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The nuclear magnetic resonance of ^{99}Ru and ^{101}Ru in hexagonal close-packed ruthenium metal

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Abstract. The nuclear magnetic resonance of ^{99}Ru and ^{101}Ru has been observed in hexagonal close-packed ruthenium metal. As both isotopes possess a nuclear quadrupole moment the field spectra show the characteristics for quadrupolar disturbed nuclear magnetic resonance. A computer simulation of the experimental spectra yields an electric field gradient of $1.09 \pm 0.06 \times 10^{17}$ V cm^{-2} in good agreement with recent band structure calculations. The isotropic and axial Knight shifts, K_{iso} and K_{ax}, deduced from these spectra are $0.49 \pm 0.02\%$ and $0.045 \pm 0.002\%$, respectively. The rather high positive isotropic Knight shift is mainly due to the Van Vleck contribution, which is presumably also responsible for the rather strong anisotropy. The measurement of the spin–lattice relaxation of the isotopes ^{99}Ru and ^{101}Ru, carried out at 4.2 K, yields spin–lattice relaxation times (T_1) of 3.7 ± 0.2 s and 3.1 ± 0.2 s, respectively.

1. Introduction

During the last decades nuclear magnetic resonance (NMR) of metals has received experimental and theoretical attention since NMR parameters such as the Knight shift and the spin–lattice relaxation times are closely related to the electronic structure of the metals. However, there are still several metals for which experimental NMR data are not yet available, for example Ru or Os. The reasons why the NMR spectra of these metals are difficult to detect are the small gyromagnetic ratio, and the low natural abundance of the NMR active isotopes. A further reason is the non-vanishing quadrupole moment for nuclei with spin $I > \frac{1}{2}$. For a non-cubic metal the quadrupole interaction may lead to an appreciable broadening of the NMR powder spectra. This is caused by the fact that the degeneracy of the $2I$ NMR transition frequencies is removed and that these depend on the relative orientation of the magnetic field with respect to the crystal axes. For a strong quadrupolar interaction this leads to very weak NMR signals for powder samples, making it often impossible to detect the signal.

As some of the transition metals, especially the elements of the Pt group, are quite commonly used as catalysts, we studied pure HCP Ru as a first step towards a characterization of bimetallic CuRu catalysts by ^{99}Ru and ^{101}Ru NMR. In course of this work (preliminary results can be found in [1]) it was possible to observe the ^{99}Ru and ^{101}Ru NMR of the pure metal for the very first time. A simulation of the recorded spectra yielded the electric field gradient and the Knight shift parameters with great accuracy. In a saturation recovery experiment the spin–lattice relaxation times for both isotopes could also be measured. The NMR data obtained experimentally allow for a comparison with theoretical NMR data, which have only recently been calculated for the longitudinal relaxation rate by Götz and Winter [2] and Markendorf *et al* [3] and for the Knight shift parameters by Götz and Winter [2]. A short description of the experiment is given below; the results are discussed in section 3.

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2. Experimental details

The NMR experiments were performed on metallic Ru powder with a purity of 99.997%. The sample was prepared by embedding the metal powder in paraffin for insulation; no thermal treatment was performed. Particles larger than 60 μm were removed from the sample.

The NMR measurements were carried out with a modified Bruker NMR spectrometer CXP at 4.2 K. The magnetic field was supplied by a superconducting solenoid. The NMR field spectra of ^{99}Ru and ^{101}Ru were recorded using the spin echo technique with the radio frequency fixed at 12.645 MHz and 14.174 MHz, respectively, and the magnetic field was varied between 5.55 T and 6.9 T within 10 h. Details of the home built sweeper unit are given elsewhere [4].

The relaxation measurements were performed by applying the saturation recovery technique followed by a spin echo sequence. Because of the very broad NMR spectra only the central line of both isotopes could be saturated.

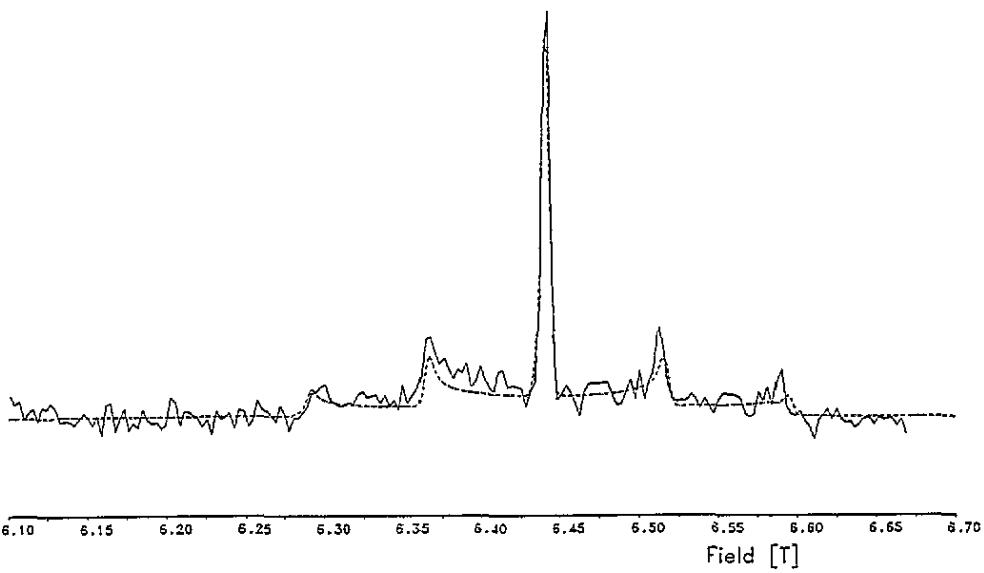

Figure 1. The spin echo profile of ^{99}Ru: NMR frequency $\nu = 12.645$ MHz; $T = 4.2$ K; ——, experiment; – – –, simulation.

Table 1. Nuclear properties of ^{99}Ru and ^{101}Ru.

	^{99}Ru	^{101}Ru
Natural abundance (%)	12.7	17.1
Nuclear spin I	$\frac{5}{2}$	$\frac{5}{2}$
γ (MHz T^{-1}) [8]	1.954	2.193
Q (10^{-24} cm^2) [9]	0.076 ± 0.007	0.44 ± 0.04

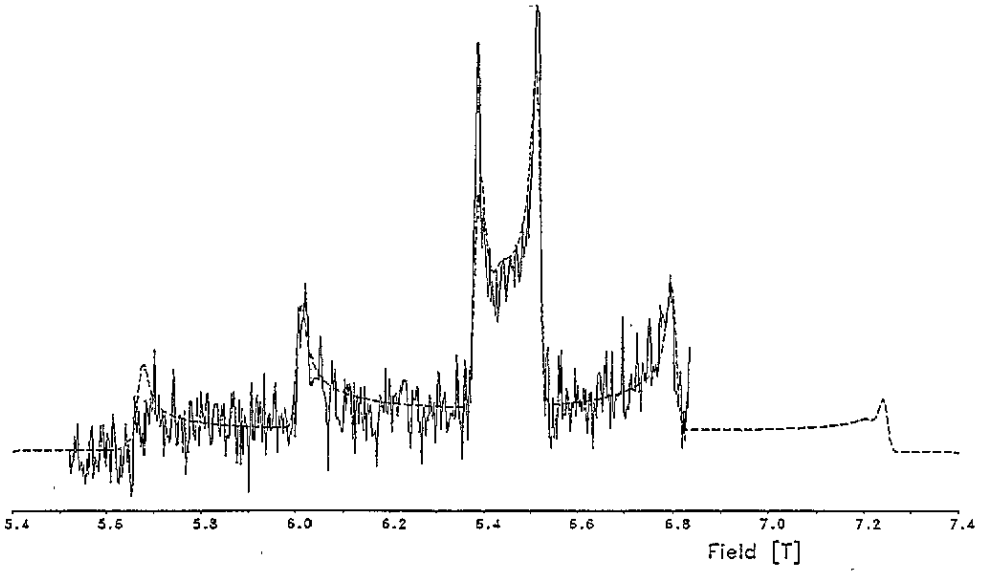

Figure 2. The spin echo profile of ^{101}Ru: NMR frequency $\nu = 14.174$ MHz; $T = 4.2$ K; ——, experiment; – – –, simulation.

3. Results and discussion

3.1. NMR spectra

The experimental NMR spectra of ^{99}Ru and ^{101}Ru are shown in figure 1 and figure 2, respectively. Both of them are typical for a quadrupole disturbed NMR spectrum of a nucleus with spin $I = \frac{5}{2}$. As can be seen from table 1, ^{101}Ru possesses the higher quadrupole moment, therefore its central line at around 6.45 T is split. Due to the limited field strength (7 T) of our magnet, one of the satellite singularities on the high-field side of the ^{101}Ru spectrum could not be detected. This satellite, according to a computer simulation, should show up at around 7.23 T. The simulation was performed in order to allow for a reliable determination of the Knight shift and quadrupole interaction parameters. The NMR resonance field for a given radio frequency is determined taking into account the Knight shift and the quadrupole part of the hyperfine Hamiltonian using first- and third-order perturbation theory, respectively [5]. To account for the various intrinsic and instrumental broadening mechanisms the resulting powder spectra are slightly broadened by a Gaussian line. Further details of the simulation are outlined elsewhere [5, 6].

The various Knight shift and quadrupole interaction parameters as obtained by the simulation are summarized in table 2. The asymmetry parameter η vanishes because of the axial symmetry of HCP Ru. The components of the Knight shift tensor K_x and K_y are identical (with the third (z) principal axis of the tensor pointing along the crystallographic c axis). Table 2 also shows the values for the isotropic Knight shift K_{iso} and the axial shift parameter K_{ax} respectively, which are defined as follows:

$$K_{iso} = \tfrac{1}{3}(K_x + K_y + K_z) \tag{1}$$

$$K_{ax} = \tfrac{1}{6}(2K_z - K_x - K_y). \tag{2}$$

Table 2. Experimental results for the quadrupole interaction and the Knightshift parameters.

	^{99}Ru	^{101}Ru	Average
η	0.0	0.0	
ν_Q (MHz)	0.30	1.74	
EFG (10^{17} V cm^{-2})	1.088	1.09	1.09
$K_x = K_y$ (%)	0.44	0.45	0.45
K_z (%)	0.57	0.59	0.58
K_{iso} (%)	0.483	0.497	0.49
K_{ax} (%)	0.043	0.047	0.045

Table 3. Results for the EFG of Ru.

	EFG (10^{17} V cm^{-2})
LAPW [11]	1.229 ± 0.14
TDPAC [10]	1.02 ± 0.03
PAC [11]	1.0 ± 0.08
NMR (this work)	1.09 ± 0.06

The simulation yields $K_{iso} = 0.49\%$ for both Ru isotopes, a value that—though being strikingly high—compares with the values of the neighbouring elements of the periodic table (HPC Ti, 0.21% at 4.2 K [6]; FCC Rh, 0.43% at 4.2 K [7]). The value of K_{iso} is in good agreement with the theoretical value of 0.526% obtained most recently by Götz and Winter [2] from band structure calculations based on local spin density functional theory. Moreover, this calculation shows that the Van Vleck contribution ($K_{iso}^{VV} = 0.534\%$) to the Knight shift determines the magnitude and the sign of K_{iso}. The dominance of the Van Vleck contributions to the Knight shift is typical for elements at the beginning and the middle of a transition metal row. Also the Van Vleck term is the main cause for the anisotropy of the Knight shift K_{ax}. The experimental value of K_{ax} (+0.045%) found for HCP Ru is again comparable to that of HCP Ti (+0.01% at 4.2 K) and HCP Tc (+0.11% at 300 K). However, the value for K_{ax} (−0.013%) obtained by the scalar relativistic calculations of Götz and Winter differs from the experimental value in sign and magnitude. It should be pointed out that the magnitude but not the sign of K_{iso} and K_{ax} deduced from our spectra depends on the chosen gyromagnetic ratio γ.

As concerns the quadrupolar interaction parameters deduced from the ^{99}Ru and ^{101}Ru spectra, it must be stated that only the quadrupole frequency

$$\nu_Q = 3e^2qQ/2I(2I-1)h$$

and neither the nuclear quadrupole moment eQ nor the electric field gradient (EFG) eq can be obtained separately from the quadrupole disturbed NMR spectra. Furthermore our experimental conditions do not allow us to determine the sign of eq. If it is assumed that the EFG is identical for the two Ru isotopes, ^{99}Ru and ^{101}Ru, a value of 5.8 for the ratio of the quadrupole moments eQ of ^{101}Ru and ^{99}Ru can be determined from the quadrupole frequencies ν_Q. This value is in good agreement with the quadrupole moments as tabulated by Carter *et al* [9] leading also to a ratio of 5.8. By using these quadrupole moments and the experimental quadrupole frequencies ν_Q the EFG is found to be $1.09 \pm 0.06 \times 10^{17}$ V cm^{-2}. This result for the EFG is in reasonable accordance (see table 3) with data from perturbed angular correlation (PAC) studies of Kotthaus and Vianden [10, 11] and it confirms the results of recent *ab initio* band structure calculations using the full potential LAPW method of Blaha and Schwarz [12].

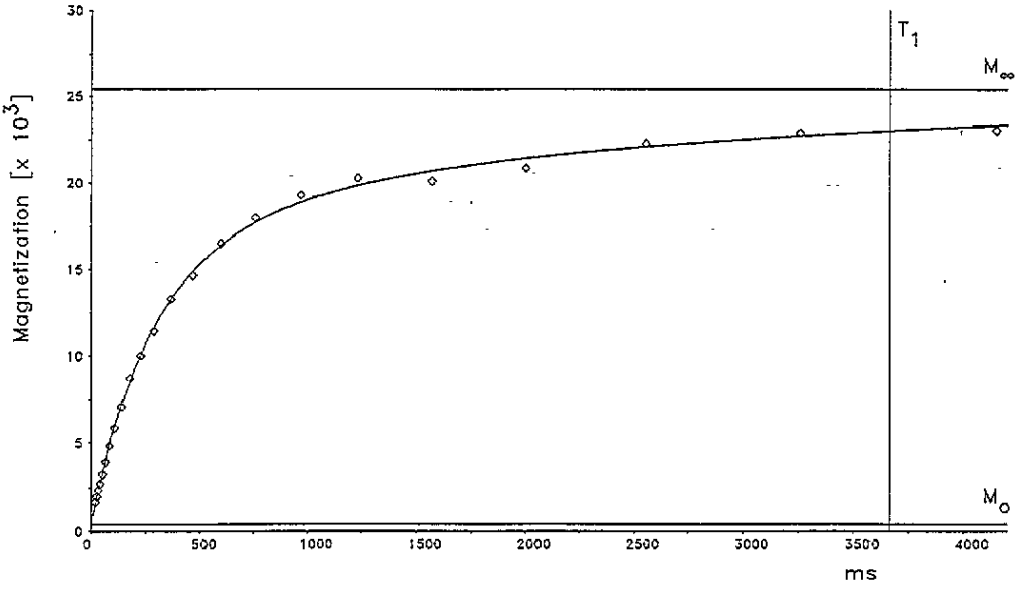

Figure 3. A T_1 experiment on ^{99}Ru: NMR frequency $\nu = 13.0111$ MHz; $T = 4.2$ K; ◇, experiment; ——, fit function $M(t)$.

3.2. Spin–lattice relaxation

Figure 3 shows the result of the saturation recovery experiment on ^{99}Ru. The solid line represents the fit function $M(t)$, which is given by

$$M(t) = M_0 + (M_\infty - M_0)(1 - ae^{-t/T_1} + be^{-6t/T_1} + ce^{-15t/T_1}) \tag{3}$$

where $M(t)$ is the magnetization at time t, M_0 is a residual magnetization, which is zero for complete saturation, and M_∞ is the equilibrium magnetization. The preexponential factors a, b and c are taken from a paper by Andrew and Tunstall [13].

The spin–lattice relaxation measurements yielded T_1 times of 3.7 s and 3.1 s for ^{99}Ru and ^{101}Ru at 4.2 K, respectively. A value of 1.2 is found for the ratio of these T_1 times. This is in reasonable accordance with the ratio $(\gamma^2(^{101}\text{Ru})/\gamma^2(^{99}\text{Ru}) = 1.26)$ that would be expected if the magnetic dipole interaction were exclusively responsible for the spin–lattice relaxation. Calculations of the T_1 relaxation rates have been performed recently for ^{99}Ru and ^{101}Ru by Götz and Winter [2] and by Markendorf and co-workers [3] in a scalar and a fully relativistic way, respectively. The results of these calculations (see table 4) indeed support the expectation that the magnetic dipole interaction dominates the spin–lattice relaxation. For ^{99}Ru and ^{101}Ru Markendorf *et al* [3] find the quadrupolar interaction to cause only 2 and 10%, respectively, of the total relaxation rate $(1/T_1)$.

4. Summary

The NMR of ^{99}Ru and ^{101}Ru could be detected for the first time in a paramagnetic metal. By simulation of the powder spectra recorded as spin echo profiles by varying the external field, accurate data for the Knight shift tensor elements and the EFG could be determined. All

Table 4. Experimental and calculated spin lattice relaxation times T_1 of ^{99}Ru and ^{101}Ru for $T = 4.2$ K.

	^{99}Ru	^{101}Ru
Gyromagnetic ratio		
γ (MHz T^{-1})	1.954	2.193
$\gamma^2(^{101}Ru)/\gamma^2(^{99}Ru)$	1.26	
T_1 (s)	3.7 ± 0.2	3.1 ± 0.2
$T_1(^{99}Ru)/T_1(^{101}Ru)$	1.2	
Theoretical results for T_1		
Fully relativistic [3]	4.4	3.2
Scalar relativistic [2]	4.1	3.0

results are in line with comparable experimental data and are—apart from the axial Knight shift component—in rather good quantitative agreement with theoretical data stemming from recent band structure calculations. These calculations could confirm the expectation that the positive Knight shift is primarily caused by its Van Vleck contribution. The ratio of the measured spin–lattice relaxation times indicates that it is dominated by the magnetic dipole interaction. This is again confirmed by the theoretical data, which represent the experimental times quite well.

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References

[1] Burgstaller A, Ebert H and Voitländer J 1993 *Hyperfine Interact.* **80** 1015
[2] Götz W and Winter H 1993 *J. Phys.: Condens. Matter* **5** 1707
[3] Markendorf R, Schober C and John W to be published
[4] Burgstaller A, Socher W, Horbach H, Gräf P and Voitländer J to be published
[5] Ebert H, Abart J and Voitländer J 1983 *J. Chem. Phys.* **79** 4719
[6] Ebert H, Abart J and Voitländer J 1986 *J. Phys. F: Met. Phys.* **16** 1287
[7] Carter G C, Bennett L H and Kahan D J 1977 *Prog. Mater. Sci.* **20** 153
[8] Raghavan P 1989 *At. Data Nucl. Data Tables* **42** 189
[9] Carter G C, Bennett L H and Kahan D J 1977 *Prog. Mater. Sci.* **20** 311
[10] Kotthaus J and Vianden R 1983 *Hyperfine Interact.* **14** 99
[11] Vianden R 1983 *Hyperfine Interact.* **15/16** 189
[12] Blaha P and Schwarz K 1988 *Phys. Rev.* B **27** 2792
[13] Andrew E R and Tunstall D P 1961 *Proc. Phys. Soc.* **78** 1