

NMR spin-lattice relaxation time in ^{205}Tl [†]

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The nuclear-magnetic-resonance (NMR) spin-lattice relaxation time T_1 of ^{205}Tl in Tl metal was measured from 1.5 to 4.2 K and at 77 K and is $T_1 T = (2.3 \pm 0.1) \times 10^{-3}$ sec K. The Korringa product is $K^2 T_1 T/S = 0.75$, indicating non- s -electron contributions to the isotropic Knight shift.

INTRODUCTION

Various aspects of the nuclear magnetic resonance properties of Tl in thallium metal over various temperature ranges have been discussed previously by a number of authors.¹⁻³ However, the behavior of the Tl spin-lattice relaxation rate in the solid phase has not previously been reported. In this paper we report measurements of the Tl spin-lattice relaxation rate from 1.5 to 4.2 K, and at 77 K, and discuss the implication of the NMR results for the nature of the conduction-electron states at the Fermi energy. The first reported NMR results are those of Bloembergen and Rowland¹ who measured the Tl Knight shift in powdered specimens at 77 K. They determined both the isotropic and anisotropic ^{205}Tl Knight shifts. Schrat-ter *et al.*² improved these values using a single-crystal specimen. From their measurement of the angular dependence of the Tl Knight shift

$$K(\theta) = K_{1s} + \frac{1}{2} K_{ax} (3 \cos^2 \theta - 1), \quad (1)$$

where θ is the angle between the applied magnetic field and the crystallographic c axis, they found for the isotropic Knight shift $K_{1s} = 1.61\%$ and for the axial Knight shift $K_{ax} = -0.096\%$.

The Knight shift is a measure of the local fields at the site of the nucleus due to the presence of the conduction electrons. There is a wide variety of interaction mechanisms between the conduction electrons and the nuclear spins which can be responsible for the experimentally measured Knight shift. Ignoring spin-orbit coupling and relativistic effects the observed Knight shift typically can be written as a sum of terms

$$K = K_s + K_{cp} + K_{orb} + K_{dia}, \quad (2)$$

where K_s includes isotropic and anisotropic contributions to the Knight shift due to the direct s -contact and spin dipole interactions, while K_{cp} is the contribution due to indirect interactions via p -electron polarization of the s -core states and polarization of conduction s electrons below the Fermi

level. K_{orb} and K_{dia} are the orbital and diamagnetic contributions to the Knight shift.

Thallium is a metal with both s and p electrons in the conduction band. The presence of p electrons is indicated experimentally by the presence of an anisotropic Knight shift. Band-structure and Fermi-surface calculations by Soven⁴ in thallium indicate that the Fermi surface and band structure of thallium bear a close resemblance to those obtained using the "free-electron" model. Departures from the predictions of this model are due to the usual effects of the finite crystal potential plus effects due to spin-orbit coupling. Relativistic effects were shown to be important in thallium due to the large atomic number ($Z = 81$) of the material. In the "free electron" model the number of electrons with s character at the Fermi surface of thallium is expected to be reduced⁵ because the conduction band contains more than one electron. Despite this reduction of the s character at the Fermi level the s -electron contribution to the isotropic Knight shift in thallium still is the main contribution because of the strong s -contact interaction. The p -core polarization contribution is also important, and it is expected to be negative for thallium.⁵ The orbital contribution to the Knight shift is proportional to the Van Vleck temperature-independent paramagnetic susceptibility.⁵ This contribution is particularly important in transition metals because of their narrow conduction band. In the case of thallium this contribution is substantially smaller because of the broad conduction band, and we will ignore it. Another orbital contribution to the Knight shift is due to the Landau-Peierls diamagnetism.⁵ This contribution is negative and it is proposed⁶ to be responsible for the large negative Knight shift observed in Bi. In the "free electron" model, K_{dia} is proportional to the Pauli susceptibility and the square of the ratio m/m^* . Using m/m^* data derived from cyclotron resonance experiments⁷ and Pauli susceptibility⁵ estimated from specific-heat data, we estimate that this contribu-

tion is less than 0.01% for the thallium and can be neglected.

EXPERIMENTAL RESULTS AND DISCUSSION

The ^{205}Tl NMR spin-lattice relaxation rate T_1^{-1} was measured in the temperature range 1.5–77 K, on 325-mesh powdered samples, using a 180° – 90° pulse sequence, and integrating the free induction decay signal. The recovery of the Tl NMR signal following this pulse sequence was followed for two decades, and it was found to be exponential in time. Measurements between 10.0 and 20.0 MHz showed the Tl relaxation rate to be field independent. From 1.5 to 77 K, T_1^{-1} was linear in temperature. We obtained $T_1T = (2.3 \pm 0.1) \times 10^{-3}$ sec K from 1.5 to 4.2 K, while at 77 K, $T_1T = (2.0 \pm 0.3) \times 10^{-3}$ sec K. The rather large experimental uncertainty in the value of T_1T at 77 K is due to the shortness of T_1 which becomes comparable to the pulse widths at this temperature.

The observed relaxation rate can also be decomposed into various terms. Following the same arguments as for the Knight shift we write

$$T_1^{-1} = T_{1s}^{-1} + T_{1cp}^{-1}, \quad (3)$$

where T_{1s}^{-1} is the s -contact interaction contribution and T_{1cp}^{-1} is the core polarization contribution to the relaxation rate. The isotropic Knight shift K_{1s} and the spin-lattice relaxation time T_{1s} due to the s -contact interaction are related through the Korringa product⁸

$$K_{1s}^2 T_1T/S = K(\alpha)^{-1}, \quad (4)$$

where $S = \mu_B^2 / \pi k_B \hbar \gamma_n^2$ and $K(\alpha)$ is an enhancement factor which decreases with increasing exchange interaction between electrons in the conduction band. The value of $K(\alpha)$ is restricted to $K(\alpha) \leq 1.0$. Using the measured values for the isotropic Knight shift $K_{1s} = 1.61\%$, and the spin-lattice relaxation time $T_1T = 2.3 \times 10^{-3}$ sec K, in the case of thallium, we find for the Korringa product, $K_{1s} T_1T/S = 0.75$. This value is less than unity, whereas the expected value from Eq. (4) for noninteracting electrons is $K(\alpha) = 1$. This indicates the existence of a negative contribution to the isotropic Knight shift which would turn out to be even larger if we assume a value for $K(\alpha)$ which is smaller than one.

Theoretical calculations of the Knight shift and spin-lattice relaxation time in the "free electron" model, taking into account the exchange interaction between the electrons, indicate that⁹ $K(\alpha) \approx 0.6$. In analyzing his experimental results on the Sn spin-lattice relaxation time in Sn metal, Dickson¹⁰ suggested that $K(\alpha)$ could be as small as 0.75. Although the experimental value of the Korringa prod-

TABLE I. Experimental value of the spin-lattice relaxation time and calculated values of the s -contact and core-polarization contributions to the isotropic Knight shift.

T_1T (sec K)	K_s (%)	K_{cp} (%)
$(2.3 \pm 0.1) \times 10^{-3}$	2.14 ± 0.02	-0.53 ± 0.02

uct for metallic Pb is 0.93, Tterlikkis *et al.*¹¹ also suggested that their calculated values for the relaxation rate and Knight shift of the Pb resonance are in better agreement with the experimental values when corrected for the electron-electron interaction effects with $K(\alpha) = 0.75$. For the analysis that follows we will assume that $K(\alpha) \approx 0.75$ is also appropriate for the case of thallium.

In order to estimate the various contributions to the isotropic Knight shift and spin-lattice relaxation time in thallium we assume, as a first approximation, that the observed relaxation rate is due to s -contact hyperfine interaction. This was found to be a good approximation in the cases of both metallic Sn,¹⁰ and Pb.¹¹ From Eq. (4), taking $K(\alpha) = 0.75$, we find an s -contact contribution to the Knight shift of $K_s = 2.14\%$. The difference between this value and the measured isotropic Knight shift we attribute to the p -electron core polarization contribution of $K_{cp} = -0.53\%$.

The validity of the previous assumption that the observed spin-lattice relaxation time is mainly due to s -contact hyperfine interaction can be checked by using the relation¹²

$$K_{cp}^2 T_{1cp} T/S = 3, \quad (5)$$

which connects the contributions to the isotropic Knight shift and spin-lattice relaxation time due to p -core polarization effects. Using the estimated value of $K_{cp} = -0.53\%$ we find that the T_{1cp}^{-1} contribution to the relaxation rate is only about 3% of the measured value and hence can be neglected. In Table I we summarize the experimental results obtained on the spin-lattice relaxation times, and the Knight-shift components calculated from this analysis. The uncertainty in the value of the Knight-shift components K_s and K_{cp} was estimated from the experimental uncertainty in the value of T_1T . From the above analysis we conclude that the s -contact interaction is the dominant term in the isotropic Knight shift and the spin-lattice relaxation time. The p -electron core polarization effect has a negligible contribution to the spin-lattice relaxation, while this analysis indicates that its contribution to the isotropic Knight shift is about 25% of the s -contact part of the Knight shift.

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