Electric Quadrupolar Contribution to the Nuclear Spin-Lattice Relaxation of Ir in Fe

G. Seewald, E. Zech, and H. J. Körner

Physik-Department, Technische Universität München, D-85748 Garching, Germany

D. Borgmann

Institut für Physikalische und Theoretische Chemie, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany

M. Dietrich

Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany

ISOLDE Collaboration

CERN, CH-1211 Geneva 23, Switzerland

We report on the first quantitative determination of the electric quadrupolar contribution to the nuclear spin-lattice relaxation in a transition metal. For ^{186}Ir and ^{189}Ir in Fe we have determined the magnetic and the electric quadrupolar part of the relaxation for magnetic fields between 0.01 and 2 T. The quadrupolar part gives information on the role of the orbital motion of the electrons for the relaxation process. Our results prove that the unexpected high relaxation rates in Fe and their magnetic field dependence are due to a nonorbital relaxation mechanism.

The nuclear spin-lattice relaxation in metals arises predominantly from the magnetic hyperfine interaction between the nuclear spins and the conduction electrons. It gives information on the density of states at the Fermi energy and the magnitude of low frequency spin fluctuations [1–3].

The interpretation of the relaxation is complicated in transition metals by the fact that several relaxation mechanisms can contribute, but only the total relaxation rate R is usually measured: According to the type of the responsible hyperfine interaction, R can be subdivided into an orbital (R_o), a Fermi-contact (R_c), a spin-dipolar (R_{sd}), a core-polarization (R_{cp}), and a quadrupolar (R_q) contribution [3,4]. The first four contributions represent together the magnetic relaxation rate R_m. R_q is due to the electric hyperfine interaction and arises from electric field gradient fluctuations at the nuclear site.

The various contributions involve quite different electronic excitations: R_c, for example, is connected to spin flips of s electrons; R_o and R_q are connected to orbital momentum changes of p or d electrons. A separate determination would, therefore, give valuable information on the relaxation process. Such information is especially desirable since experiment and theory are in serious disagreement for several transition metal systems [5,6].

In this situation, one can make use of two special features of R_q: R_q can be determined separately and it is so closely related to R_o that R_o can be estimated from R_q [4,7]. This offers the unique possibility to decompose *experimentally* the relaxation into an orbital and a nonorbital part.

This possibility is used here for the first time. It is used to study the origin of two still unsolved problems in the nuclear spin-lattice relaxation in Fe: (i) The relaxation rates are usually larger than predicted by *ab initio* calculations. This effect is especially prominent and well documented for the $5d$ impurities in Fe [6]. (ii) For magnetic fields below 1 T there is a so far unexplained magnetic field dependence due to which the relaxation in zero field is typically 3 to 10 times faster than at high fields [8–10].

This work is also the first experimental determination of R_q in a transition metal, although the presence of this contribution to the relaxation in transition metals is meanwhile well established in the theoretical work [4,7,11–13]. In Ref. [14] the relaxation of ^{97}Mo in Mo was interpreted by the presence of a quadrupolar contribution. But the quadrupole moment of ^{97}Mo [15], which was not known at that time, does not support this interpretation. A quadrupolar contribution to the relaxation was also reported for ^{103}Ru in Ru [11,16]. But no quantitative conclusions are possible since the relaxation data on ^{103}Ru were interpreted in terms of the "high temperature limit" which is not justified for that experiment.

R_m and R_q can be separated by using the scaling of R_m and R_q with the square of the magnetic and the quadrupole moment, respectively [4]:

$$R = (R_m/g^2)g^2 + (R_q/N_q)N_q, \qquad (1)$$

$$g = \frac{\mu}{I}, \qquad N_q = \frac{Q^2(2I+3)}{I^2(2I-1)}. \qquad (2)$$

I, μ, g, and Q are the spin, the magnetic moment, the g factor, and the quadrupole moment of the respective isotopes. We assume that μ is given in nuclear magnetons and Q in barns. g and N_q are then dimensionless quantities. R_m/g^2 and R_q/N_q are isotope independent measures

of the magnetic and the quadrupolar part of the relaxation. They can be determined from the relaxation rates of two isotopes of the same element with different nuclear moments using Eq. (1). However, only for a few isotopes with large quadrupole moment and small magnetic moment is there a measurable quadrupolar contribution at all. For most isotopes, R_q can be neglected with respect to R_m [7].

We have chosen radioactive ^{189}Ir ($I^\pi = 3/2^+$) and ^{186}Ir ($I^\pi = 5^+$) as the most suitable isotope pair for our problem. One of the largest (Q/μ) ratios among all available 5d isotopes leads to a particularly large electric quadrupolar contribution to the relaxation of ^{189}Ir. On the other hand, the very convenient decay properties of ^{186}Ir allow particularly precise relaxation measurements by nuclear magnetic resonance on oriented nuclei (NMR-ON). The relaxation measurements on the two isotopes were performed in the same sample in the same experiment with the same technique. They are thus directly comparable.

An Fe single crystal disk, 2.2 mm thick and 12 mm in diameter, was used as host. The disk plane was perpendicular to the [110] direction. Since the probe nuclei were implanted into the first 50 nm, much attention was paid to the surface preparation. The final cleaning of the surface was performed by a sequence of Ar$^+$ ion sputtering and annealing steps.

^{186}Hg and ^{189}Hg, the precursors of ^{186}Ir and ^{189}Ir, were implanted at the on-line mass separator ISOLDE at CERN. The Hg isotopes were produced in spallation reactions using the 1 GeV CERN PS-booster proton beam and the liquid Pb target. The implantation voltage was 60 kV, and the implantation dose was about 0.6×10^{14} cm^{-2} and 1.6×10^{14} cm^{-2} for $A = 186$ and $A = 189$, respectively. After the implantation the sample was annealed for 1/2 h at 970 K, before it was mounted into a ^{3}He-^{4}He dilution refrigerator and cooled down to temperatures in the 10 mK range. The external magnetic field B_{ext} was applied in the disk plane parallel to the [100] direction.

For each isotope first the magnetic and electric hyperfine splitting frequencies were measured by NMR-ON and modulated adiabatic fast passage on oriented nuclei. They agreed well with the known hyperfine field and the electric field gradient of Ir in Fe [17], and the known magnetic and quadrupole moments of ^{186}Ir and ^{189}Ir [18].

In relaxation measurements by the NMR-ON technique [19] the anisotropy of the γ radiation in the decay of oriented probe nuclei is used to monitor the time dependence of the nuclear orientation. The rf field at the NMR resonance frequency is applied first without frequency modulation (FM). Virtually no nuclear spins are excited because of the large inhomogeneous broadening of the hyperfine splitting, and the nuclear spins are in thermal equilibrium. At the time t_{on} the FM is switched on and the nuclear orientation is partly destroyed. After some time a new equilibrium is reached. At the time t_{off} the FM is switched off and the nuclear orientation relaxes back to the thermal equilibrium value.

Typical NMR-ON time spectra for ^{186}Ir and ^{189}Ir are shown in Fig. 1. The relaxation constants and the rf field strengths were determined from these time spectra via *least squares fit*. To describe the time dependence of the γ anisotropy the rate equations for the population numbers of the sublevels were solved [19]. These rate equations were extended by the rf transition probabilities [9] and by the transition rates of the quadrupolar part of the relaxation [4].

The magnetic and electric quadrupolar relaxation rates, R_m and R_q, are conveniently given as inverse Korringa constants, so that the Korringa relation is given by $(T_1 T)^{-1} = (R_m + R_q)$. The ratios $R_m^{(186)}/R_m^{(189)}$ and $R_q^{(186)}/R_q^{(189)}$ are known from the scaling of the relaxation rates with the nuclear moments. With this additional information the four rates $R_m^{(186)}$, $R_m^{(189)}$, $R_q^{(186)}$, and $R_q^{(189)}$ were determined from the combined ^{186}Ir and ^{189}Ir relaxation data.

Whereas the magnetic relaxation can be characterized by a single constant, R_m, one has to specify two constants for the quadrupolar relaxation: $R_q^{(1)}$ and $R_q^{(2)}$, the contributions to R_q that arise from $\Delta I_z = \pm 1$ and $\Delta I_z = \pm 2$ transitions, respectively [4]. The relaxation of ^{189}Ir was measured at $B_{\text{ext}} = 0.2$ T by exciting either all three subresonances of the quadrupolar split NMR spectrum or only the ν_1 subresonance. From a comparison of this data $R_q^{(1)}/R_q^{(2)} = 0.17(9)$ could be deduced. This uncertainty in $R_q^{(1)}/R_q^{(2)}$ is the main contribution to the error of R_q.
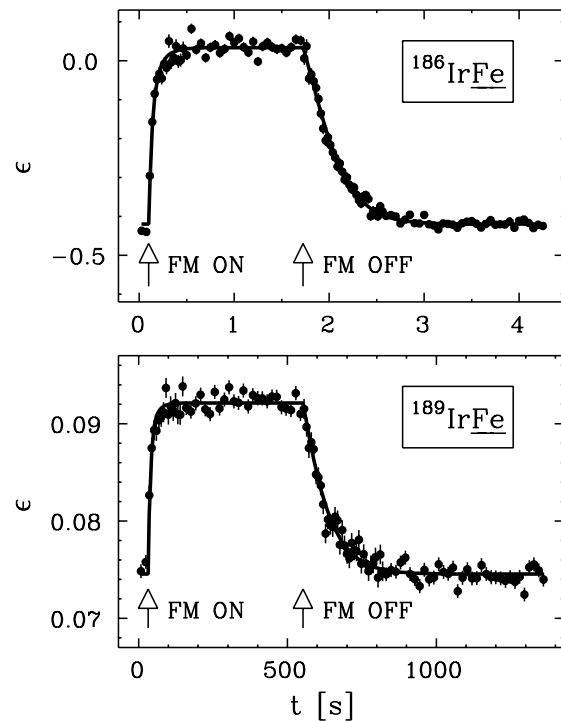

FIG. 1.   NMR-ON time spectrum (γ anisotropy ϵ versus time during a FM off-on-off cycle) for ^{186}Ir and ^{189}Ir. $B_{\text{ext}} = 0.2$ T. The arrows mark the times at which the FM was switched on and off.

It is also known that, due to the hyperfine anomaly, the Fermi-contact interaction in general does not scale exactly with g. This may have consequences for the scaling of R_m. The hyperfine anomaly can be estimated moderately well, but the extent to which the Fermi-contact interaction participates in the nuclear spin-lattice relaxation is *a priori* not known. Therefore, we give the final results for several extreme cases: for example, for a scaling of R_m with g^2 (corresponding to a pure noncontact interaction), or for a scaling with ν_m^2 (corresponding to an almost pure contact interaction).

To calculate $R_m^{(186)}/R_m^{(189)}$ and $R_q^{(186)}/R_q^{(189)}$ we used $\nu_m^{(189)}/\nu_m^{(186)} = 0.12900(4)$, $g^{(189)}/g^{(186)} = 0.1174(19)$, and $Q^{(186)}/Q^{(189)} = 2.902(11)$. R_m/g^2 and R_q/N_q were deduced using $g^{(186)} = 0.773(12)$ and $Q^{(189)} = 0.878(10)$ b. The quadrupole moments were taken from Ref. [18]. The zero field magnetic resonance frequencies in Fe were measured in this work: $\nu_m^{(186)} = 794.68(20)$ MHz, $\nu_m^{(189)} = 102.512(17)$ MHz. The g factors were derived using $\nu_m^{(193)} = 119.00(5)$ MHz [20], $g^{(193)} = 0.1061(4)$ [21], and estimating the hyperfine anomaly with the help of the Moskowitz-Lombardi rule [22] and the ratio of the contact to the total hyperfine field [23].

To check the reproducibility of our results the relaxation of ^{186}Ir was measured at $B_{ext} = 0.1$ and 0.5 T for five different rf power levels, varying the power by a factor of 32. As expected, the deduced Korringa constants proved to be independent of the temperature and the rf power.

About 60% to 80% of the ^{189}Ir relaxation are due to R_q. In contrast, R_m is responsible for more than 98% of the relaxation of ^{186}Ir. This allows one to determine R_m even if only the ^{186}Ir relaxation was measured. The measured magnetic and quadrupolar relaxation constants for B_{ext} between 0.01 and 1 T are shown in Fig. 2. In addition, R_m was also determined at 2 T.

The form and magnitude of the field dependence of R_m are similar to many previous relaxation experiments on polycrystalline Fe samples. One difference is that the relaxation rates are constant up to $B_{ext} \leq 0.27$ T due to the screening of B_{ext} by the demagnetization field. We take here the relaxation rate at 2 T as the high field limit. R_q was extrapolated to 2 T assuming that the form of the magnetic field dependence is the same for R_m and R_q. Table I summarizes the final results for R_m and R_q at zero field and at 2 T. The high field limit for R_m is in moderate agreement with previous results on Ir in Fe and is about 4 times larger than predicted by the *ab initio* calculations [6].

The orbital relaxation was deduced from the following relation [2,4]:

$$(R_o/g^2) \leq 7.70(R_q/N_q). \tag{3}$$

This relation is valid for cubic symmetry and d electrons, which dominate the orbital relaxation for the heavy $5d$ impurities [24]. The close relationship between R_o and R_q arises from the fact that in both cases the nuclear spin in-
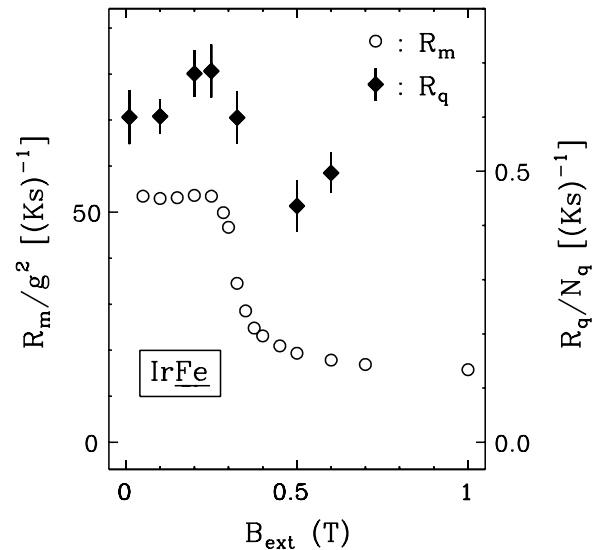

FIG. 2. The reduced magnetic and electric quadrupolar relaxation rates of Ir in Fe as a function of B_{ext} applied along [100]. Because of the choice of the ordinate scales, the relative magnitude of the rates in the figure reflects the situation for ^{189}Ir. The R_q data were obtained assuming a ν_m^2 scaling of R_m and $R_q^{(1)}/R_q^{(2)} = 0.17$.

teracts with the electron orbital moment and the radial part of the interaction is given by a r^{-3} dependence. Table I lists the deduced R_o's for zero field and 2 T. The orbital relaxation rate from the *ab initio* calculations of Ref. [24], $R_o^{(th)}$, is also listed.

A recent fully relativistic *ab initio* calculation of R_q (and R_o) for the $5d$ impurities in Fe is, in principle, also available [13]. However, the results cannot, in our opinion, be correct, since the ratio $(R_o/g^2)/(R_q/N_q)$ comes out much larger (up to a factor of 30) than the factor 7.7 in Eq. (3), and the latter relation has been confirmed by previous fully relativistic calculations [11,12].

The relaxation mechanism in Fe was discussed so far controversially: According to the *ab initio* calculations the orbital relaxation is dominant for transition metal impurities. These calculations are believed to reproduce at least the trend of the systematics [6]. On the other hand, it was repeatedly suggested that direct and indirect spin wave mechanisms play a decisive role [6,9,25]. This would imply primarily spin excitations, that is, nonorbital relaxation. However, both the *ab initio* calculations and the proposed spin wave mechanisms fail to explain the magnitude and the field dependence of the relaxation rates.

The decomposition of the relaxation into an orbital and a nonorbital part now reveals the following: (i) Experiment and *ab initio* calculations are in reasonable agreement for the orbital part of the relaxation, at least at high fields. (ii) There is a significant field dependence of R_q, but it is at least 5 times smaller than that of R_m. We propose that this is a secondary effect, invoked perhaps via the spin-orbit coupling. (iii) The unexpectedly large magnetic relaxation rates and the magnetic field dependence are

TABLE I.   Magnetic, electric quadrupolar, and orbital part of the nuclear spin-lattice relaxation of Ir in Fe. All relaxation rates are in $(Ks)^{-1}$.

	$B_{ext} = 0$	$B_{ext} = 2$ T	$R(0)/R(2\,\text{T})$
R_m/g^2	53.4(17)	13.81(69)	3.87(15)
R_q/N_q	0.63(12)[a]...0.79(18)[b]	0.45(12)[a]...0.51(15)[b]	1.30(15)[c]...1.60(15)[d]
R_o/g^2	$\leq 4.8(9)^a...6.0(13)^b$	$\leq 3.5(9)^a...3.9(11)^b$	–
$R_o^{(th)}/g^2$	3.3[e]	3.3[e]	1.0

[a]Obtained assuming $R_m \propto \nu_m^2$.
[b]Obtained assuming $R_m \propto g^2$.
[c]Obtained assuming $R_m(2\,\text{T}) \propto g^2$ and $[R_m - R_m(2\,\text{T})] \propto \nu_m^2$.
[d]Obtained assuming $R_m(2\,\text{T}) \propto \nu_m^2$ and $[R_m - R_m(2\,\text{T})] \propto g^2$.
[e]Calculated R_o from Ref. [24].

mainly due to a nonorbital relaxation mechanism. Thus, the *ab initio* calculations themselves seem to be correct but obviously an important mechanism is missing in these calculations. The nonorbital nature of this mechanism will be important information for the further investigation of this subject. Furthermore, R_q rather than R_m appears to be in Fe the appropriate quantity used to investigate the local band structure.

To summarize, we have determined for the first time in a transition metal the electric quadrupolar part of the conduction electron contribution to the nuclear spin-lattice relaxation. This part gives information on the nature of the relaxation process. This was demonstrated for an unresolved problem in the nuclear spin-lattice relaxation of the 5d impurities in Fe: Whereas the *ab initio* calculations predict that the orbital part dominates the relaxation in these systems, our measurements show that the bulk of the magnetic relaxation and its magnetic field dependence are of nonorbital origin.

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