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

R. Bucklisch and D. Ploumbidis

Institut für Atom- und Festkörperphysik der Freien Universität Berlin

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

$$K_s = \frac{8\pi}{3} \chi_s \Omega \langle |\Psi_s(0)|^2 \rangle_{E_F}, \quad (1)$$

where χ_s is the spin susceptibility for the s-electrons, Ω is the atomic volume, and $\langle |\Psi_s(0)|^2 \rangle_{E_F}$ 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]

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

R_{1m} is the magnetic relaxation induced by the interaction between the nuclear dipole moment and the time-dependent magnetic fields, and R_{1Q} 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_{1m} :

$$R_{1m} = \frac{64}{9} \pi^3 h^3 \gamma_e^2 \gamma_n^2 \langle |\Psi_s(0)|^2 \rangle_{E_F} \cdot N^2(E_F) K_B T, \quad (3)$$

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

$$R_{1m} = T K_s^2 \frac{4\pi K_B}{h} \frac{\gamma_n^2}{\gamma_e^2}. \quad (4)$$

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:

$$R_{1m} = T K_s^2 \frac{4\pi K_B}{h} \frac{\gamma_n^2}{\gamma_e^2} K(\alpha). \quad (5)$$

We consider now the electric quadrupole contribution R_{1Q} to the relaxation rate R_1 . The main contribution to R_{1Q} 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_{1Q} in some cases [6].

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

Reprint requests to Ass. Prof. Dr. D. Ploumbidis, Freie Universität Berlin, Institut für Atom- und Festkörperphysik, Königin-Luise-Str. 28/30, D-1000 Berlin 33.

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 be-

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.

cause 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.

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

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

Now the constancy and the magnitude of $K(\alpha)$ indicate that the magnetic contact hyperfine interaction is the most dominant contribution to

$K(^{115}\text{In})$ 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 $K(^{115}\text{In})$ 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.

- [1] C. H. Townes, C. Herring, and W. D. Knight, *Phys. Rev.* **77**, 852 (1950).
- [2] D. Ploumbidis, *Z. Phys.* **B29**, 61 (1977).
- [3] T. E. Faber, *Sol. St. Commun.* **1**, 41 (1963).
- [4] J. Korringa, *Physica* **16**, No. 7–8, 601 (1950).
- [5] C. P. Slichter, *Principles of Magnetic Resonance*, Springer-Verlag Berlin 1980, p. 149.
- [6] F. A. Rossini and W. D. Knight, *Phys. Rev.* **178**, 641 (1969).
- [7] D. Ploumbidis and T. Sutter, *Phys. Stat. Sol. (b)* **91**, 185 (1979).
- [8] D. Ploumbidis and R. Bucklisch (in preparation for publication).
- [9] M. v. Hartrott, J. Höhne, D. Quitmann, J. Rossbach, E. Wehreter, and F. Willeke, *Phys. Rev. B* **19**, 3449 (1979).