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1995 J. Phys.: Condens. Matter 7 4561

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Nuclear spin–lattice relaxation in ruthenium

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Received 2 March 1995

Abstract. The spin–lattice relaxation rate T_1^{-1} of hexagonal close packed ruthenium has been calculated on the basis of full-relativistic linear muffin tin orbital band structure calculations. For the stable isotopes ^{99}Ru and ^{101}Ru the results are in accord with experiment. The ratio between the theoretical relaxation rates of ^{101}Ru and ^{99}Ru is 1.36. This ratio exhibits, in comparison with the corresponding γ_N^2 ratio of 1.26, an additional quadrupole relaxation at ^{101}Ru , which is in line with the large quadrupole moment of ^{101}Ru . Surprisingly, however, the experimental ratio of 1.19 is lower than 1.26. A large discrepancy opens between theory and experiment for the ^{103}Ru relaxation which has been measured by nuclear orientation. Consideration of the dominant quadrupole relaxation rate in the evaluation of the experimental data improves the agreement.

1. Theory

We present a calculation of the nuclear spin–lattice relaxation times T_1 of different Ru isotopes and their comparison with experimental data. In this section only the basic formulae of the nuclear relaxation by relativistic conduction electrons are introduced.

In the spin-temperature approximation the relaxation rate T_1^{-1} is given as [1]

$$\frac{1}{T_1} = \frac{1}{2} \frac{\sum_{m,m'} W_{m,m'} (E_m - E_{m'})^2}{\sum_m E_m^2} \quad (1)$$

$$W_{m,m'} = \frac{2\pi}{\hbar} \sum_{k,k'} |\langle m'k' | H_{\text{hf}} | mk \rangle|^2 k_{\text{B}} T \delta(E_k - E_{\text{F}}) \delta(E_{k'} - E_{\text{F}}) \quad (2)$$

where E_m are the nuclear Zeeman energies, $W_{m,m'}$ is the total transition probability between the Zeeman levels E_m and $E_{m'}$, and E_{F} is the Fermi energy. It is convenient to split the hyperfine interaction Hamiltonian H_{hf} , describing the interaction between the nuclei and the electrons, into magnetic and quadrupole interactions:

$$H_{\text{hf}} = H_{\text{mag}} + H_{\text{q}} \quad (3)$$

$$H_{\text{mag}} = \frac{e c \tau \mu_0 \gamma_N \mathbf{I} (\boldsymbol{\sigma} \times \mathbf{r} / r)}{4\pi r^2} \quad (4)$$

$$H_{\text{q}} = -\frac{1}{6} \sum_{i,j} \frac{e^2 Q}{4\pi \epsilon_0 I (2I - 1)} \left[\frac{3}{2} (I_i I_j + I_j I_i) - \delta_{ij} I^2 \right] \left(\frac{3x_i x_j - r^2 \delta_{ij}}{r^5} \right). \quad (5)$$

Table 1. Nuclear gyromagnetic ratio $\gamma_N/2\pi$, nuclear quadrupole moment Q , nuclear spin I , ratios $A_l = \{(\mathcal{T}_l^{-1})_q/(\mathcal{T}_l^{-1})_m\}l$ with $l = p, d$ and $A = [(\mathcal{T}_1^{-1})_q/(\mathcal{T}_1^{-1})_m]$, see table 3.

	$\gamma_N/2\pi$ (MHz/T)	Q (barn)	I/\hbar	Ref.	A_p	A_d	A
^{99}Ru	-1.956	0.076	5/2	[6]	0.012	0.0034	0.004
^{101}Ru	-2.192	0.44	5/2	[6]	0.31	0.091	0.11
^{103}Ru	-1.016	0.59	3/2	[9]	10.9	3.1	3.8

Here τ is the pseudoscalar matrix exchanging the major and minor component in the Dirac spinor. The nucleus is determined by the gyromagnetic ratio γ_N , the spin operator I with the components I_i and the quadrupole moment Q , see table 1, while the properties of the electrons are expressed by the spin operator σ , the space vector r with the components x_i and the charge $-e$.

Using a product ansatz for the nuclear and electronic coordinates of the wavefunction, $|mk\rangle = |m\rangle|k\rangle$, the nuclear part of the transition probability (2) can be calculated analytically and the electronic part contains an integration over the angles, resulting in selection rules for the angular momentum, densities of states at the Fermi energy and radial integrals which are the so-called hyperfine coupling constants

$$H_\kappa = 2\mu_B \frac{\mu_0}{4\pi} \frac{2m_0c}{\hbar} \int_0^R dr g_\kappa f_\kappa. \quad (6)$$

The integration runs up to the Wigner-Seitz radius R ; g_κ and f_κ are the radial parts of the major and minor components in the Dirac spinor at the Fermi energy, respectively. The band calculations were performed on the basis of the full-relativistic linear muffin tin orbital method (RLMTO) from Skriver [2].

Explicit formulae and a more extensive description of the theory, as well as its application to other hexagonal close packed (HCP) transition metals are reported in [3,4].

2. Results

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

Table 2. Densities of states n_κ in states per atom Ryd, hyperfine coupling constants H_κ in 10^2 T in the relativistic case, and H_l in 10^2 T in the non-relativistic case for Ru.

κ	l	n_κ	n_l	n_l [8]	H_κ	H_l	H_l
-1	0	0.1075	0.1075	0.142	-18.219	12.146	11.597
1	1	0.2457	0.7385	0.784	5.866	2.772	2.672
-2	1	0.4928	0.7385	0.784	-2.691	2.772	2.672
2	2	3.7890	10.3234	10.506	2.689	0.863	0.8446
-3	2	6.5344	10.3234	10.506	-1.683	0.863	0.8446

The results for the densities of states and for the hyperfine coupling constants H_κ are given in table 2. For comparison, the corresponding non-relativistic hyperfine coupling constants H_l in the notation of Asada and Terakura [5] are also presented.

Table 3. Spin-lattice relaxation rate $(T_1 T)^{-1}$ in $(\text{sK})^{-1}$.

		^{99}Ru	^{101}Ru	^{103}Ru
Diagonal contributions	Magnetic	0.0522	0.0655	0.0141
	Quadrupole	0.0002	0.0065	0.0485
Non-diagonal contributions	Magnetic	-0.0041	-0.0051	-0.0025
	Quadrupole	0.0000	0.0001	0.0000
Core polarization contributions		0.0063 [8]	0.0079 [8]	—
Total		0.0546	0.0749	0.0601
Total, $(H\parallel c)$		0.05399 [8]	0.07403 [8]	—
Total, $(H\perp c)$		0.05930 [8]	0.08116 [8]	—
Total, exp.		0.064 [7]	0.077 [7]	0.035 [9]

Because the HCP double-point symmetry group has only three irreducible extra representations, different angular momenta appear in the same representation and cause non-diagonal contributions in the relaxation rate. The diagonal and non-diagonal contributions to the relaxation rate are listed in table 3.

Götz and Winter [8] have calculated the relaxation rates for two orientations of the external magnetic field with respect to the crystal axis c . Our results are averaged over all angles β between the external magnetic field and the crystal c axis, i.e. $\sin^2 \beta = 2/3$ for ^{99}Ru and ^{101}Ru . For ^{103}Ru $\beta = 0$ was used, in line with the experimental conditions. If we add the core polarization contributions from Götz and Winter [8] our relaxation rates are between the results of Götz and Winter for the two orientations. Our densities of states are somewhat smaller than those of Götz and Winter, but our hyperfine fields are slightly larger.

Burgstaller [7] obtained a relaxation time T_1 of 3.7 s in ^{99}Ru and 3.1 s in ^{101}Ru at a temperature of 4.2 K. These results agree rather well with our theoretical values.

The ratio of our theoretical relaxation rates between ^{101}Ru and ^{99}Ru is 1.36; the data of [8] yield 1.37. For purely magnetic relaxation the ratio is 1.26, according to the γ_N in table 1. The ratio of 1.36 is due to an additional quadrupole contribution, which in ^{101}Ru is about $0.006 \text{ s}^{-1} \text{ K}^{-1}$ both in [8] and in our calculation, i.e. a fraction of 10%, whereas it is negligible in ^{99}Ru , due to a smaller Q value. In contrast, the experimental $1/T_1$ ratio of 1.19 seems to indicate an additional relaxation mechanism in ^{99}Ru .

The relaxation time T_1' in ^{103}Ru has been measured by Green and Stone with a low-temperature electric quadrupole orientation technique [9]. They found $T_1' = 7100(1000) \text{ s}$ at $T = 1.85(14) \text{ mK}$. For the constant of Korringa relaxation they present a value of $T_1 T = 3T_1' T = 39(6) \text{ sK}$ which is too large by far in comparison with our theoretical result. The factor three includes only the magnetic scattering. The rate $1/T_1' T$, however, which was measured in a pure quadrupole spectrum, is caused by a magnetic relaxation rate $R^{\mathcal{Q},m}$ as well as by quadrupole scattering $R^{\mathcal{Q},q}$

$$\frac{1}{T_1' T} = R^{\mathcal{Q},m} + R^{\mathcal{Q},q}. \quad (7)$$

Here the first superscript denotes the nuclear spectrum and the second superscript denotes the relaxation mechanism. The total rate $1/T_1 T$ in table 3 represents relaxation in a pure Zeeman spectrum and is caused again by magnetic and quadrupole scattering:

$$\left(\frac{1}{T_1 T} \right)^{\text{total}} = R^{\mathcal{Z},m} + R^{\mathcal{Z},q}. \quad (8)$$

The ratios between the rates in the pure quadrupole spectrum and in the pure Zeeman spectrum are given by

$$R^{Q,m}/R^{Z,m} = 3 \quad (9)$$

$$R^{Q,q}/R^{Z,q} = 2 \quad (10)$$

for magnetic and quadrupolar scattering, respectively. The latter ratio is valid for nuclear spin $I = 3/2$ and, if the electronic parts of the transition probability for the transitions $m' - m = \pm 1$ and $m' - m = \pm 2$ are equal, $W_1 = W_2$ which is exact in the spherical case. With the help of (7)–(10) we obtain for the relaxation rate

$$\left(\frac{1}{T_1 T} \right) \approx \frac{1}{T T_1'} (3R^m + 2R^q)^{-1}. \quad (11)$$

Here $R^{m(q)} = (T_1^{-1})^{m(q)}/T_1'^{-1}$ is the amount of magnetic (quadrupolar) relaxation in a Zeeman spectrum. According to our calculations, $R^m = 0.19$ and $R^q = 0.81$. Entering these values into (11) we translate the experimental value $T_1' T$ into the experimental Korringa relaxation value $T_1 T$. Our theoretical relaxation rate for ^{101}Ru is larger than the experimental value $(T_1 T)_{\text{exp}}^{-1} = 0.035 \text{ s}^{-1} \text{ K}^{-1}$ which has been corrected by formula (11), but the agreement is better than the original value in [9].

The final three columns in table 1 contain the ratios of the quadrupole relaxation rate to the magnetic relaxation rate. A_p and A_d are estimated by (19) in [4], which is related to the Obata ratio [10], but which includes the orbital relaxation by p and d states, respectively; A is the result of numerical calculation. In all cases the value of A is nearer to A_d , indicating much stronger relaxation by d states than by p states.

Acknowledgment

We are grateful to A Burgstaller for providing us with experimental data prior to publication.

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