The Influence of Ni on the NMR-properties of ^{209}Bi in Liquid Bi-Ni Alloys

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We present detailed experimental results concerning the temperature and concentration dependence of the ^{209}Bi-Knight shift and the NMR linewidth in liquid Bi-Ni. The measurements are carried out in an external magnetic field of about 39 KG over the concentration range (0–35) at.-% Ni at temperatures from 400 K to 1300 K. According to our experimental results there are no localized magnetic moments in the liquid Bi-Ni system. The experimental results are discussed in the framework of theories on metallic alloys.

1. Introduction

Measurements of the solvent Knight shift K in solid alloys containing transition metals often aim at investigating the occurrence of local moments and the NMR satellite structure related with it [1]. In liquid alloys of nontransition metals with 3d elements, so-called "magnetic impurities", the near-neighbour atomic structure causing NMR satellites is destroyed. But the polarization of the surrounding electron gas, caused by the magnetic moments of the impurities, influences both the Knight shift of the solvent nucleus and the relaxation time of the NMR process. To our knowledge the present paper describes the first investigation of the ^{209}Bi-Knight shift in the liquid Bi-Ni system. This work is carried out in the frame of a systematic study of the electronic properties of liquid simple metal alloys containing transition metals.

2. Experimental Details

The measurements were carried out using a cw-NMR spectrometer operating at 27 MHz. The external magnetic field, which was calibrated with deuterium NMR, has been generated by a superconducting solenoid. The high temperature furnace in the present case was constructed using a Pt-10% Rh wire bifilar heating element. More details concerning this high field and high temperature NMR spectrometer are published elsewhere [2, 3].

In this investigation we used metals (Bi and Ni) with a purity of 99.999% (Ventron Corporation). Alloys of required composition were left for about 60 h at 1150 °C in an Al_2O_3 container sealed in a Quarz tube under vacuum, to get a uniform distribution of the components.

To avoid complications from the radio-frequency skin effect, the samples were prepared as powders. After sieving only particles with a diameter of less than 50 µm were used in the NMR experiment. The metallic particles were mixed with an equal volume of Al_2O_3 powder to provide electrical insulation between them and to prevent the metallic droplets from coalescing above the melting point. The sample temperature was measured using a Pt-PtRh thermocouple to an accuracy of about ±0.6%. Standard corrections for the cw-NMR line shape have been carried out.

3. Experimental Results

The ^{209}Bi-Knight shift K as a function of temperature in liquid Bi-Ni alloys is shown in Figure 1. The 60 at.% Bi–40 at.% Ni alloy shows at room temperature strong magnetic properties like those of ferromagnetic materials. The melting point ($T_m \approx 1340$ K) of this alloy lies relatively high. Liquid Bi-Ni alloys with Ni concentrations higher than 40 at.% will, due to their high melting point, be the subject of a further study, using NMR-instruments under construction which will work reasonably at temperatures higher than 1400 K. It can be seen from Fig. 1 that for many alloys in the supercooled state the function $K_{Bi}(T)$ has the same temperature coefficient as above the melting

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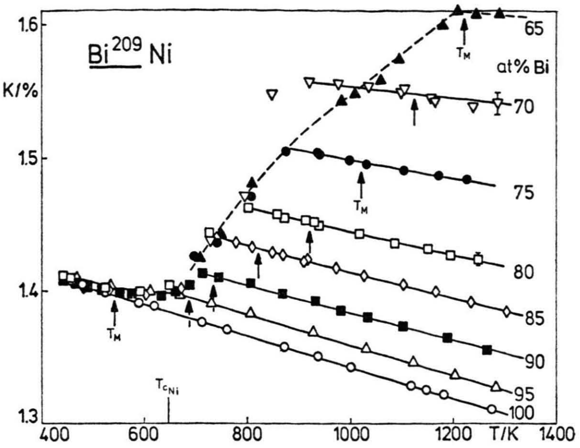

Fig. 1. Temperature dependence of the ^{209}Bi Knight shift K for liquid Bi-Ni alloys. Concentrations are shown in at.-% Bi. T_M indicates the melting point for different alloys. T_C is the Curie temperature for the pure Ni metal.

point. Below a characteristic temperature for every alloy (which seems to be a solidification temperature of a part of the alloy) $K_{Bi}(T)$ decreases rapidly with decreasing temperature, and approaches the Knight shift of liquid pure Bi metal.

Figure 2 shows the concentration dependence of the Bi-NMR linewidth ΔB in liquid Bi-Ni at 1000 K. We plotted the function $\Delta B(c)$ at the temperature $T = 1000$ K because all considered alloys are at this temperature in the liquid state. For higher temperatures the signal-to-noise-ratio was reduced so that no reasonable linewidth evaluation was possible from the corresponding line shape.

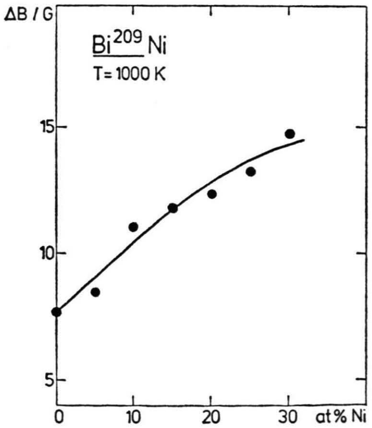

Fig. 2. The NMR linewidth ΔB of ^{209}Bi in liquid Bi-Ni alloys as a function of the Ni concentration c.

4. Discussion

4.1. Pure Metal

It is usually assumed that in nontransition metals the only important contribution to the Knight shift K is the contact term K_s given by

$$K_s = (8\pi/3)\,\chi_p \Omega P_F\,, \tag{1}$$

where χ_p is the conduction electron spin susceptibility, Ω is the atomic volume and $P_F = \langle|\Psi_s(0)|^2\rangle_{E_F}$ is the average probability density at the nucleus of s-like, Fermi surface electrons.

The experimental Knight shift K_{Bi} of ^{209}Bi in liquid Bi metal at the melting point has been published by several authors. There is a very good agreement between the other values and that found in our experiment:

C. P. Flynn and E. F. W. Seymour [4]

$$K_{Bi} = (1.41 \pm 0.015)\%\,,$$

L. E. Drain [5]

$$K_{Bi} = (1.41 \pm 0.01)\%\,,$$

Present work

$$K_{Bi} = (1.398 \pm 0.002)\%\,.$$

It is of particular interest to compare experimental with theoretical values of K_{Bi}. Heighway and Seymour [5], using the zero-order pseudopotential theory, calculated K_{Bi}. They give two different values:

$$K_{Bi}(1) = 1.73\% \quad \text{and} \quad K_{Bi}(2) = 1.57\%\,,$$

corresponding to two different values of the spin susceptibility χ_p which they used in their calculations. For $K_{Bi}(1)$ they used the free electron χ_p value with an electron-electron enhancement as given by Rice [6], and for $K_{Bi}(2)$ they used χ_p values deduced from the measured total susceptibilities [7].

Ford and Styles [8] calculated the contact density ΩP_F by explicitly orthogonalizing the conduction electron pseudowave-functions to the ionic core states. They extracted the χ_p values from the measured susceptibilities by subtracting estimates of the diamagnetic contributions from the ion cores and conduction electrons. They give two values for K_{Bi}:

$$K_{Bi}(\mathrm{I}) = 1.03\% \quad \text{and} \quad K_{Bi}(\mathrm{II}) = 0.73\%\,.$$

$K_{\mathrm{Bi}}(\mathrm{I})$ is calculated using a single orthogonalized-plane-wave (OPW), while $K_{\mathrm{Bi}}(\mathrm{II})$ includes the effects of the first-order correction terms.

More recently, in 1978, Styles and Tranfield [9] also calculated the contact density ΩP_{F} as in [8], but in this case using a nonlocal pseudopotential method within the framework of the nearly-free electron model. The χ_{P} values used by these authors for the calculation of K_{Bi} are given in the work of Dupree and Geldart [10], who calculated χ_{P} from the free-electron value with a suitable correction for exchange enhancement. Styles and Tranfield give for K_{Bi} the value

$$K_{\mathrm{Bi}} = 0.950\,\%\,.$$

This value lies about 32% lower than our experimental one. Styles and Tranfield present in their work the calculation of the Knight shift at the melting point for 18 nontransition metals; the average deviation of the calculated from the experimental values lies within 15% for most of the other metals.

The comparison between the measured K_{Bi} value and the calculated one by the authors mentioned above, shows that the best theoretical value for K_{Bi} is given by Heighway and Seymour [5]. It is $K_{\mathrm{Bi}}(2) = 1.52\%$ which lies about 12% higher than the experimental one, while $K_{\mathrm{Bi}}(1) = 1.73\%$, given in the same work, lies about 24% higher than the experimental value. The calculated values $K_{\mathrm{Bi}}(\mathrm{I})$ and $K_{\mathrm{Bi}}(\mathrm{II})$ given by Ford and Styles (s. above) lie about 26% and 48% lower than the measured value, respectively.

In all the above calculations core polarization, orbital and diamagnetic contributions to the Knight shift have not been considered. These contributions, however, are expected to be significant in liquid pentavalent Bi (with five conduction electrons per atom) whose conduction electron states may tend to have rather p-like character.

Furthermore, for the evaluation of χ_{P} different approaches have been used. Although the values obtained agree within 5% it is possible that the values of χ_{P} used in the calculation for the Knight shift may be responsible for significant errors. It is well known that a direct measurement of χ_{P} for metals is very difficult. There are only two cases where a direct measurement of χ_{P} was possible using electron spin resonance: for the alkali metals Li and Na [10]. On the other hand, accurate a priori calculations of χ_{P} for the different metals do not exist.

From Fig. 1 the temperature coefficient K_{Bi} of the ^{209}Bi-Knight shift in pure liquid Bi metal, can be determined for an extensive temperature range (400–1350) K. Earlier reports give $K_{\mathrm{Bi}}(T)$ for temperatures up to 770 K only [10].

We find

$$\varkappa_{\mathrm{Bi}} = \frac{1}{K_0}\,\frac{\mathrm{d}K}{\mathrm{d}T} = -\,8.7 \cdot 10^{-5}\,\mathrm{K}^{-1}$$

where K_0 is the ^{209}Bi Knight shift at the melting point. This value for $\varkappa_{\mathrm{Bi}}$ agrees very well with earlier experimental values given by Heighway and Seymour [5] and by Ford and Styles [8]. The calculated values for $\varkappa_{\mathrm{Bi}}$ given by these authors are:

$\varkappa_{\mathrm{Bi}} = -\,2.6 \cdot 10^{-5}\,\mathrm{K}^{-1}$ Heighway and Seymour,

$\varkappa_{\mathrm{Bi}} = -\,6.1 \cdot 10^{-5}\,\mathrm{K}^{-1}$ Ford and Styles.

They disagree strongly with the experimental value.

4.2. *Alloys*

We discuss now the observed behaviour of the ^{209}Bi-Knight shift in dependence of the Ni concentration in the liquid Bi-Ni system.

The change of K_{Bi} due to the presence of the Ni atoms is shown in Fig. 3 where we plotted

$$\Delta K_{\mathrm{Bi}}/K_{\mathrm{Bi}} = [K_{\mathrm{Bi}}(\mathrm{alloy}) - K_{\mathrm{Bi}}]/K_{\mathrm{Bi}}$$

versus Ni-concentration at 1200 K. $K_{\mathrm{Bi}}(\mathrm{alloy})$ is the Knight shift of ^{209}Bi in the Bi-Ni alloy and K_{Bi} is the ^{209}Bi-Knight shift in pure liquid Bi.

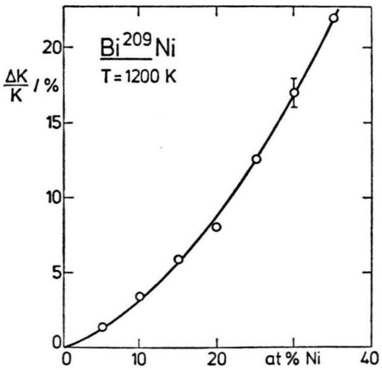

Fig. 3. The relative change of the ^{209}Bi-Knight shift in liquid Bi-Ni as a function of the Ni concentration.

There is no theoretical work concerning calculations of the solvent Knight shift as a function of the solute concentration for concentrated liquid alloys of nontransition with transition metals.

Earlier NMR investigations in liquid alloys containing simple and transition metals are restricted only to small concentrations of the transition elements (usually up to 6 at.%) [11], [12]. In these investigations $\Delta K/K$ has been found to increase linearly with the concentration of the transition metal impurity. There is a more recent report of NMR studies in the liquid Bi-Mn system with Mn concentrations c up to about 12 at.%, Dupree et al. [13]. In the Bi-Mn system $\Delta K_{\mathrm{Bi}}/K_{\mathrm{Bi}}$ shows a linear behaviour at low Mn concentrations, but at 11 at.% Mn the concentration coefficient $\mathrm{d}(\Delta K_{\mathrm{Bi}})/\mathrm{dc}$ decreases significantly. The Mn impurity susceptibility in this system, which has been obtained from the measured susceptibility corrected for background contributions of the Bi matrix, Dupree et al. [13], shows a Curie-Weiss behaviour.

The Mn impurities in Bi metal possess a local magnetic moment and exhibit a Kondo temperature $T_{\mathrm{K}} \approx 50$ K. The NMR studies in liquid Bi-Mn show that the Mn solute atoms effect very strongly the ^{209}Bi-Knight shift. So a concentration of 3 at.% Mn causes a relative change of the ^{209}Bi-Knight shift $\Delta K_{\mathrm{Bi}}/K_{\mathrm{Bi}} = 33\%$, which is really a very significant effect.

Now for the liquid Bi-Ni system our experimental results give for a 3 at.% Ni concentration a $\Delta K_{\mathrm{Bi}}/K_{\mathrm{Bi}} = 0.66\%$; this relative change for the ^{209}Bi-Knight shift in liquid Bi-Ni is considerably smaller than the corresponding one for the liquid Bi-Mn system. The $\Delta K_{\mathrm{Bi}}/K_{\mathrm{Bi}}$ value in liquid Bi-Ni at 1200 K is very close to the value of $\Delta K_{\mathrm{Al}}/K_{\mathrm{Al}}$ at 1233 K found by Flynn et al. [12] in a liquid Al-Ni system of 3 at.% Ni concentration. The Ni impurities in liquid Al do not give rise to localized magnetic moments and this is also the case for the Ni impurities in liquid Bi. There are several indications for the nonexistence of localized magnetic moments in the studied liquid Bi-Ni system. Firstly, the experimental magnetic susceptibility χ as a function of temperature found by Tamaki [14] in liquid pure Bi and Bi-Ni alloys for Ni concentrations up to 27% yields a χ_{corr} which is not proportional to the inverse temperature (T^{-1}). χ_{corr} is the value of the measured susceptibility χ corrected for background contributions of the Bi matrix. Secondly, the χ values for liquid Bi-Ni given by Tamaki [14] are two orders of magnitude smaller than the χ values for liquid Bi-Mn given by Dupree et al. [13] for equal transition metal concentrations. In addition as our results presented in Fig. 4 show there is no proportionality between $\Delta K_{\mathrm{Bi}}/K_{\mathrm{Bi}}$ and T^{-1} in the liquid Bi-Ni system either.

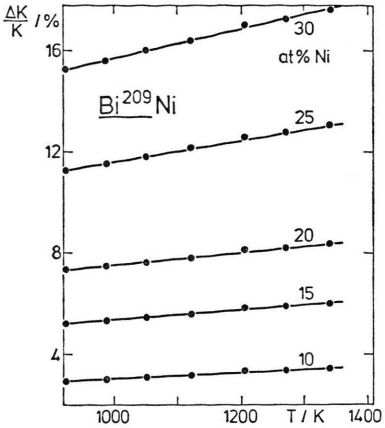

Fig. 4. The relative change of the ^{209}Bi-Knight shift in liquid Bi-Ni as a function of temperature for different Ni concentrations.

According to the above considerations there is no local magnetic moment in liquid Bi-Ni. However, experimental NMR results concerning liquid Bi alloys with *simple metals*, for example liquid Bi-In alloys investigated by Seymour and Styles [15], show that the change of the ^{209}Bi-Knight shift due to simple metal concentration variation is one order of magnitude *smaller* than the ^{209}Bi-Knight shift change due to equal Ni concentration variation in liquid Bi-Ni.

In summary then we find that the Ni solute atoms in liquid Bi-Ni do not give rise to localized magnetic moments in contrast to Mn in liquid Bi-Mn, but cause Knight shift and susceptibility changes which are larger by one order of magnitude compared to those changes due to solute simple metals.

A further interesting point in our experimental results is the nonlinear dependence of the relative change of the ^{209}Bi-Knight shift as a function of the Ni concentration, as it is shown in Figure 3.

In terms of the Anderson model [16], concerning dilute impurities of transition elements in nonmagnetic metals, the total susceptibility may be written

$$\chi = \chi_{\mathrm{h}} + c \frac{\mu_{\mathrm{B}}^2 N_{\mathrm{d}}(E_{\mathrm{F}})}{1 - (U + 4J) N_{\mathrm{d}}(E_{\mathrm{F}})/10} = \chi_{\mathrm{h}} + c\,\eta\,\mu_{\mathrm{B}}^2 N_{\mathrm{d}}(E_{\mathrm{F}}),$$

where χ_{h} is the host-metal susceptibility, c the transition atom impurity concentration, μ_{B} the Bohr magneton, $N_{\mathrm{d}}(E_{\mathrm{F}})$ the density of virtual bound states of the Fermi surface, and U and J are the Coulomb and exchange integrals between two d orbitals on the same atom in the metal environment, ($\eta = 1/[1-(U+4J)N_{\mathrm{d}}(E_{\mathrm{F}})/10]$ is the enhancement factor).

This model predicts for dilute alloys a linear dependence between magnetic susceptibility χ and concentration c of the magnetic impurity. Experimental results in liquid Al-X and Cu-X alloys (X for V, Cr, Mn, Fe, Co and Ni) for X-concentrations up to 6 at.% have confirmed this prediction [12], [17]. But for higher transition metal concentrations the linearity between χ and c does not exist as the experimental results given by Tamaki [14] show. Tamaki finds for the liquid Bi-Ni system that the d-electron contribution to the magnetic susceptibility depends nonlinearly upon the Ni concentration. This result is in very close agreement with our ^{209}Bi-Knight shift measurements shown in Fig. 3 where the change of the Bi-Knight shift is a nonlinear function of the Ni concentration. It means that the Bi-Knight shift change *follows* the magnetic susceptibility change caused by the variation of the 3d magnetic atom concentration. As said above there is need for theoretical treatment referring to the Knight shift dependence upon the transition metal concentration in *nondilute* liquid alloys with a simple metal solvent.

This nonlinear dependence of the ^{209}Bi-Knight shift upon the Ni concentration in liquid Bi-Ni is supposed to be due to three essential mechanisms.

a) An increase of the Ni-solute concentration causes an increase of the density of states at the Fermi energy $N_{\mathrm{Bi-Ni}}(E_{\mathrm{F}})$ because of the very high density of states $N_{\mathrm{Ni}}(E_{\mathrm{F}})$ which is characteristic for Ni metal [18].

b) With an increasing number of core polarized Ni atoms the polarization of the conduction electrons increases, too.

c) There is an isotropic transferred hyperfine interaction $A(r)\,\boldsymbol{I}\cdot\boldsymbol{S}$ between a solute spin $\boldsymbol{S}$ and a Bi nuclear spin $\boldsymbol{I}$ separated by a distance r. The effects of the solute spins superimpose nonlinearly at increased Ni concentrations. Thus the Ni solute atoms in Bi-Ni simultaneously influence both factors (susceptibility and contact density) in the Knight shift and cause its nonlinear behaviour, as it is shown in Figure 3. Further experimental results concerning relaxation time and structure factor in liquid Bi-Ni will aid to detailed quantitative discussions.

4.3. *The NMR Linewidth*

We discuss here the influence of the Ni atoms on the ^{209}Bi-NMR-linewidth in the liquid Bi-Ni system. As Fig. 2 shows, a Ni concentration variation of 30 at.% causes a linewidth change of about 100%, whereas the ^{209}Bi-Knight shift change for equal Ni concentration variation amounts to about 20%. The hyperfine field at a ^{209}Bi nucleus in Bi-Ni with small Ni concentrations depends on the instantaneous position of the Bi nucleus near Ni atoms, and on the Ni atom spin orientation. Fluctuations of this hyperfine field with frequencies higher than the Larmor frequency ω_0 of the nuclear precession in an applied field may contribute to the resonance linewidth. A field of magnitude $|B_z|$ fluctuating randomly in a time τ effects the transverse relaxation time T_2 by

$$\frac{1}{T_2} = \gamma_n{}^2 B_z{}^2 \tau, \tag{3}$$

where γ_n is the nuclear gyromagnetic ratio, Slichter [19]. Such fields arise because the resonating nucleus moves relative to its neighbours and relative to the solute atoms by diffusion with the correlation time τ. Now in dilute alloys the hyperfine fields at the ^{209}Bi nucleus caused by the Ni impurities superimpose linearly (there is a negligibly small impurity-impurity interaction), and the linewidth increases linearly with impurity concentration. But for higher Ni concentration the Ni moments interact directly or through the electron gas by an indirect exchange coupling, which will cause the spins to topple away from their quantized orientations in the applied field. For a sufficiently strong coupling, the correlation time associated with the toppling may become much shorter than to the Larmor period and the correlation time for diffusive motion. Thus, solute atoms in close association no longer contribute to nuclear relaxation, and the NMR linewidth concentration coefficient must become smaller with increasing impurity concentration. This agrees very well with our experimental results shown in Fig. 2, where the linewidth concentration coefficient $\alpha = \mathrm{d}(\Delta B)/\mathrm{d}C$ in the higher concentration range decreases with increasing Ni concentration.

Acknowledgement

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