Nuclear Magnetic Resonance of ^{198}Au and ^{199}Au Oriented in a hcp Cobalt Single Crystal at Low Temperatures

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(Received 6 July 1988)

We report the first observation of quadrupole-interaction–resolved nuclear magnetic resonance on oriented nuclei in a hexagonal Co host. The radioactive isotopes ^{198}Au and ^{199}Au were mass-separator implanted into a hcp Co single crystal and nuclear magnetic resonance was detected via the anisotropy of the γ radiation at temperatures of ~ 10 mK. These experiments have shown that hcp Co might be the best host matrix for the determination of the electric quadrupole moments of heavy radioactive nuclei with resonance precision.

PACS numbers: 76.80.+y, 75.50.Cc, 76.60.−k

Since its discovery in 1966 by Matthias and Holliday,[1] the technique of nuclear magnetic resonance on oriented nuclei (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 mainly applied for the measurement of ground-state magnetic moments of short-lived radioactive isotopes, using mostly Fe and Ni as host matrices. The obtained accuracy is for many systems comparable to that of laser-spectroscopy methods. Presently, the interest in nuclear structure investigations concentrates more and more on nuclei far from stability, where new regions of spherical, deformed, or superdeformed nuclei are expected. For such investigations, several facilities for on-line implantation and nuclear orientation are now operating or are under construction.

Electric quadrupole moments of radioactive nuclei are interesting as they provide information on single-particle aspects and on deformation parameters. Up to now no equivalent techniques have been established with which quadrupole splittings of radioactive nuclei in metal matrices could be measured with resonance precision. "Pure" quadrupole resonance on oriented nuclei in a noncubic nonmagnetic metal has not been observed yet, most probably because of the missing enhancement factor for the rf field together with typically small γ anisotropies.

The difficulties due to the small γ anisotropies and the missing enhancement factor can be overcome by use of a ferromagnetic (or antiferromagnetic) matrix in which an electric field gradient (EFG) exists in addition to a large magnetic hyperfine field. Then, the magnetic interaction provides a large degree of orientation at the "convenient" temperature of ~ 10 mK and the enhancement factor for the rf field, while the electric interaction splits the NMR-ON resonance into a set of $2I$ subresonances. If the quadrupole splitting is large enough in comparison to the resonance linewidth (caused mainly by inhomogeneous broadening) it may be possible to resolve the resonance structure and thus to determine the quadrupole splitting with resonance precision.

The first experiments in this context were performed with Fe and Ni matrices.[2] They were based on the fact that for high-Z impurities in (cubic) Fe and Ni a small EFG exists which arises from an unquenched orbital momentum and is thus collinear with the hyperfine field. These EFG's are so small, however, that the subresonance structure could be resolved only for a few selected low-spin isotopes.

Thus other magnetic matrices with larger EFG's would be desirable. Two well-known crystals which fulfill this condition are hcp Co and hcp Gd. In a recent Letter, Ebeling *et al.*[3] reported the first observation of a NMR-ON resonance in Gd. They supposed that, for quadrupole-interaction–resolved NMR-ON (QI-NMR-ON) hcp Gd could be superior to hcp Co as Co undergoes a hcp-fcc phase transition at $\sim 400\,^{\circ}$C, which restricts annealing to temperatures below the transition temperature. Further experiments showed, however, that the implantation behavior of heavy elements into Gd is complicated and, e.g., the NMR-ON resonances of ^{198}Au and ^{199}Au in Gd could not be detected.[4] Recently, Roman *et al.*[5] reported the first NMR-ON experiment of ^{160}Tb in a Tb matrix. Here, because of the large EFG originating from electrons in the $4f$ shell, the quadrupole subresonances are separated by several hundred MHz. In this case, it is difficult to find the higher quadrupole subresonances, the amplitudes of which are in general much smaller than that of the lowest subresonance. Actually, Roman *et al.*[5] found only the lowest

subresonance. They could determine the quadrupole splitting only via the offset from the magnetic hyperfine splitting, which was possible as the magnetic moment had already been known. Meanwhile, Marshak *et al.*[6] reported the observation of the second quadrupole subresonance of Tb:^{160}Tb with a double-resonance technique. However, neither Gd nor Tb will be ideal matrices for future on-line measurements.

Here we report the first QI-NMR-ON experiments with hcp Co as host matrix. The isotopes ^{198}Au and ^{199}Au were mass-separator implanted simultaneously into a hcp-Co single crystal, and NMR-ON measurements were performed at $T\sim 10$ mK. The quadrupole subresonance structure could be resolved well for both isotopes, not only on annealed but also on unannealed samples, the resonance linewidths of the unannealed samples being only slightly larger than those of the annealed samples.

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

$$W(\theta)=1+f\sum_k B_k(\nu_M,\nu_Q,T)A_kP_k(\cos\theta)Q_k. \quad (1)$$

The parameters B_k describe the degree of orientation; they depend on the temperature T and on the magnetic and electric hyperfine splitting frequencies

$$\nu_M=|g\mu_N B_{\rm hf}/h|, \quad \nu_Q=e^2qQ/h, \quad (2)$$

where g and eQ are the nuclear g factor and the spectroscopic quadrupole moment, and $B_{\rm hf}$ and eq are the magnetic hyperfine field and the EFG, respectively. For hcp Co, $\nu_M\gg|\nu_Q|$, the degree of orientation is mainly fixed by the ratio $h\nu_M/k_BT$ and nearly independent of ν_Q. The parameters A_k in Eq. (1) are products of the normally used angular correlation coefficients F_k and deorientation coefficients U_k; they depend on the specific properties of the nuclear decay cascade. The parameter f describes, in a two-site model, the fraction of nuclei which are subject to the full hyperfine interaction, while the residual fraction of nuclei, $1-f$, sees a negligibly small hyperfine interaction. In NMR-ON experiments the resonant change of $W(\theta)$ is used as the detector for NMR. In the case of a combined magnetic dipole plus electric quadrupole interaction there exists a set of $2I$ subresonances. (Here I is the spin of the oriented state.) The center of the subresonance corresponding to rf transitions between state $|m\rangle$ and $|m+1\rangle$ is given by, with the assumption that the $m=I$ state lies lowest in energy,

$$\nu_{m\to m+1}=\nu_M+\Delta\nu_Q(m+\tfrac{1}{2}), \quad (3)$$
$$\Delta\nu_Q=3\nu_Q/[2I(2I-1)],$$

where $\Delta\nu_Q$ is the subresonance separation. It should be noted that, in contrast to "normal" NMR, the subresonance amplitudes depend on the specific properties of the decay cascade and the direction of observation. This is due to the fact that the observable is a mixture of rank-2 and rank-4 tensors, whereas the observable in normal NMR experiments is the magnetization, i.e., a rank-1 tensor.

Samples were prepared from a hcp-Co single crystal available commercially. Disks with a diameter of ~ 10 mm and a thickness of ~ 0.2 mm were spark cut from the crystal, the c axis being oriented parallel to the plane of the disk. (This geometry was chosen in order to avoid nuclei being implanted into closure domains.) The disks were fist mechanically polished with 1-, 0.5-, and 0.25-μm diamond paste and then electropolished for 8-10 min in H_3PO_4 (concentration 85%).

Implantations of ^{198}Au and ^{199}Au were carried out with use of the mass separator at Universität Konstanz at a voltage of 350 kV and total doses between 40 and 50 μC/cm^2. After the implantation one sample was annealed for 6 h at 360 °C in high vacuum, soldered with GaIn to one side of the Cu cold finger of an adiabatic demagnetization cryostat, and cooled to a temperature of ~ 10 mK. The temperature was monitored with a Co(hcp):^{60}Co thermometer soldered to the other side of the cold finger. A magnetic field of 100 G was applied parallel to the c axis of the crystals to establish that the soldered joints were normal conducting. The γ rays were detected with four $\sim$100-cm^3 Ge(Li) detectors which were placed at 0°, 90°, 180°, and 270° with respect to the c-axis of the single crystals. From the analysis of the γ anisotropies according to Eq. (1) the full-field fraction f was found to be 0.93(3) and 0.87(7) for ^{198}Au and ^{199}Au, respectively.

Figure 1 shows NMR-ON spectra of the 412-keV transition of ^{198}Au measured at 0°, and 180° (top) and 90° and 270° (bottom). The quadrupole-interaction substructure is well resolved. The following features are evident: (i) The subresonance amplitudes are different for 0° and 90°. This is due to the fact that the $k=2$ and $k=4$ contributions to the resonance destruction enter with different weights for 0° and 90°, which, in addition, depend on the specific sublevel transition (and on the temperature). (ii) The resonance linewidth of the "inner" resonances (corresponding to sublevel transitions between $m=\pm 1$ and $m=0$), $\Gamma_i=0.99(14)$ MHz, is smaller than the linewidth of the "outer" resonances (transitions between $m=\pm 2$ and $m=\pm 1$), $\Gamma_o=1.46(6)$ MHz. (For the determination of the linewidths the frequency distribution of the sinusoidal frequency modulation has been taken into account.) The difference in the linewidths must be ascribed to quadrupolar effects. Thus, the linewidth can be separated into a magnetic (Γ_M) and a quadrupolar contribution (Γ_Q), the latter entering according to Eq. (3) with a factor $(m+\frac{1}{2})^2$:

$$\Gamma_i=(\Gamma_M^2+0.5^2\Gamma_Q^2)^{1/2}, \quad \Gamma_o=(\Gamma_M^2+1.5^2\Gamma_Q^2)^{1/2}. \quad (4)$$

With the experimental linewidths quoted before, we find $\Gamma_M=0.91(17)$ MHz and $\Gamma_Q=0.76(11)$ MHz. The rela-

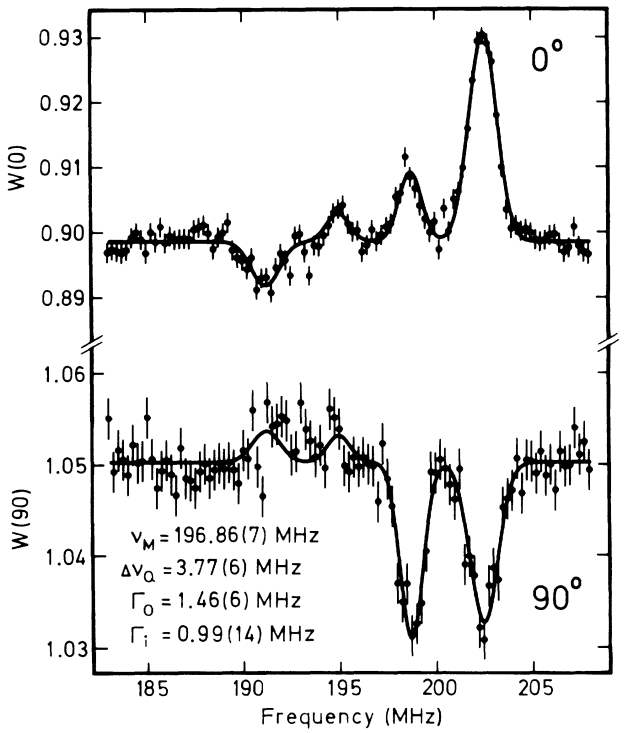

FIG. 1. NMR-ON resonances of the 412-keV transition of ^{198}Au in hcp Co measured with frequency steps 0.25 MHz, total modulation bandwidth 1.0 MHz, and total counting time 30 h. Top: 0°+180°. Bottom: 90°+270°. The different subresonance amplitudes for 0° and 90° are due to the different weights of the $k=2$ and $k=4$ contributions in the γ anisotropy.

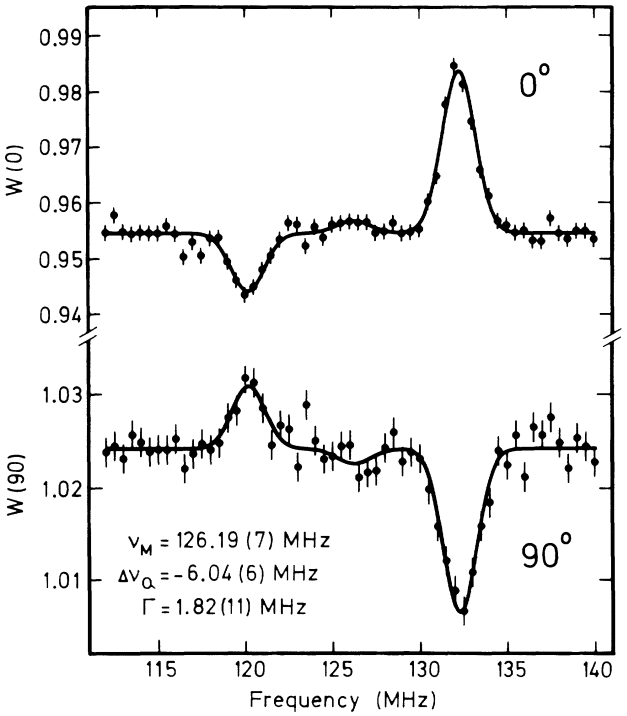

FIG. 2. NMR-ON resonances of the 158-keV transition of ^{199}Au in hcp Co measured with frequency steps 0.5 MHz, total modulation bandwidth 1.5 MHz, and total counting time 19 h. Top: 0°+180°. Bottom: 90°+270°. The similar structure for 0° and 90° is due to the fact that the $k=4$ contribution to the γ anisotropy vanishes for a $\frac{3}{2}$ state.

tive linewidths, Γ_M/ν_M and Γ_Q/ν_Q are strongly different, namely, 5×10^{-3} and 5×10^{-2}, respectively. These data indicate that lattice imperfections in the neighborhood of the impurity atoms influence the EFG much stronger than the magnetic hyperfine field.

Figure 2 shows NMR-ON resonances of the 158-keV transition of ^{199}Au. Here, there is no difference in the subresonance amplitudes for 0° and 90°. This is due to the fact that the $k=4$ coefficient in Eq (1) vanishes for the ground-state spin of $\frac{3}{2}$. The second subresonance corresponding to transitions between $m=-\frac{1}{2}$ and $+\frac{1}{2}$ has a small amplitude, as the resonant equilibration of these substates influences the γ anisotropy only indirectly via the induced change of the population probabilities of the $+\frac{3}{2}$ and $-\frac{3}{2}$ substates. The quadrupole interaction can, however, easily be determined from the positions of the first and third subresonances. The linewidth of the outer lines (transitions between $m=\pm\frac{3}{2}$ and $m=\pm\frac{1}{2}$) is $\Gamma_o=1.9(1)$ MHz. This is larger than 1.40(16) MHz which would be expected by taking into account the data for ^{198}Au and scaling according to the ratio of the magnetic and electric hyperfine splittings. No explanation for this feature can be given at present.

A second experiment was performed with a sample which was not annealed after the implantation. The full-field fractions were found to be 0.90(4) and 0.91(13) for ^{198}Au and ^{199}Au, respectively, i.e., similar to those of the annealed samples. The linewidths were found to be larger by ~10%, whereas the resonance amplitudes were smaller by a factor of ~3. The quadrupole substructure

TABLE I. Results for ^{198}Au in hcp Co.

Sample	f	$\Delta\nu_Q$ (MHz)	ν_M (MHz)	Γ_o (MHz)	Γ_i (MHz)
Annealed	0.93(3)	−3.77(6)	196.86(7)	1.46(6)	0.99(14)
Unannealed	0.90(4)	−3.68(7)	196.89(8)	1.61(10)	1.47(22)
Average	···	−3.73(5)	196.87(5)	···	···

TABLE II. Results for ^{199}Au in hcp Co.

Sample	Transition energy (keV)	f	$\Delta\nu_Q$ (MHz)	ν_M (MHz)	Γ_o (MHz)
Annealed	158	0.87(7)	−6.04(6)	126.19(7)	1.82(11)
	208	...	−6.05(10)	126.14(10)	2.04(12)
Unannealed	158	0.91(9)	−6.01(7)	126.15(7)	2.10(10)
	208	...	−6.06(11)	126.03(11)	2.45(15)
Average		...	−6.03(5)	126.15(5)	...

could be resolved well. The detailed results are compiled in Tables I and II. With the average quadrupole splittings, the ratio of quadrupole moments of ^{198}Au and ^{199}Au is now deduced to be

$$Q(^{198}\text{Au})/Q(^{199}\text{Au}) = +1.24(2),$$

which is smaller than 1.37(3) deduced from QI-NMR-ON measurements with Fe hosts,[7] but in good agreement with 1.26(3) deduced by Herzog *et al.* from nuclear-orientation experiments with Cd and Zn matrices.[8] The origin for the discrepancy with the QI-NMR-ON experiments with Fe cannot be explained at present. We think that, most probably, the quadrupole splitting of Fe:^{198}Au could be incorrect, as it has been deduced from a spectrum in which the quadrupole substructure is not well resolved, with the assumption of one unique linewidth for the four quadrupole subresonances.

Taking the quadrupole moment of ^{197}Au, $Q = 0.547(16)$ b (Ref. 9), and the quadrupole splittings of ^{197}Au and ^{199}Au in Fe, $\nu_Q = -1.50(5)$ MHz (Ref. 10) and $-1.52(2)$ MHz (Ref. 11), respectively, we deduce the spectroscopic quadrupole moment of ^{198}Au to be

$$Q(^{198}\text{Au}) = +0.68(2) \text{ b}.$$

The EFG of Au in hcp Co is found to be

$$eq(\text{Co(hcp):Au}) = -0.90(4)\times 10^{17} \text{ V/cm}^2,$$

which is larger by a factor of 7.9(1) than the EFG of Au in Fe.

In summary, our experiments have shown that quadrupole-interaction-resolved NMR-ON spectroscopy with a hcp-Co host lattice can be performed well. The EFG is large enough that the quadrupole substructure of heavy elements can be resolved well. In this way, ratios of quadrupole moments and, if the field gradient can be calibrated, absolute values of quadrupole moments can be determined with high precision. By a refined surface treatment of the crystals it should be possible to reduce the experimental linewidths further. Thus, for on-line measurements of quadrupole moments of nuclei far from stability, hcp Co is probably the best matrix known at present. Moreover, systematic studies of the magnetic hyperfine interaction in hcp Co together with known data in fcc Co might yield interesting information on the differences in the magnetic properties of these phases.

We are indebted to Professor H.-J. Körner for his interest and support of this work. We also wish to thank E. Smolic and J. Hesol for experimental help. This work was supported by the German Federal Minister for Research and Technology (BMFT) under the Contract No. 06 TM 178/I, and, partly, by the Kernforschungszentrum Jülich, and the Walther Meissner Institut für Tieftemperaturforschung, Garching.

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