⁵⁾ also behaves similarly in the two systems. The phase diagram⁽⁶⁾ and thermodynamic properties⁽⁷⁾ are less similar however,

Experimental

Our samples were prepared in situ from 99.999% Bi and 99% BiBr₃ which was recrystallized from HBr. The measurements were carried out over a frequency range of 12 MHz - 50 MHz using standard pulsed NMR techniques with a boxcar integrator and a computer for noise averaging.

Results

The bismuth shifts are shown for several concentrations as a function of temperature in fig. 1. The shift decreases with concentration quite rapidly and is only very slightly temperature dependent at these concentrations, unlike the Bi-BiI₃ mixtures whose shift is shown for the 75% Bi sample for comparison. For concentrations less than 80% Bi the ^{209}Bi resource became very difficult to observe because of the short relaxation time. We were able to clearly observe the resonance for 'pure' BiBr₃, unlike BiI₃ where the resonance was not detectable, but the value of the shift depended upon the sample preparation, presumably due to small departures from stoichiometry. The error bars shown cover the range of values found in this material. The free induction decay rate, T_2^{*-1} ,

*Permanent address : Physics Department, Oregon State University, Corvallis, Oregon, U.S.A.

(assumed equal to the spin-lattice relaxation rate, T_1^{-1} , in these liquids) is also shown as a function of temperature in figure 1. For 80% Bi the rate has increased by about a factor five relative to pure bismuth and decreases rapidly with increasing temperature. This too is unlike Bi-BiI₃ since the relaxation rate for this material increases with temperature and is little different from pure bismuth near this composition.

Discussion

The conductivity of all the concentrations shown in figure 1 is still metallic being ~ 1500 ($\Omega \text{ cm}$)⁻¹ for the 80% alloy. In a nearly free-electron metal the shift, K , is related to the relaxation by the Korringa relation $K^2 T_1 T = \text{constant}$. When the mean free path is comparable to the lattice

spacing the relaxation may be enhanced⁽⁸⁾ because of incipient localization of the conduction electrons but the strong temperature dependent relaxation observed for the 80% alloy cannot be due to conduction electrons since the shift and conductivity barely alter whilst the relaxation changes by a factor ~ 2 . ²⁰⁹Bi has a large quadrupole moment and in a system where there are time varying electric field gradients this will lead to quadrupolar relaxation, the rate being given by

$$T_1^{-1} = f(I) \left(\frac{e^2 q Q}{h} \right)^2 \tau_c \quad (\omega \tau_c < 1) \quad (1)$$

where $\left(\frac{e^2 q Q}{h} \right)$ is the electric field gradient, τ_c is the characteristic time over which the field gradient remains constant and $f(I)$ is a function of the nuclear spin⁽⁹⁾ and ω the resonance frequency. (In liquids $\omega \tau_c$ is usually $\ll 1$ and this was checked by measuring $T_2^* (= T_1)$ at two frequencies a factor four apart). In metals quadrupolar relaxation is usually weak and has a much smaller temperature dependence than observed for this alloy⁽¹⁰⁾, for instance adding a similar percentage of copper to bismuth gives a quadrupolar relaxation rate more than an order of magnitude smaller. Since both large field gradients and long correlation times are required, it seems likely that BiBr₃ molecules are being formed for short times in the alloy. An estimate of the lifetime of those molecules may be made by using the field gradients measured in solid BiBr₃⁽¹²⁾ viz. $e^2 q Q/h = 266$ MHz with the additional relaxation observed for the 80% alloy in (1). Since those Bi nuclei which have three bromine atoms associated with them will be most effective in the relaxation a concentration factor must be included in (1). We have assumed that this is just the number of Bi

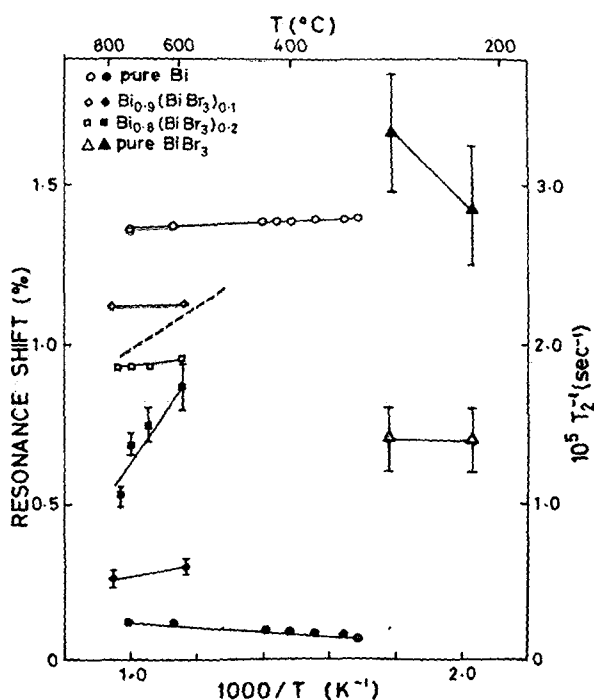


Figure 1: ²⁰⁹Bi shift and relaxation rates for Bi-BiBr₃ mixtures. The empty symbols are shifts and the filled symbols relaxation rates. The shift data for Bi_{0.75}(BiI)_{0.25} is shown for comparison. (-----)

nuclei with 3 nearest neighbours of bromine (~ 0.2 for the 90% alloy) and find that $\tau_c \sim 3.8 \times 10^{-11}$ sec at 600°C decreasing to $\sim 1.7 \times 10^{-11}$ sec at 800°C for the 20% alloy and somewhat shorter, $\sim 1.2 \times 10^{-11}$ sec at 600°C decreasing to 0.7×10^{-11} sec, for the 10% alloy. The rapid decrease in relaxation rate is now readily explained in terms of a reduced lifetime for the "molecular" BiBr_3 association, which is expected, as the temperature increases.

The Knight shift is given by

$$K = \frac{8\pi}{3} \beta^2 N(E_F) \Omega \langle |\psi(0)|^2 \rangle_F \quad (2)$$

where $N(E_F)$ is the electronic density of states at E_F and $\langle |\psi(0)|^2 \rangle_F$ the average electronic probability amplitude at the nucleus normalized to a volume Ω .

In alloys the change in the Knight shift with composition are usually due to changes in all the terms in (2), however in this case if BiBr_3 "molecules" are being formed one can calculate the variation of the density of states as BiBr_3 is added to Bi and this is shown in fig. 2 together with the observed shift at 600°C and that for the BiI_3 alloys. There is semiquantitative agreement between the shift and calculated density of states implying that the main contribution to the change in Knight shift in this system is the density of states.

Conclusion

Although the conductivities of the Bi-BiBr_3 and Bi-BiI_3 systems are very similar in the metal rich region their microscopic properties are very different. We have shown that in Bi-BiBr_3 , BiBr_3 "molecules" are formed with a comparatively long lifetime and that the density of states follows the free-electron value once the formation of "molecules" is recognised. Molecular formation

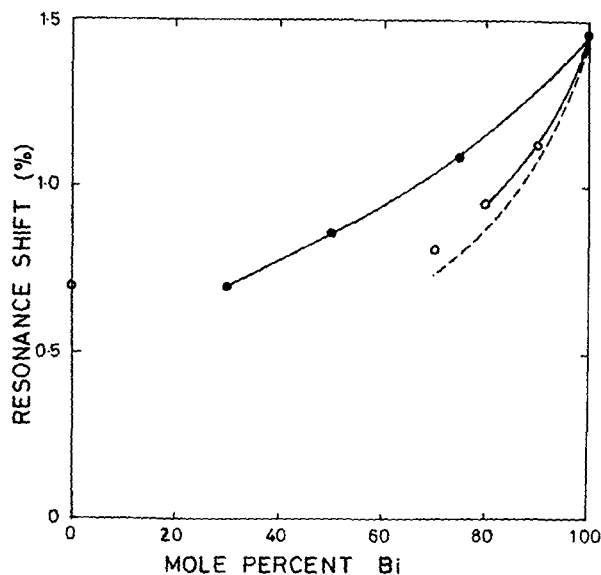


Figure 2: ^{209}Bi shift versus concentration for \circ Bi-BiBr_3 , \bullet Bi-BiI_3 at 600°C . The normalized free-electron $N(E_F)$ for Bi-BiBr_3 is shown dashed.

does not seem to occur in metal rich Bi-BiI_3 mixtures whose microscopic behaviour is still not understood. The more marked formation of molecules in Bi-BiBr_3 than in Bi-BiI_3 might perhaps be expected since the excess entropy for Bi-BiBr_3 is always negative indicating strong bonding effects whereas it is positive for Bi-BiI_3 down to excess metal concentrations of $\sim 40\%$ Bi.

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