Calculated Spin-lattice Relaxation of $^{103}$Ru Compared with Low Temperature Quadrupole Orientation Measurements*

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The spin-lattice relaxation time $T_1$ in $^{103}$Ru has been determined on the basis of the Dirac theory and strict relativistic band structure calculations. The low temperature relaxation time $T_{1t}$ of $^{103}$Ru in an axially symmetric quadrupole field and the quadrupole moment $Q$ have been measured by Green and Stone using the technique of low temperature quadrupole orientation. For the usual reference value $T_2$ $T_1$, which corresponds to relaxation in a Zeeman spectrum, they obtain 39(6) sK, which exceeds our value by 134%. This large discrepancy is attributed to the fact that the spin relaxation by direct quadrupole scattering of conduction electrons, the so-called Mitchell contribution, is dominant. According to our calculations it amounts to 81% of the total relaxation rate. This contribution could not be included in the evaluation of the experimental data.

Key words: Low temperature quadrupole orientation, Axially symmetric quadrupole field, Constant of Korringa relaxation, Zeeman spectrum, Obata relation.

I. Introduction

We present a calculation of the nuclear spin-lattice relaxation time $T_1$ of $^{103}$Ru in Ru metal and its comparison with experimental data [1] obtained by the technique of low temperature quadrupole orientation.

The motivation for our studies was to test whether a microscopic Dirac theory based on self-consistent band structure calculations within local density approximation [2] is able to describe nuclear relaxation processes which are dominated by quadrupole scattering.

Concerning the investigation of electric quadrupole relaxation, the orientation measurements of Green and Stone [1] are very useful:

Firstly, they were done by means of an orientation technique, that works without a magnetic resonance. Green and Stone used the low temperature quadrupole orientation technique and detected the time variation of the $\gamma$-ray anisotropy for which an effective relaxation time $T_{1t}$ is defined [3, 4]. In NMR/NQR measurements of materials with considerable quadrupole coupling between nuclei and conduction electrons the static line broadening renders it difficult to saturate the resonance lines. Examples are the 5d metals with HCP crystal structure, discussed in [2]. As the quadrupole scattering correlates to some extent with the static interaction, the low temperature quadrupole orientation technique is valuable for our aim.

Secondly, $^{103}$Ru has a nuclear spin of $I = 3/2$ in the ground state. Therefore in a quadrupole spectrum the spin-lattice relaxation is described by a single exponential, which simplifies the considerations.

In the following we describe and calculate the relaxation times $T_2$ and $T_t$ referring to NQR/NMR measurements in a quadrupole spectrum and a Zeeman spectrum, respectively, in the presence of strong quadrupole scattering in order to compare them with the nuclear orientation data.

The theoretical investigation shows that for the $^{103}$Ru isotope electric quadrupole transitions contribute mostly to the relaxation. In order to distinguish the considered processes from various quasipolar phonon mechanisms we specify quadrupole relaxation throughout this paper as the direct quasielastic scattering of conduction states at the nucleus by virtue of electric quadrupole hyperfine interactions, known as Mitchell relaxation [5].

II. Magnetic and Quadrupole Relaxation in Different Nuclear Spectra

In this section the nuclear spin-lattice relaxations in NQR and NMR in the presence of strong quadrupole scattering are compared.
In the experiments of Green and Stone [1] the $^{103}\text{Ru}$ activity has been produced by irradiation with thermal neutrons. The $^{103}\text{Ru}$ concentration was in a range in which already several orientation studies have been made, showing that thermalizing spin-spin interactions are certainly absent [6]. For the absence of a nuclear spin temperature, the rate equations of the differences $p_m$, between the momentary and the equilibrium populations of the nuclear quadrupole levels $|m\rangle$ provide the proper theoretical starting point. The description is simplified by using the differences $n_m$ between the populations of two adjacent levels. In the NQR case $n_m$ is given by

$$n_m = (p_m - p_{m-1}) + (p_{m-1} - p_{m-2})$$

because of the twofold degeneracy of each level. The transitions between the nuclear levels are induced by the hyperfine interactions

$$H_{hf} = H_{mag} + H_q.$$  

The Dirac hyperfine operator

$$H_{mag} = \frac{e\tau\mu_0}{4\pi r^2} \hbar \gamma_N I(\sigma \times \hat{r})$$  

describes the magnetic interaction of electrons with the nuclear dipole moment. In the nonrelativistic case it corresponds to the Fermi contact, dipole and orbital interaction. Here $\tau$ is the relativistic pseudoscalar matrix, $\gamma_N$ the nuclear gyromagnetic ratio, $I$ and $\sigma$ are the nuclear and the electron spin operator, respectively, $e$ is the electron charge and $\hat{r}$ the unit vector $r/r$ in real space. The operator $H_q$ is the quadrupole interaction:

$$H_q = -\frac{3e^2 Q}{4I(2I-1)r^3} \sum_M (-1)^M T_{2M}(I) T_{2-M}(\hat{r}),$$

$$T_{20}(I) = \sqrt{2/3} (3I_z^2 - I^2),$$

$$T_{2\pm 1}(I) = \mp (I \pm I_z I_z \pm I_z),$$

$$T_{2\pm 2}(I) = I_z^2, \quad T_{2M}(\hat{r}) = \frac{8\pi}{15} Y_{2M}(\hat{r})$$

with the quadrupole moment $Q$, the irreducible tensor components of the electronic field gradient operators $T_{2M}(\hat{r})$ and the irreducible tensor components of the nuclear spin $T_{2M}(I)$. The quantity $e^2$ is equal to $e^2/4\pi\varepsilon_0$ and $Y_{2M}(\hat{r})$ are spherical harmonics.

For a nuclear spin $I = 3/2$ the rate equation for the population difference in the NQR case as given by (1) yields a single exponential decay with a time constant

$$\left(\frac{1}{T_1}\right)_q = \left(\frac{1}{T_1}\right)_{mag} + \left(\frac{1}{T_1}\right)_q.$$

Here and in the following the superscript $Q$ refers to the nuclear quadrupole energy levels and the subscript $q$ to the quadrupole relaxation. No superscript is used in the case of relaxation in a spectrum of Zeeman levels. It is well known that the magnetic transition rate $(1/T_1)_q^{mag}$ for relaxation in NQR is three times the relaxation rate $(1/T_1)_q^{mag}$ in the Zeeman spectrum, which follows easily from the rate equation for (1). For $(1/T_1)_q^{Q}$ we obtain

$$\left(\frac{1}{T_1}\right)_q = 2e^2 Q^2 \left(\frac{3}{4I(2I-1)}\right)^2 12(W_{q1} + W_{q2}),$$

where the factor 12 arises from the $T_{2-1}(I)$ and $T_{2-2}(I)$ nuclear transitions. The quantities $W_{qM}$ are electronic quadrupole transition probabilities

$$W_{qM} = \frac{2\pi}{\hbar} \sum_{k,k'} |\langle k'| T_{2M}(\hat{r})|k\rangle|^2 \cdot k_B T \delta(E_k - E_F) \delta(E_k - E_k)$$

between the Bloch states $|k\rangle$ and $|k'\rangle$ near the Fermi energy $E_F$.

We now turn to the problem of how the quadrupole relaxation $(1/T_1)_q^{Q}$ changes if we pass over to a Zeeman spectrum, where the Korringa relaxation time $T_1$ is defined. The corresponding quadrupole relaxation rate $(1/T_1)_q^{Q}$ is given by [21]

$$\left(\frac{1}{T_1}\right)_q = e^2 Q^2 \frac{9(2I + 3)}{40I^2(2I-1)} (W_{q1} + 4W_{q2}).$$

To compare it with (9) we can use the approximation $W_{q1} = W_{q2}$, which is valid for spherical symmetry. If the symmetry is reduced to HCP this remains usually a good approximation for metals, see e.g. [2]. Under this approximation and for $I = 3/2$, (9) and (11) yield the ratio $(T_1)_q/T_1 = 2$. Hence we obtain the simple formula

$$T_1 = (2R_q + 3(1 - R_q)) T_1^{Q}$$

for the conversion of the relaxation time constant $T_1^{Q}$ measured in NQR to the Korringa relaxation time $T_1$ for nuclei with a spin $I = 3/2$ in the presence of a considerable amount $R_q = (T_1^{-1})_q/T_1^{-1}$ of quadrupole relaxation. The quantity $(1 - R_q)$ represents the amount of magnetic relaxation $(1/T_1)_q^{mag}/T_1^{-1}$. An estimation of $R_q$ will be given by (25). Note that for van-
ishing Mitchell relaxation \( R_q = 0 \) (i.e. pure magnetic relaxation), (12) yields the well known relation 
\[
T_1 = 3 T_1^q.
\]
Here a comment on spin temperature is appropriate. For \( I = \frac{3}{2} \) nuclei in the NQR case the quadrupole relaxation time (9) is not changed if spin-spin interactions establish a temperature in the spin system on a time scale much shorter than \( T_1 \). Applying the expression
\[
\left( \frac{1}{T_1} \right)^q = \frac{1}{2} \sum_{m,M} W_{m,m+M} (E_m - E_{m+M})^2,
\]
for the relaxation rate in spin temperature approximation [7, 8] to Mitchell relaxation in a quadrupole spectrum with the energies \( E_m \) we obtain
\[
\left( \frac{1}{T_1} \right)^q = e^4 Q^2 \left( \frac{27(12 I^2 + 12 I - 17)}{56 I^2(2I-1)^2} W_q + \frac{54(I^2 + I - 2)}{7I^2(2I-1)^2} W_2 \right),
\]
where the \( W_q \) are again given by (10). This is identical to (9) for \( I = \frac{3}{2} \), which is expected because equilibrating spin processes are resonant (i.e. energy conserving) flips within the nuclear spin system. In a quadrupolar two-level system this type of flips can not change the level population. Thus the assumption of thermal equilibrium is not necessary for the application of (9) to nuclei with a spin 3/2. For larger nuclear spins (14) is useless because the nonequidistant level spacing in quadrupole spectra destroys the resonance condition for spin-spin interactions which may change the level populations. Hence the spin-lattice relaxation will not follow a single exponential.

III. Relativistic Formulation and Practical Calculations

In this section the formulation of the nuclear spin-lattice relaxation by relativistic conduction electrons and some computational details are sketched. All expressions refer to the relaxation in a Zeeman spectrum, i.e. the Korringa relaxation. The corresponding relaxation time in the quadrupole spectrum is then given by (12).

In the preceding section we were dealing with the nuclear contributions to the relaxation. Here we describe the electronic scattering parts. The Korringa relaxation rate \( 1/T_1 \) is according to the interactions (3) and (4–7) in (2) the sum of two contributions:
\[
\left( \frac{1}{T_1} \right) = \left( \frac{1}{T_1} \right)_{\text{mag}} + \left( \frac{1}{T_1} \right)_{\text{q}}.
\]
The magnetic relaxation rate \( (1/T_1)_{\text{mag}} \) is essentially given by (10) replacing \( T_{1m} \) (\( \hat{\rho} \)) by \( H_{\text{mag}} \). The Mitchell relaxation rate \( (1/T_1)_{\text{q}} \) is described by (10, 11). These transition probabilities have to be evaluated with theBloch states \( |k\rangle \) of the electrons. The band states \( |k\rangle \) are expanded with respect to symmetrized Dirac four component spinors, containing the relativistic spin-orbit basis functions of the representations of the double point symmetry group \( D_{3h} \), presented in [9]. In the resulting formulae the hyperfine coupling constants, that we defined as
\[
\mu_0 \frac{\hbar}{4\pi} \int_0^{r_{\text{WS}}} \frac{(g_x f_{x^*} + g_{x^*} f_x)}{r^2} dr,
\]
and the quantities
\[
n_{x'x}^r = n_{x'x}^r (E_F) = \sum_k c_{\gamma,\gamma'}^* (k) c_{\gamma',\gamma} (k) \delta (E_k - E_F)
\]
occur. The quantities \( n_{x'x}^r \) are in the diagonal case \( x = x' \) the partial densities of states (DOS) of \( x \) orbitals of the representation \( I \), and in the nondiagonal case the so-called mixed (or off diagonal) DOS containing the expansion coefficients \( c_{\gamma,\gamma'}^r (k) \) of the Bloch states. The symbols \( g_x \) and \( f_x \) denote the radial parts of the major and the minor component in the Dirac spinor at the Fermi energy. The integrals are taken from zero to the radius of the Wigner-Seitz sphere \( r_{\text{WS}} \). We label the formulae for the contributions to the relaxation rates by the orbital angular momenta \( l \). The diagonal relaxation rates are denoted by one superscript \( l \) and the off diagonal rates by two. According to a basis set, which contains s, p, and d states, the magnetic relaxation rate is
\[
\left( \frac{1}{T_1} \right)_{\text{mag}} = \left( \frac{1}{T_1} \right)^s_{\text{mag}} + \left( \frac{1}{T_1} \right)^p_{\text{mag}} + \left( \frac{1}{T_1} \right)^d_{\text{mag}}
\]
and the quadrupole rate is given by
\[
\left( \frac{1}{T_1} \right)_{\text{q}} = \left( \frac{1}{T_1} \right)^p_{\text{q}} + \left( \frac{1}{T_1} \right)^d_{\text{q}} + \left( \frac{1}{T_1} \right)^{pd}_{\text{q}}.
\]
As an example we present here the expression for the magnetic contribution $(1/T_1)_{\text{mag}}^p$:

$$
(1/T_1)_{\text{mag}}^p = \frac{4 \pi k_B T}{h} (h \gamma_n^2) \{ H_{11} \frac{4}{9} (n_{11}^s)^2 
+ H_{22}^2 - \frac{3 \sqrt{2}}{2} (2(n_{22}^s - 2)^2 + 3 n_{22}^s n_{-22}^s - 2) 
+ H_{11}^2 \frac{2}{16} (n_{11}^s n_{-22}^s + 3 n_{11}^s n_{22}^s + \text{Re}(n_{11}^s)^2) 
- H_{11} H_{1-2} \frac{4 \sqrt{2}}{9} \text{Re}(n_{11}^s n_{1-2}^s) 
+ H_{1-2} H_{-2-2} \frac{8 \sqrt{2}}{45} \text{Re}(-2 n_{11}^s n_{-22}^s n_{22}^s - 2) 
+ 3 n_{-22}^s n_{22}^s)
+ H_{11} H_{-2-2} \frac{3 \sqrt{2}}{2} (n_{11}^s n_{22}^s)^2 \}.
$$

(21)

The symbol $\text{Re}$ denotes the real part of the mixed DOS product. The complete formulae are presented in [2, 10]. Please note that for the present application the angle $\beta$ between the external magnetic field and the $c$-axis in [2] must be set to zero, because we want to compare the relaxation in the axially symmetric quadrupole field with the relaxation in a Zeeman spectrum in the case that the electronic scattering rates are equal (see Section II). That is fulfilled, if the external magnetic field coincides with the fixed principal axis of the axially symmetric electric field gradient tensor, i.e. with the crystalline $c$-axis. (Otherwise the electronic transitions contain additional terms $\sim \sin^2 \beta$ which do not occur in the relaxation rate in the quadrupole spectrum.)

Furthermore we define some useful magnetic coupling constants. Our hyperfine coupling constants are not directly comparable with the constants commonly used in the literature because we use here a relativistic theory. The following combinations of the $H_{xx}$ yield the usual coupling constants in the nonrelativistic limit:

$$
H_s = -\frac{2}{3} H_{-1-1},
$$

(22)

$$
H_{1-1} = \frac{H_{xx}}{\kappa + 1}, \quad \kappa = \{l-1-1\}.
$$

(23)

For non $s$ terms we define one uniform coupling constant for a given $l$

$$
H_l = \frac{H_l^1 + (l + 1) H_l^1}{2l + 1}.
$$

(24)

$H_s$ and $H_l$ are the relativistic counterparts of $^{103}\text{Ru}$.

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In this section the numerical results are presented and compared with the experiment.

In the numerical calculations of $T_1 T$ the magnetic moment $|\mu| = 0.200 \mu_\text{B}$ from [18] and the quadrupole moment $Q = 0.59 b$ from [1] have been used. The numerical results are presented in Table 1. The commonly used hyperfine coupling constants $H_s, H_p,$ and $H_d$ are related by (22–24) to the (diagonal) relativistic coupling constants $H_{xx}$. In line (1/$T_1 T)_{\text{mag}}^{(a)}$ the magnetic (quadrupolar) $\times \times$-contributions are listed. Non-diagonal contributions (last column) correspond to terms with more than two different $\times$’s. The last but one line in Table 1 contains the sum of all magnetic (mag) and quadrupole (quad) contributions and the total relaxation rate.

Our product of the Korringa relaxation time with temperature $(T_1 T)_{\text{total}}$, as given in the last line of Table 1, is by more than a factor of two too small in comparison with [1]. The discrepancy between theory and experiment is larger than that in other 3d, 4d, and 5d transition metals with HCP structure [2, 11, 12].
Since the relaxation rates of the stable isotopes $^{99}$Ru and $^{101}$Ru, which we calculated in the same manner as described here [19], deviate only by about 10% from the experimental value measured by NMR [20], the reason must be connected with the peculiarities of $^{103}$Ru and the measurement. In this connection we discuss two peculiarities that may contain the seeds of an explanation of the discrepancy.

Firstly, a striking feature of $^{103}$Ru is, that the decisive relaxation mechanism has Mitchell character. This relaxation by quadrupole scattering of conduction electrons amounts 81% in a Zeeman spectrum, as may be seen in Table 1. In $^{99}$Ru and $^{101}$Ru this mechanism contributes for example by about 1% and 10%, respectively. The portion $R^q_q$ of quadrupole relaxation may be estimated without having to perform band structure calculations. Calculating all contributions to $T_i$ which arise from direct scattering of conduction states with p or d character for spherical symmetry, the nonrelativistic theory yields the following generalised Obata formula:

$$R^q_q \text{estim} = \frac{(T_i^{-1})^q_q}{(T_i^{-1})_{\text{total}}} = \left[0.55 \left(\frac{2I-1}{2I+3}\right)\left(\frac{\mu}{Q}\right)^2 s_i + 1\right]^{-1} \quad (25)$$

with the nuclear magnetic moment $\mu$ in units of nuclear magnetons and $Q$ in barns. As distinguished from Obata [21] an $l$ dependence appears in (25) because of the contribution from orbital relaxation. Assuming relaxation either by p or by d states only, $s_i$ has the values $s_p = 13/3$ or $s_d = 15$, respectively. $(T_i^{-1})_{\text{total}}$ is the sum of magnetic dipolar, orbital and quadrupole relaxation by conduction states with $l$-character. For practical use of $R^q_q \text{estim}$ some knowledge of the electronic microstructure is favorable to choose the right value $s_i$ in (25). Here the assumption of dominant d scattering, i.e. $s_i = s_d = 15$ or a little smaller, is often good for transition metals in the middle of each d period. Expression (25) yields a Mitchell portion of $R^q_q \text{estim} = 0.76 \pm 76\%$ for scattering by d states only, in good agreement with the microscopically computed value. These dominant relaxation processes are not included in the theory of Bacon et al. [4], by which Green and Stone [1] determined the Korringa relaxation time from the measured time constant $T_i$ for the behavior of the radiation intensity in zero direction.

Secondly, the theory of Bacon et al. [4] assumes a magnetic spectrum with $(2I+1)$ nuclear levels in ferromagnetic materials, whereas the $T_i$ measurement in $^{103}$Ru was performed in a weak magnetically disturbed quadrupole spectrum. The NQR relaxation time $T^Q_q$ in the presence of strong quadrupole relaxation is related by (12) to the Korringa $T_i$. According to our calculations it amounts to $T^Q_q T = 7.6\text{ sK}$. The actually measured value [1] $T_i T = 13\text{ sK}$ lies in between the values $T^Q_q T$ and $T_i T$ which we calculated.

In view of the very good agreement of $T_i$ between theory and experiment for the two stable isotopes of Ru [19] we attribute the reason for the remaining difference between theory and experiment in $^{103}$Ru to these quadrupole effects.

V. Conclusions

The spin-lattice relaxation time of $^{103}$Ru has been determined with Dirac theory on the basis of self-consistent relativistic LMTO band structure calculations.
The theoretical results exhibit an overwhelming amount of Mitchell relaxation. The results were compared with data from low temperature quadrupole orientation measurements. The differences between theory and experiment are attributed to quadrupole effects. A generalized Obata ratio has been introduced in order to estimate the portion of Mitchell relaxation.

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