Drastic Enhancement of Nuclear Magnetic Resonance in a hcp Cobalt Single Crystal Magnetized Perpendicular to the c Axis

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Nuclear magnetic resonance on oriented nuclei was performed for the first time using as host matrix a hexagonal Co single crystal magnetized perpendicular to the c axis. The radioactive isotope ^{191}Pt was implanted using the mass separator ISOLDE-3 at CERN. In comparison to the case of magnetization parallel to the c axis, a drastic enhancement of the resonance signal was observed. This observation opens new possibilities for precise measurements of nuclear moments of short-lived isotopes far from stability.

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Among the different methods for the measurement of the hyperfine splitting of radioactive isotopes in a ferromagnetic host lattice the most precise technique is nuclear magnetic resonance on oriented nuclei (NMR-ON).¹ This is due to the fact that the detection of NMR via the change of the radiation pattern of β or γ radiation allows impurity concentrations far below the ppm level. Thus, since its discovery in 1966 by Matthias and Holliday,¹ NMR-ON has been used for numerous precise determinations of the magnetic hyperfine interaction of radioactive nuclei in a ferromagnetic host lattice, yielding highly precise and reliable results on magnetic hyperfine fields, nuclear magnetic dipole moments, and information on the nuclear spin-lattice relaxation in very dilute alloys. In recent years the NMR-ON technique has been applied mainly for the measurement of ground-state magnetic moments of short-lived radioactive isotopes, using mostly Fe and Ni as host matrices. The accuracy of the deduced magnetic moments is for many systems comparable to that of laser-spectroscopy methods.

Precise electric quadrupole moments of short-lived radioactive nuclei could up to now only be determined with laser-spectroscopy methods, which, however, are not applicable to all elements. Thus, a new method would be desirable with which electric quadrupole splittings of radioactive nuclei in metal matrices could be measured with resonance precision. Then, ratios of electric quadrupole moments, and, if the electric-field gradient can be calibrated, also absolute values of electric quadrupole moments, could be determined. Several approaches have been tried,²⁻⁷ which, up to now, did not lead to a new method with a broad application range. All these approaches have the common feature that a host matrix is used in which an electric-field gradient (EFG) exists in addition to a large magnetic hyperfine field. Then, the

magnetic interaction provides (i) a large degree of orientation at the "convenient" temperature of ~ 10 mK and (ii) the enhancement factor for the rf field (see below), while the electric interaction splits the NMR-ON resonance into a set of $2I$ subresonances.

Recently, the first successful NMR-ON experiment with a hexagonal Co single crystal as host matrix was reported:⁷ All quadrupole subresonances of ^{198}Au and ^{199}Au could be resolved well. Thus it was very promising that hcp Co could be a good matrix for precise measurements of quadrupole moments of radioactive nuclei. The relatively small resonance amplitudes, however, seemed to be the limiting factor for the detection of new resonances.

In this Letter we report the observation that, compared to the case for which the external magnetic field is applied parallel to the c axis (0° geometry), the resonance amplitudes are strongly enhanced if the hcp-Co single crystal is magnetized perpendicular to the c axis (90° geometry). This enhancement may be decisive for the detection of new NMR-ON resonances.

The angular distribution of γ rays emitted in the decay of oriented nuclei is most conveniently written as

$$W(\theta) = 1 + f \sum_k B_k(v_M^{\text{eff}}, v_Q^{\text{eff}}, T) A_k P_k(\cos\theta) Q_k, \quad (1)$$

where f is the so-called full-field fraction and A_k are products of the angular correlation coefficients F_k as normally defined and the deorientation coefficients U_k . The parameters B_k describe the degree of orientation; they depend on the temperature T and on the (effective) magnetic and electric hyperfine splitting frequencies

$$v_M^{\text{eff}} = |g\mu_N B^{\text{eff}}/h|, \quad v_Q^{\text{eff}} = e^2 q^{\text{eff}} Q/h, \quad (2)$$

where g and eQ are the nuclear g factor and the spectroscopic quadrupole moment, and B^{eff} and eq^{eff} are the

effective magnetic field and the effective EFG, respectively. These are given by

$$\mathbf{B}^{\text{eff}} = \mathbf{B}_{\text{HF}}(\vartheta) + \mathbf{B}_0, \quad (3a)$$

$$eq^{\text{eff}} = eqP_2(\cos\vartheta), \quad (3b)$$

where ϑ is the angle between the direction of the magnetization $\mathbf{M}$ and the crystal c axis. For the validity of Eq. (3b), it has to be assumed that the quadrupole interaction is small compared to the magnetic interaction, $|v_Q| \ll v_M$, and no impurity-ion EFG is present.

In NMR-ON experiments the resonant change of $W(\theta)$ is used as the detector for NMR. For a combined magnetic dipole plus electric quadrupole interaction of an oriented state with spin I there exists a set of $2I$ subresonances. The center of the subresonance corresponding to rf transitions between state $|m\rangle$ and $|m+1\rangle$ is, assuming that the $m = -I$ state lies lowest in energy, given by

$$\nu_{m \rightarrow m+1} = \nu_M^{\text{eff}} + \Delta\nu_Q^{\text{eff}}(m + \frac{1}{2}), \quad (4)$$

$$\Delta\nu_Q^{\text{eff}} = \frac{3\nu_Q^{\text{eff}}}{2I(2I-1)},$$

where $\Delta\nu_Q^{\text{eff}}$ is the subresonance separation.

The resonance amplitude, which is a decisive parameter for the measurement, depends directly on the rf power at the nuclear site. [Strictly, it depends on the ratio of the reduced matrix elements for the rf coupling (driving the spin system towards deorientation) and the spin-lattice relaxation (driving the spin system towards thermal-equilibrium orientation).] The maximum rf power which can be applied is, however, limited by the cooling power and heat impedances of the normally used ^3He - ^4He dilution refrigerators in the millikelvin region. In this context the enhancement factor for the rf field plays an important role. It is normally explained by rewriting Eq. (3a) as follows:

$$\mathbf{B}^{\text{eff}} = \mathbf{B}_{\text{HF}}(\vartheta) + \mathbf{B}_0 = (B_{\text{HF}}/B_0 + 1)\mathbf{B}_0 = F\mathbf{B}_0, \quad (5)$$

which can be interpreted by noting that the external magnetic field B_0 at the nuclear site is enhanced by a factor F . This holds also for the rf field B_1 , implying a factor F^2 for the enhancement of the rf power. This interpretation is, however, misleading, as the crystal anisotropy energy is disregarded. The enhancement factor can be calculated easily from energy considerations, taking into account the known angular dependence of the anisotropy energy for hcp Co, $E = K_1 \sin^2\vartheta + K_2 \sin^4\vartheta$, where again ϑ is the angle between the magnetization and the crystal c axis, which is the easy axis for magnetization. For $K_2 = 0$, a straightforward calculation yields

$$F^{\parallel} = \frac{B_{\text{HF}}}{B_0 + B_A} + 1 \text{ for } \mathbf{B}_0 \parallel \mathbf{c}, \quad (6)$$

$$F^{\perp} = \frac{B_{\text{HF}}}{B_0 - B_A} + 1 \text{ for } \mathbf{B}_0 \perp \mathbf{c},$$

where B_A is an anisotropy field, defined as the magnetic field which is necessary for complete orientation of the magnetization in the case $\mathbf{B}_0 \perp \mathbf{c}$ axis. For $K_2 \neq 0$, Eq. (6) also holds, with a slightly different definition of B_A . It is now obvious that the maximum value for the enhancement factor is obtained when the crystal is magnetized perpendicular to the c axis for $B_0 \sim B_A$, which is of the order of 17 kG for hcp Co. Then, the enhancement factor is comparable in magnitude to low-field enhancement factors obtained with Fe and Ni as host lattices, for which case the enhancement factors are large enough for successful NMR-ON measurements.

Samples were prepared from a hcp-Co single crystal available commercially. Disks with a diameter of ~ 10 mm and a thickness of 1–2 mm were spark cut from the crystal, the c axis being oriented parallel to the plane of the disk. The disks were first mechanically polished with 1-, 0.5-, and 0.25- μm diamond paste, then electropolished, and finally chemically polished.

The implantations of ^{191}Pt ($T_{1/2} = 2.8$ d) were carried out at the mass separator ISOLDE-3 at CERN with an accelerating voltage of 60 kV. Two samples were annealed after the implantation (2.5 h at 360°C in high vacuum), and one sample was not annealed. In all cases the single-crystal sample was soldered with In to one side of the Cu cold finger of a ^3He - ^4He dilution refrigerator with top-loading facility, the c axis perpendicular or parallel to the direction of the external magnetic field B_0 , and cooled down to ~ 10 mK. The temperature was measured with a $^{60}\text{CoCo}(\text{hcp})$ thermometer, with the crystal c axis parallel to B_0 . The γ rays were detected with four $\sim 100\text{-cm}^3$ Ge(Li) detectors which were placed at 0°, 90°, 180°, and 270° with respect to the external magnetic field B_0 . For the case $\mathbf{c} \perp \mathbf{B}_0$, the magnetization of the $^{191}\text{PtCo}$ sample was measured via the γ anisotropy for B_0 up to 20 kG, which was the limit given by the superconducting magnet. It was found that the magnetization was nearly saturated at 18 kG, thus implying that the maximum enhancement factor should be expected in this field region.

Figure 1 (top) shows the NMR-ON spectrum of the 351-keV transition measured on an annealed sample for $B_0(\perp \mathbf{c}) = 20$ kG, with an applied rf power $P_{\text{rf}} = 10$ mW. The quadrupole structure is well resolved, yielding $\Delta\nu_Q^{\text{eff}} = -6.30(6)$ MHz and $\nu_M^{\text{eff}} = 228.01(6)$ MHz. After these measurements, the crystal was mounted with $\mathbf{c} \parallel \mathbf{B}_0$. With $P_{\text{rf}} = 10$ mW, no NMR-ON resonance signal could be detected. All further 0°-geometry measurements were therefore performed with $P_{\text{rf}} = 32$ mW. (This was the upper limit for the rf power keeping the nonresonant eddy-current heating and hence warmup of the sample tolerable.) For $B_0 = 6$ kG the two lower NMR-ON resonances could now be detected at $\nu_1 = 220.83(2)$ and $\nu_2 = \nu_M^{\text{eff}} = 234.15(4)$ MHz (Fig. 1, bottom, left and middle). Despite the fact that the rf power in the measurement with 90° geometry is smaller by a factor of ~ 3 , the resonance amplitudes are larger by a factor of ~ 2 ,

FIG. 1. Variation of the γ anisotropy $\Delta\epsilon$ vs applied rf frequency $\{\epsilon = [W(0^\circ) + W(180^\circ)]/[W(90^\circ) + W(270^\circ)]\}$. Top: "Normal" NMR-ON spectrum for $B_0(\perp c) = 20$ kG measured with $P_{rf} = 10$ mW. Measurement time 300 s per frequency interval (fi) (0.5 MHz). Bottom: $B_0(\parallel c) = 6$ kG. Left and middle: "Normal" spectra measured with $P_{rf} = 32$ mW. Measurement times 600 s/fi (left) and 1500 s/fi (middle). Right: Triple-resonance spectrum (for explanation, see text); measurement time 1800 s/fi. It should be noticed that the resonance amplitudes for the 90° -geometry measurement are by a factor of ~ 2 larger although the rf power is by a factor of ~ 3 smaller, which is the consequence of the larger enhancement factor for the rf field in the 90° geometry.

which is the consequence of the larger enhancement factor for the rf field. For a high-precision measurement of the third subresonance the "normal" NMR-ON technique is not appropriate as the (theoretical) maximum amplitude is small for all temperatures. Therefore, for the first time, a triple-resonance technique was applied using three rf generators: The frequencies of two generators were fixed at 220.83 and 234.15 MHz, both with a frequency-modulation bandwidth of ± 1 MHz, in order to saturate the ν_1 and ν_2 resonances, while the frequency of the third generator was varied as in "normal" NMR-ON experiments. In this way, the third subresonance could be resolved well at $\nu_3 = 247.67(6)$ MHz (Fig. 1, bottom, right). Further measurements of the ν_1 and ν_2 resonances were performed for the second annealed sample and the unannealed sample for $B_0(\parallel c) = 1, 3.5$, and 6 kG. No dependence of the deduced quadrupole subresonance separation frequencies $\Delta\nu_Q$ on

B_0 was observed.

The results for $\Delta\nu_Q^\parallel$ for the three different samples are $+13.45(8)$ MHz (unannealed sample), $+13.32(9)$ MHz (annealed sample), and $+13.39(6)$ MHz (triple resonance), which are in perfect agreement. The data show that annealing has no influence on the quadrupole splitting. The average value for $B_0 \parallel c$ is $\Delta\nu_Q^\parallel = +13.39(4)$ MHz, from which the quadrupole splitting frequency is found to be $\nu_Q = +26.78(8)$ MHz. With this value, for $M \perp c$, $\Delta\nu_Q^\perp = -6.69(2)$ MHz would be expected according to Eq. (3b). The corresponding data for $B_0(\perp c) = 16, 18$, and 20 kG are $-5.75(6)$, $-6.17(5)$, and $-6.30(6)$ MHz, respectively; i.e., slightly smaller than expected, with an increasing trend. The deviation may be partly due to the fact that the magnetization M was not completely aligned in the direction of B_0 , even at $B_0 = 20$ kG. (The demagnetization field of this sample was estimated to be ~ 2 kG.) On the other hand, it cannot be anticipated *a priori* that the quadrupole interaction actually follows a $P_2(\cos\vartheta)$ dependence. A slight nonaxiality of the EFG for $M \perp c$ would be sufficient to explain the decrease of $|\Delta\nu_Q^\perp(90^\circ)|$, as pointed out by Enokiya, who found a similar behavior for Co in hcp Co.⁸ In addition, a (small) directional-independent EFG could exist due to an unquenched orbital momentum of the 5d electrons at the Pt sites, as observed, e.g., for Au and Ir in Fe and Ni. A precise study of these effects was not the aim of this work.

As a byproduct, with $\nu_M^\parallel = 235.2(1)$ MHz, $\nu_M^\perp = 232.6(1)$ MHz, and $\mu = -0.501(5)\mu_N$ (Ref. 9), the hyperfine fields of Pt in hcp Co are deduced to be $B_{HF}^\parallel = -923.8(9.2)$ kG, $B_{HF}^\perp = -913.6(9.1)$ kG, and $B_{HF}^\perp - B_{HF}^\parallel = -10.2(6)$ kG. The isotropic part of the hyperfine field is, assuming a $P_2(\cos\vartheta)$ angular dependence, $B_{HF}^{iso} = (B_{HF}^\parallel + 2B_{HF}^\perp)/3 = -917.0(9.2)$ kG, which is a factor of 1.12 larger than the hyperfine field of Pt in fcc Co [$B_{HF}^{fcc} = -818(17)$ kG; Ref. 10, recalculated]. These data are compiled in Table I, together with the respective values for Co. It should be noticed that (i) the ratio $B_{HF}^{iso}/B_{HF}^{fcc}$ is different, (ii) the ratio $(B_{HF}^\parallel - B_{HF}^\perp)/B_{HF}^{iso}$ is different, and (iii) $B_{HF}^\parallel - B_{HF}^\perp$ has opposite sign. Thus, the anisotropy of the hyperfine field in hcp Co and the ratio to the hyperfine field in fcc Co seem to be strongly dependent on the probe.

Summarizing, our experiments have shown the following: (i) The resonance amplitudes for NMR-ON measurements with hcp Co as host matrix are enhanced drastically if the crystal is magnetized perpendicular to the c axis. This gain can be decisive for the detection of new NMR-ON resonances on systems with short spin-lattice relaxation times, for which a larger rf power is necessary to obtain a considerable resonant deorientation of the spin system. In addition to the magnetic hyperfine interaction, the quadrupole interaction frequency can be determined, with a high precision for the 0° geometry. Thus, ratios of quadrupole moments, and, if the field gradient can be calibrated, absolute values of quadrupole

TABLE I. Magnetic hyperfine fields of Co and Pt in hcp and fcc Co.

	$B_{\text{HF}}^{\parallel}$ (kG)	$B_{\text{HF}}^{\perp}$ (kG)	$B_{\text{HF}}^{\text{iso}}$ (kG)	$B_{\text{HF}}^{\parallel} - B_{\text{HF}}^{\perp}$ (kG)	$(B_{\text{HF}}^{\parallel} - B_{\text{HF}}^{\perp})/B_{\text{HF}}^{\text{iso}}$	$B_{\text{HF}}^{\text{fcc}}$ (kG)	$B_{\text{HF}}^{\text{iso}}/B_{\text{HF}}^{\text{fcc}}$
CoCo	-218.2(4) ^a	-226.2(4) ^a	-223.5(4) ^a	+8.0(1) ^a	$-3.6(4) \times 10^{-2}$	-215.5(4) ^a	+1.037(2)
PtCo	-923.8(9.2)	-913.6(9.1)	-917.0(9.2)	-10.2(6)	$+1.1(1) \times 10^{-2}$	-818(17) ^b	+1.12(2)

^aReference 11, recalculated^bReference 10, recalculated.

moments can be determined with high precision. (ii) The anisotropy of the hyperfine field in hcp Co and the ratio of the isotropic part to the hyperfine field in fcc Co can be strongly dependent on the impurity element. A systematic study of these hyperfine fields could provide an important contribution for the understanding of magnetic properties in the fcc and hcp phases of Co and stimulate new magnetic-band-structure calculations.

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