Nuclear Spin-Lattice Relaxation and Knight Shift in Liquid In-Zn System

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Z. Naturforsch. **36a**, 1155—1157 (1981); received September 30, 1981

The nuclear spin-lattice relaxation time T_1 and the Knight shift K of ^{115}In in the liquid In-Zn system have been measured over the temperature range (450—900) K. The Korringa correction factor $K(\alpha)$ is found to be temperature independent. The electric quadrupolar contribution to the relaxation rate is concluded to be very small (about 6% of the measured relaxation rate).

1. Introduction

Measurements of the spin-lattice relaxation time T_1 and the Knight shift K in liquid metals and alloys contribute to a deeper understanding of the internal motions and the electronic structure of these materials. There are various mechanisms which can contribute to K and T_1.

In most nontransition metals the dominant mechanism which couples the nuclear magnetic moment with the magnetic fields due to the conduction electrons is the contact hyperfine interaction. In this case K is given by

$$K_\mathrm{s} = \frac{8\pi}{3}\chi_\mathrm{s}\Omega\langle|\Psi_\mathrm{s}(0)|^2\rangle_{E_\mathrm{F}}, \qquad (1)$$

where χ_s is the spin susceptibility for the s-electrons, Ω is the atomic volume, and $\langle|\Psi_\mathrm{s}(0)|^2\rangle_{E_\mathrm{F}}$ is the probability density of s-electrons at the nuclear site averaged over the Fermi surface [1].

Other contributions to K such as the orbital K_orb and core polarization K_cp are much weaker than K_s in simple metals. In transition metals K_orb or K_cp can be the main part of K and they can have a dominant temperature dependence in comparison to the other contributions [2].

The spin lattice relaxation rate $R_1 = 1/T_1$ is the sum of two significant parts [3]

$$R_1 = R_{1\mathrm{m}} + R_{1\mathrm{Q}}. \qquad (2)$$

$R_{1\mathrm{m}}$ is the magnetic relaxation induced by the interaction between the nuclear dipole moment and the time-dependent magnetic fields, and $R_{1\mathrm{Q}}$ is the quadrupolar relaxation, induced by the coupling between the nuclear electric quadrupole moment and the time dependent electric field gradients. Korringa [4] derived first the expression for $R_{1\mathrm{m}}$:

$$R_{1\mathrm{m}} = \frac{64}{9}\pi^3 h^3 \gamma_\mathrm{e}^2 \gamma_\mathrm{n}^2 \langle|\Psi_\mathrm{s}(0)|^2\rangle_{E_\mathrm{F}} \cdot N^2(E_\mathrm{F}) K_\mathrm{B} T, \qquad (3)$$

where γ_e is the electronic gyromagnetic ratio, γ_n is the nuclear gyromagnetic ratio, $\langle|\Psi_\mathrm{s}(0)|^2\rangle_{E_\mathrm{F}}$ is as in (1), $N(E_\mathrm{F})$ is the density of states at the Fermi surface for s-electrons, K_B is the Boltzmann constant and T is the temperature. $R_{1\mathrm{m}}$ is related to K_s of (1) by the Korringa relation [4]:

$$R_{1\mathrm{m}} = T K_\mathrm{s}^2 \frac{4\pi K_\mathrm{B}}{h}\frac{\gamma_\mathrm{n}^2}{\gamma_\mathrm{e}^2}. \qquad (4)$$

This equation is derived in the frame of the independent-electron approximation. For the effects of electron correlation and exchange on the Knight shift and the relaxation time accounts a correction factor $K(\alpha)$ introduced in (4) [5]. In this case a modified Korringa relation can be applied:

$$R_{1\mathrm{m}} = T K_\mathrm{s}^2 \frac{4\pi K_\mathrm{B}}{h}\frac{\gamma_\mathrm{n}^2}{\gamma_\mathrm{e}^2} K(\alpha). \qquad (5)$$

We consider now the electric quadrupole contribution $R_{1\mathrm{Q}}$ to the relaxation rate R_1. The main contribution to $R_{1\mathrm{Q}}$ in liquid metals is the thermal modulation of the charge distribution around a nucleus by diffusional and vibrational motion. A direct quadrupolar relaxation caused by the conduction electrons has been estimated to be a mechanism capable of providing less than 1% of the observed $R_{1\mathrm{Q}}$ in some cases [6].

Now an important purpose of this work is to evaluate the contributions of the various mecha-

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nisms to R_1 and K in the liquid In-Zn system. Much recent activity on NMR studies of the liquid Indium alloys has been centered on development and testing of physical models describing the electronic structure and other physical properties [7–9]. In this paper we report the first measurements of the Knight shift K and the spin lattice relaxation time T_1 for the ^{115}In isotope in liquid In-Zn for the temperature range (450–900) K. In addition to the measurements, an evaluation of the various mechanisms responsible for the observed values of K and T_1 is presented.

2. Results

Figure 1 shows the measured Knight shift of ^{115}In in liquid In-Zn as a function of temperature. The choice of the concentration range in the vicinity of 50 at.-% In is because of our earlier NMR studies in the In-Hg liquid system [7]. We found at 50 at.-% Hg an absolute maximum of the ^{115}In-Knight shift there, which is not the case for the In-Zn system. Experimental details and preparation of the NMR samples are described elsewhere [8].

As Fig. 1 shows, for temperatures below the melting point T_m of the In-Zn alloys, $K(^{115}\text{In})$ decreases rapidly with decreasing temperature and tends to values close to those of $K(^{115}\text{In})$ in pure Indium. This can be explained, if one supposes that the In-Zn alloy for temperatures lower than the melting point consists of two systems. One system is solidified Zn or Zn-In (in a solid Zn-In no In-NMR-signals can be easily observed, mainly because of quadrupolar line broadening) and the other is almost pure liquid Indium in which In-NMR is detectable. Detailed measurements concerning Knight shift and relaxation time in the liquid In-Zn system as functions of concentration are subject of a further work.

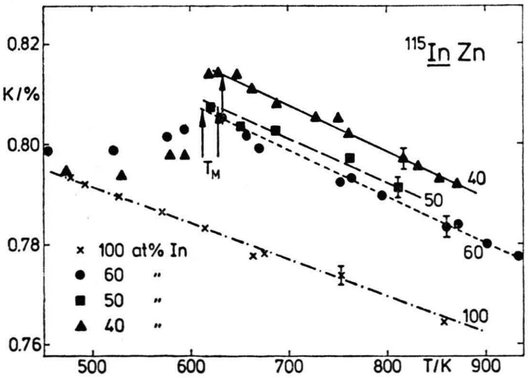

Fig. 1. The experimental Knight shift K for ^{115}In in liquid In-Zn system as a function of temperature for several concentrations. (T_M: melting point).

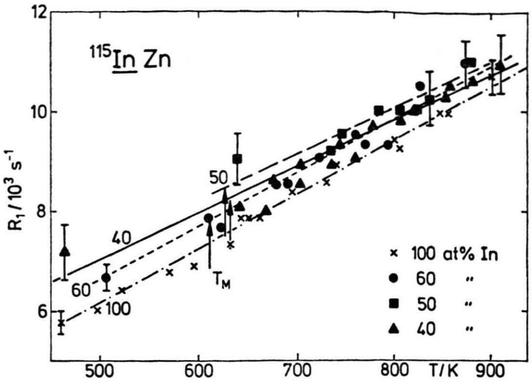

Fig. 2. The experimental relaxation rate $R_1 = 1/T_1$ for ^{115}In in liquid In-Zn system as a function of temperature for the same concentrations as for the Knight shift in Figure 1.

Our experimental results for the spin-lattice relaxation rate $R_1 = 1/T_1$ as a function of temperature for the ^{115}In-NMR in the liquid In-Zn system, are plotted in Figure 2.

On the assumption that (5) describes adequately our system for $K(^{115}\text{In})$ and T_1 we calculated the

Table 1. The calculated values for the correction factor $K(\alpha)$ for different concentrations and temperatures for the liquid In-Zn system. The corresponding values of Knight shift $K(^{115}\text{In})$ and relaxation time T_1 are also given.

T(K)	K(%)	T_1(ms)	$K(\alpha)$
40 at. % In			
650 ± 0.4%	0.8124 ± 0.3%	0.119 ± 5%	1.07 ± 5%
700 ± 0.4%	0.8078 ± 0.3%	0.112 ± 5%	1.07 ± 5%
800 ± 0.4%	0.7985 ± 0.3%	0.102 ± 5%	1.05 ± 5%
900 ± 0.4%	0.7892 ± 0.3%	0.093 ± 5%	1.05 ± 5%
50 at. % In			
650 ± 0.4%	0.8053 ± 0.4%	0.116 ± 5%	1.12 ± 5%
700 ± 0.4%	0.8010 ± 0.4%	0.110 ± 5%	1.11 ± 5%
800 ± 0.4%	0.7924 ± 0.4%	0.099 ± 5%	1.10 ± 5%
850 ± 0.4%	0.7880 ± 0.4%	0.095 ± 5%	1.09 ± 5%
60 at. % In			
650 ± 0.4%	0.8034 ± 0.4%	0.122 ± 5%	1.07 ± 5%
700 ± 0.4%	0.7987 ± 0.4%	0.114 ± 5%	1.08 ± 5%
800 ± 0.4%	0.7894 ± 0.4%	0.102 ± 5%	1.08 ± 5%
900 ± 0.4%	0.7801 ± 0.4%	0.092 ± 5%	1.09 ± 5%

correction factor $K(\alpha)$. The values of $K(\alpha)$ for several temperatures and concentrations are given in Table 1.

3. Discussion

As Table 1 shows $K(\alpha)$ is a constant within experimental error over the entire temperature range and the several concentrations. The Korringa relation predicts that the product $K_s{}^2 T_1 T$ is a constant (cf. (4)) and this is what we also find from our experimental results. We give for this product for the 50 at.-% In—50 at.-% Zn system a representative value:

$$K^2 T_1 T = 4.95 \cdot 10^{-6} (\mathrm{sK}).$$

Now the constancy and the magnitude of $K(\alpha)$ indicate that the magnetic contact hyperfine interaction is the most dominant contribution to $K(^{115}\mathrm{In})$ and T_1 for the liquid In-Zn system. It is expected that there is an electric quadrupolar contribution to T_1. From our experimental results and their interpretation in connection with the Korringa relation appears that the quadrupolar contribution to R_1 is negligibly small. We can make an estimate of the quadrupolar rate R_{1Q} assuming that (4) is valid for the liquid In-Zn system, that is we assume that $K(\alpha) = 1$. With the measured values for $K(^{115}\mathrm{In})$ and T_1 we get R_{1m} from (4). Equation (2) gives then with the experimentally determined $R_1 = 1/T_1$ the value for R_{1Q}. So we find that the quadrupolar relaxation rate R_{1Q} amounts to about 6% of the measured entire relaxation rate R_1.

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft.

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