Dependence of the Electric Field Gradient of Ir in Fe on the Direction of Magnetization with respect to the Crystallographic Axes

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The electric quadrupole interaction of ^{188}Ir ($I^\pi = 1^-$; $T_{1/2} = 41.5$ h) in a Fe single crystal was measured for magnetization parallel to the crystallographic [100], [110], and [111] axes. Contrary to all previous experiments, a strong dependence of the electric field gradient on the direction of the magnetization with respect to the crystallographic axes was observed for the first time. [S0031-9007(97)02493-9]

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The electric field gradient (EFG) at the site of impurity nuclei in cubic ferromagnetic hosts such as Fe, Ni, and fcc-Co has been the subject of many investigations, both experimental [1–9] and theoretical [5,10,11]. It was first observed by nuclear magnetic resonance (NMR) of ^{191}Ir and ^{193}Ir in polycrystalline dilute ferromagnetic alloys of Fe and Ni [1,5]. Both isotopes have nuclear spin $I = \frac{3}{2}$. The measured NMR spectrum consisted of a central line ($m = -\frac{1}{2} \rightarrow +\frac{1}{2}$ transition) and two satellite lines ($m = -\frac{3}{2} \rightarrow -\frac{1}{2}$ and $m = +\frac{1}{2} \rightarrow +\frac{3}{2}$ transitions). The separation between the central line and each of the satellite lines was observed to be ~ 2.5 MHz in Fe and ~ 1.4 MHz in Ni. The splitting was interpreted as being due to an electric quadrupole interaction (EQI). The EQI frequency is defined as

$$\nu_Q = e^2 q Q / h, \quad (1)$$

where $eq = V_{zz}$ (henceforth denoted as EFG) is the principal component of the traceless EFG tensor and eQ is the nuclear spectroscopic quadrupole moment. If the EQI is collinear with the magnetic hyperfine interaction, the magnetic resonance frequency is split into a set of $2I$ equidistant subresonances, where I is the nuclear spin. The subresonance separation is given by

$$\Delta\nu_Q = 3\nu_Q / [2I(2I - 1)]. \quad (2)$$

The satellite resonances were considerably broader than the central line. Mainly, the following two explanations were discussed: (i) The additional broadening is due to lattice inhomogeneities. (ii) The EFG depends on the direction of the magnetization with respect to the crystal axes. To explore whether the second possibility was the origin for this broadening, Aiga and Itoh prepared single crystal alloys of Fe-0.3% Ir by the stress annealing method. The NMR measurements yielded exactly the same spectra as observed for the polycrystal samples

[5]. Thus Aiga and Itoh concluded that the quadrupole interaction is almost independent of the direction of the magnetization, and even if there is some anisotropy, it is of the order of, or less than, a few hundred kHz. Johnston and Stone performed NMR on oriented nuclei (NMR-ON) measurements on ^{192}Ir diffused in a Ni single crystal. They also reported the EQI to be independent of the direction of the magnetization [4].

The existence of an EFG in a cubic ferromagnetic host lattice has been attributed to an unquenched orbital momentum produced by the spin-orbit interaction of the nd electrons [5,10,11]. For Ir in Ni, Demangeat [10] reported Hartree-Fock calculations of the EFG. According to his calculations a large anisotropy with respect to the crystallographic axes is expected, which was viewed to be in disagreement with the experimental data [5]. Gehring and Williams [11] examined the effects of the spin-orbit coupling using an extension of the Wolff-Clogston approach. In the general framework of their model, the EFG may, depending on the relative sizes of the spin-orbit coupling, the crystal field, and the exchange splitting, depend on the direction of the magnetization with respect to the crystal axes. Led by the experiments suggesting the EFG to be invariant, they concluded that the effects of the crystal field can be neglected.

For $I = \frac{3}{2}$ ^{197}Au in Fe, spin echo (SE) experiments showed a similar resonance structure as observed for ^{191}Ir and ^{193}Ir , a relatively narrow central line and two broadened satellite lines [8,9]. For radioactive $I = \frac{3}{2}$ ^{199}Au in Fe, NMR-ON measurements were reported in which a similar quadrupole-split resonance structure had been observed. The ratio of quadrupole splittings $\nu_Q(^{199}\text{AuFe})/\nu_Q(^{197}\text{AuFe})$ differed, however, from the ratio of quadrupole moments $Q(^{199}\text{AuFe})/Q(^{197}\text{AuFe})$ [12]. This was interpreted such that the SE and NMR-ON

methods probe different contributions to the total (broad) hyperfine interaction with different weights. In this way different average quadrupole interactions are obtained.

Meanwhile, a new measurement technique has been established with which the EQI of radioactive nuclei can be measured with high precision, even if it is hidden within the inhomogeneous magnetic broadening: modulated adiabatic passage on oriented nuclei (MAPON) [13,14]. Recent MAPON measurements on ^{192}Ir and ^{198}Au in polycrystal Fe and Ni samples showed that the average quadrupole interaction depends strongly on the external magnetic field B_{ext} [15,16]. It was speculated that this could be due to a strong dependence of the EFG on the direction of the magnetization. There is a hint in the literature that such an effect might actually exist: Chaplin and Hutchison [17] reported MAPON experiments on ^{60}Co as a dilute impurity in Fe single crystals. They observed broad asymmetric distributions of $\Delta\nu_Q$ for the [100], [110], and [111] directions, the maxima of the distributions being different, however, by only few kHz. (The widths of the distributions were much larger.) In our opinion, these data are not conclusive, as the measured average quadrupole interaction in this case is only of the order of kHz (instead of MHz for Au and Ir). Such small quadrupole interactions might actually originate from lattice inhomogeneities, especially if the observed distributions are broad and asymmetric. Therefore, measurements of the quadrupole splitting of Ir or Au in Fe single crystals were necessary. As the EFG for IrFe is larger than for AuFe , measurements on an Ir isotope were preferred. As the best isotope for this purpose, ^{188}Ir was chosen. Actually, a strong anisotropy of the EQI was observed.

A Fe single-crystal slice was cut from a single-crystal rod, the surface normal being parallel to a [110] axis. The [100], [110], and [111] crystallographic axes then lie in the plane of the surface of the sample. Thus, by rotating the crystal in its position at the cold finger of the dilution refrigerator, the magnetization can be forced parallel to the [100], [110], and [111] axes with an external magnetic field. Much attention was paid to a high surface quality which was obtained by mechanical polishing and electropolishing steps. The sample of $^{188}\text{IrFe}^{(\text{sc})}$ was prepared at the mass separator ISOLDE at CERN by implanting ^{188}Hg with $E = 60$ keV. The implanted nuclei (total number $\sim 5 \times 10^{12}$; size of the beam spot $\sim 5 \times 5$ mm 2) are distributed within a layer of ~ 5 nm width in a depth of ~ 25 nm underneath the crystal surface. The impurity concentration in this layer is ~ 0.05 at. %; i.e., the criteria for a dilute alloy are well fulfilled. The following decay chain is relevant:

As ^{188}Ir is fed in the decay of ^{188}Pt , the longer half-life of ^{188}Pt of 10.2 days allowed an integral measurement time of about 4 weeks. After the implantation, the sample was annealed for 2 h at 600 °C. Using a ^3He - ^4He -dilution

refrigerator with a top-loading facility, the sample was cooled to temperatures near 10 mK. For the NMR-ON measurements, the radio frequency (rf) was frequency modulated, with a modulation bandwidth $\Delta\nu^{\text{rf}}$ between ± 0.4 and ± 1.0 MHz. The MAPON measurements were performed as described in Ref. [18].

Three experiments were performed, for which the [100], [110], and [111] crystallographic axes had been adjusted parallel to the external magnetic field. The γ rays emitted in the decay of $I^\pi = 1^-$ ^{188}Ir were measured with Ge detectors placed at 0°, 90°, 180°, and 270° with respect to the polarizing field. The temperature of the sample was measured with a $^{60}\text{CoCo}^{(\text{hcp})}$ thermometer. For all experiments, the sequence was as follows: (i) measurement of the magnetization behavior via the γ anisotropy as a function of B_{ext} , (ii) NMR-ON measurements for different values of B_{ext} in the saturation region of the magnetization, (iii) a MAPON measurement with a magnetic field in the saturation region of the magnetization. Typical measurement times for NMR-ON and MAPON spectra were ~ 3 days.

In the first experiment, the crystal was aligned with the [100] axis (direction of easy magnetization) parallel to B_{ext} . Here, saturation of the γ anisotropy was obtained for $B_{\text{ext}} \geq 0.5$ kG. NMR-ON spectra were measured for $B_{\text{ext}} = 1$ kG ($\Delta\nu^{\text{rf}} = \pm 1.0$ MHz) and $B_{\text{ext}} = 4$ kG ($\Delta\nu^{\text{rf}} = \pm 0.4$ MHz). The 4 kG spectrum is shown in Fig. 1 (top). In addition to the sharp resonances [inhomogeneous linewidth $\Gamma_{(\text{inh})} = 1.24(12)$ MHz], there is a weak resonant background. This is probably due to a small fraction of ^{188}Ir nuclei for which the lattice defects introduced by the implantation have not been healed out completely by the annealing procedure. The centers of the sharp resonance and hence the deduced quadrupole interaction are not affected by this background. The results for the quadrupole splitting are $\Delta\nu_Q^{(\text{NMR-ON})} = -6.99(43)$ and $-6.80(14)$ MHz for $B_{\text{ext}} = 1$ and 4 kG, respectively. A MAPON measurement was performed for $B_{\text{ext}} = 1$ kG. The derivative of a measured MAPON spectrum yields directly the distribution of the quadrupole interaction $P(\Delta\nu_Q)$ [14]. It is shown in Fig. 2 (top). Here again, a sharp distribution peaking at $\Delta\nu_Q^{(\text{MAPON})} = -6.93(6)$ MHz [half-width $\Gamma_{\Delta\nu_Q} = 1.12(21)$ MHz] is superimposed to a broad background. The result for the sharp component is in perfect agreement with the less precise NMR-ON results.

Next, the [110] axis was aligned parallel to B_{ext} . The saturation of the γ anisotropy was obtained for $B_{\text{ext}} \geq 1.5$ kG. NMR-ON spectra were measured for $B_{\text{ext}} = 2$ and 4 kG. The 4 kG spectrum is shown in the middle part of Fig. 1. The inhomogeneous linewidth of the sharp resonances is $\Gamma_{(\text{inh})} = 1.00(7)$ MHz. Again, the broad resonant background is visible. The results for the quadrupole splitting are $\Delta\nu_Q^{(\text{NMR-ON})} = -4.39(11)$ and $-4.38(16)$ MHz for $B_{\text{ext}} = 2$ and 4 kG, respectively. The MAPON measurement was performed for

FIG. 1. NMR-ON resonance of $^{188}\text{IrFe}^{(\text{sc})}$ measured for magnetization parallel [100] (top), [110] (middle), and [111] (bottom). $\Delta\epsilon$ is the change of the γ anisotropy of the 2215 keV γ transition. The spectra for [100] and [110] were measured with a modulation bandwidth of $\Delta\nu^{\text{rf}} = \pm 0.4$ MHz. In comparison with the inhomogeneous linewidths of $\Gamma_{(\text{inh})}^{([100])} = 1.24(12)$ MHz and $\Gamma_{(\text{inh})}^{([110])} = 1.00(7)$ MHz, there is no considerable broadening by the rf modulation. The spectrum for [111] was measured with $\Delta\nu^{\text{rf}} = \pm 1.0$ MHz. Here, in comparison to $\Gamma_{(\text{inh})}^{([111])} = 1.35(13)$ MHz, a considerable broadening by the rf modulation is introduced. The dashed line represents the frequency distribution obtained by unfolding the rf modulation. The inhomogeneous broadening is about the same for all directions.

$B_{\text{ext}} = 2$ kG. The derivative of the MAPON spectrum is shown in Fig. 2 (middle). The sharp distribution peaks at $\Delta\nu_Q^{(\text{MAPON})} = -4.37(4)$ MHz [$\Gamma_{\Delta\nu_Q} = 1.17(18)$ MHz].

For alignment of the [111] axis parallel to B_{ext} , the γ anisotropy was saturated for $B_{\text{ext}} \geq 1.7$ kG. The NMR-ON spectrum measured for $B_{\text{ext}} = 2$ kG is shown in Fig. 1 (bottom). Here, the rf modulation bandwidth was chosen $\Delta\nu^{\text{rf}} = \pm 1.0$ MHz. Therefore the linewidth of the experimental spectrum is additionally broadened. After unfolding the rf modulation, the dashed curve in Fig. 1 is obtained. The inhomogeneous linewidth [$\Gamma_{(\text{inh})} = 1.35(13)$ MHz] is similar to those observed for the [100] and [110] directions. The MAPON measurement was performed for $B_{\text{ext}} = 2$ kG. The result is shown in Fig. 2 (bottom). The sharp distribution peaks at $\Delta\nu_Q^{(\text{MAPON})} = -3.80(7)$ MHz [$\Gamma_{\Delta\nu_Q} = 0.74(23)$ MHz].

A compilation of the results is given in Table I. All quadrupole splitting frequencies obtained from the MAPON measurements are in perfect agreement with the NMR-ON results. In the saturation region for the magnetization, no dependence of $\Delta\nu_Q$ on B_{ext} is observed. For the present case of $I = 1$, $\nu_Q = 2\Delta\nu_Q/3$. The final re-

FIG. 2. Derivatives of the MAPON spectra for $^{188}\text{IrFe}^{(\text{sc})}$, which represent the distribution of the quadrupole splitting $P(\Delta\nu_Q)$. The widths are $\Gamma_{\Delta\nu_Q}^{([100])} = 1.12(21)$ MHz, $\Gamma_{\Delta\nu_Q}^{([110])} = 1.17(18)$ MHz, and $\Gamma_{\Delta\nu_Q}^{([111])} = 0.74(23)$ MHz.

sults are

$$\begin{aligned}\nu_Q^{([100])} &= -4.61(4) \text{ MHz}, \\ \nu_Q^{([110])} &= -2.91(3) \text{ MHz}, \\ \nu_Q^{([111])} &= -2.53(5) \text{ MHz}.\end{aligned}$$

The ratios are

$$\nu_Q^{([100])} : \nu_Q^{([110])} : \nu_Q^{([111])} = 1 : 0.631(9) : 0.549(12).$$

Taking $Q(^{188}\text{Ir}) = +0.484(6)$ b [19], the absolute values of the EFG are $-0.394(6) \times 10^{17}$, $-0.249(4) \times 10^{17}$, and $-0.216(5) \times 10^{17}$ V/cm² for the [100], [110], and [111] directions, respectively. [The average EFG from the NMR measurements on ^{193}Ir in polycrystal Fe is $-0.281(6) \times 10^{17}$ V/cm².]

Thus, contrary to the results of previous experiments [5], the EQI of Ir in Fe is strongly anisotropic with respect to

TABLE I. Measured magnetic and quadrupole splittings of $^{188}\text{IrFe}$ as a function of the crystallographic axes.

Direction	B_{ext} (kG)	$\nu_{\text{mag}}^{(\text{NMR-ON})}$ (MHz)	$\Delta\nu_Q^{(\text{NMR-ON})}$ (MHz)	$\Delta\nu_Q^{(\text{MAPON})}$ (MHz)
[100]	1	316.15(22)	-6.99(43) ^a	-6.93(6)
	4	315.73(7)	-6.80(14) ^b	
[110]	2	315.81(5)	-4.39(11) ^c	-4.37(4)
	4	315.37(8)	-4.38(16) ^b	
[111]	2	315.81(11)	-3.83(23) ^a	-3.80(7)

^amodulation bandwidth $\Delta\nu^{\text{rf}} = \pm 1.0$ MHz.

^b $\Delta\nu^{\text{rf}} = \pm 0.4$ MHz.

^c $\Delta\nu^{\text{rf}} = \pm 0.5$ MHz.

the crystallographic axes. According to the calculations of Ref. [11], the EQI associated with the unquenched orbital momentum is isotropic only if the spin-orbit interaction is much smaller than the host d -band width and much larger than the crystal field. These conditions were viewed to be fulfilled in general for the $5d$ elements in Fe and Ni [5,11]. This presumption has to be revised.

As a by-product, information on the dependence of the magnetic hyperfine field on the direction of the magnetization is obtained. The magnetic hyperfine splitting frequency ν_{mag} is connected with the hyperfine field B_{HF} by

$$\nu_{\text{mag}} = |g\mu_N[B_{\text{HF}} + (1 + K)(B_{\text{ext}} - B_{\text{dem}})]/h|, \quad (3)$$

where g is the nuclear g factor, K is the resonance shift parameter which includes Knight shift and diamagnetic shielding, and B_{dem} is the demagnetization field. (Within the present accuracy it is sufficient to reduce the demagnetization tensor to the approximation with demagnetization fields, which differ only slightly for the [100], [110], and [111] directions.) With the experimental data listed in column 3 of Table I, and taking into account the demagnetization fields calculated numerically, we get

$$\begin{aligned} B_{\text{HF}}^{([100])} - B_{\text{HF}}^{([110])} &= -0.8(8) \text{ kG}, \\ B_{\text{HF}}^{([111])} - B_{\text{HF}}^{([110])} &= +0.4(8) \text{ kG}. \end{aligned}$$

Thus, an anisotropy, if existent, is very small in comparison to the absolute value of $B_{\text{HF}}(\text{IrFe}) = -1373(7) \text{ kG}$ [7].

On the condition that the EFG's in Fe and Ni depend on the direction of magnetization many unresolved problems in this context can now be explained: (i) The different average quadrupole interactions as measured by zero-field spin echo and NMR-ON experiments are due to the different weight of the contributions from the different crystal axes. This is due to the fact that the enhancement factor for the rf field depends on the angle between the magnetization and the crystallographic axes. (ii) The magnetic field dependence of the average quadrupole interaction of ^{192}Ir in polycrystal Fe is an immediate consequence of the anisotropy of the EFG. With decreasing external magnetic field, the magnetizations of the single crystal domains rotate gradually towards [100] directions, which is accompanied by an increase of the average EFG. The observed magnetic-field dependence of the average EQI for ^{192}Ir in Ni [15] and ^{198}Au in Fe [16] indicates that the EFG is anisotropic in these systems also. (iii) There are systems such as OsFe [20] and AuNi [16] for which a broad distribution for the quadrupole interaction has been observed by MAPON experiments. Here, the EFG's for different directions of the magnetization could be strongly different and could even have an opposite sign. Then the broad distribution with a large contribution around $\nu_Q^{(\text{eff})} = 0$ could immediately be understood. In addition, it is then obvious why it has been found to be impossible to resolve the EQI in the polycrystal samples of OsFe and AuNi .

In summary, for Ir as dilute impurity in cubic Fe, the EFG at the impurity site depends on the direction of

magnetization with respect to the crystallographic axes. We think that such a directional dependence exists also for other dilute alloys of nd elements in Fe, Ni, and fcc-Co. From theory, the EFG depends on the strength of the spin-orbit coupling, the crystal field, and the exchange splitting. The strength of these interactions and hence the EFG and its directional dependence are specific for the impurity-host combination. Thus, systematic studies on nd elements in single crystals of Fe and Ni may yield valuable new information on the electronic structure at the impurity site, especially the interplay between the spin-orbit interaction, the crystal field, and the exchange interaction.

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