New method for the determination of the sign and magnitude of electric quadrupole splittings. II. The electric field gradient of Co in hcp and fcc Co

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The 0°−90° differential resonance displacement $\overline{\Delta\nu}=\overline{\nu(0)}-\overline{\nu(90)}$ and the 0° total resonance displacement $\overline{\nu(0)}-\nu_M$ of the NMR-ON (oriented nuclei) resonances of ^{60}Co in hcp Co have been measured at a temperature $T=10(1)$ mK as $+57(6)$ kHz and $+0.44(9)$ MHz, respectively. Using the relations $\nu_Q=c_1\overline{\Delta\nu}$ and $\nu_Q=c_2(\overline{\nu(0)}-\nu_M)$, where c_1 and c_2 are calculable constants, the quadrupole splitting $\nu_Q=e^2qQ/h$ is deduced as $-3.1(4)$ MHz. In combination with NMR data on ^{59}Co*Co* (hcp) the electric field gradient (EFG) in hcp Co is found to be $-0.30(3)\times10^{17}$ V/cm^2. The negative sign supports the correlation of EFG's in hcp transition metals reported recently. For ^{60}Co*Co* (fcc) a small positive quadrupole splitting $\nu_Q=+0.75(39)$ MHz was observed.

I. INTRODUCTION

For systems of impurity nuclei in a ferromagnetic host lattice such as Fe, Ni, Co, or Gd a small quadrupole interaction (QI) $\nu_Q=e^2qQ/h$ may be superimposed to a much larger magnetic hyperfine splitting $\nu_M=|g\mu_N B_{\rm hf}/h|$. In part I (preceeding paper)[1] it has been shown that the sign and magnitude of ν_Q can be determined from the 0°−90° differential resonance displacement of the NMR-ON (nuclear magnetic resonance on oriented nuclei) resonances, even if $|\nu_Q|$ is so small (in comparison to the inhomogeneous linewidth Γ) that neither the quadrupole subresonances can be resolved nor an asymmetry of the resonance spectrum can be detected. Such conditions are present for hcp Co. From NMR measurements on stable ^{59}Co in hcp Co (Ref.2), the absolute value of the QI was measured as $|\nu_Q(^{59}\text{Co}Co)|=2.90(7)$ MHz. The sign of ν_Q, however, could not be determined because of fundamental principles. Especially for the better understanding of electric field gradients (EFG's) in noncubic metals,[3−6] the sign of the QI is an interesting quantity. Here we report on the measurement of sign and magnitude of the QI of ^{60}Co in hcp Co. We further present data for ^{60}Co in fcc Co.

II. EXPERIMENTAL DETAILS

The ^{60}Co*Co* (hcp) sample was prepared in the following way. From a hcp Co single crystal rod a disk (diameter 5 mm, thickness 0.1 mm) was spark cut, the *c* axis being oriented perpendicular to the disk plane. The disk was mechanically and electrolytically polished to a final thickness of ~9 μm and neutron irradiated at the Munich research reactor FRM for ~10 min in a neutrom flux of 10^{13} *n*/sec cm.^{2} After the neutron irradiation the crystal was annealed for 24 h at 350 °C. (For $T>380$ °C a phase transition hcp→fcc takes place.)

The ^{60}Co*Co* (fcc) sample was prepared by neutron irradiation of a Co foil (area 8×8 mm^2, thickness 2 μm; purchased from Goodfellow Metals LTD). After the irradiation the Co foil was annealed for 24 h at 650 °C. The cooling down to room temperature was performed within a few minutes. In this way it could be assured that the growing of hcp regions was suppressed completely.

After the heat treatment the samples were soldered to the cold finger of an adiabatic demagnetization cryostat and cooled to a temperature of 10 mK. Details of the cryostat are given in Ref. 7. Parallel to the foil plane of the samples a small external magnetic field $B_0=0-7$ kG could be applied. In the case of fcc Co this external field is necessary to orient the ferromagnetic domains and thus to establish a unique direction of the hyperfine field. For hcp Co a spontaneous magnetization parallel to the *c* axis is present; i.e., in our case perpendicular to the foil plane.

Perpendicular to B_0 the rf field B_1 was applied with either a one-turn or a double-turn

Helmholtz-type rf coil, the direction of the rf field being parallel to the foil plane too. The rf was 100 Hz−1 kHz frequency modulated with a total bandwidth $\Delta f_t = 100-200$ kHz. The frequency was varied continuously (sweep-mode) or in steps (step-mode) over the resonance region. The frequency resolution and measurement time per frequency interval were chosen as 20−100 kHz and 10−40 sec/100 kHz, respectively. The γ rays were detected with three 7.5 cm diam $\times$7.5 cm NaI (Tl) detectors which were placed at $\theta=0°$, 90°, and 180° with respect to B_0. The γ-ray counts of the 1.17- and 1.33-MeV γ transitions were selected with single-channel discriminators, accumulated in a multichannel analyzer as a function of the rf-center freqency, and recorded onto magnetic tape. Details of the NMR-ON data processing are given in Refs. 7 and 8. The final analysis of the data was performed at the Amdahl 470 computer of the IPP in Garching.

III. EXPERIMENTAL RESULTS

A. ^{60}Co*Co* (hcp)

Figure 1 shows NMR-ON spectra measured for $B_0=0$ kG at $\theta=0°$ (top) and $\theta=90°$ (bottom). The temperature of the sample varied slightly between ~9 and 11 mK. The parameters were the following: frequency range 125.2−128.8 MHz; frequency resolution 0.1 MHz per channel; counting time 40 sec/100 kHz; rf input power $P_{rf}=7$ dBm ($\hat{=}5$ mW); rf modulation width $\Delta f_t=100$ kHz. The measurements were performed in step-mode[7] in the following sequence: 125.2, 125.3, . . . , 128.7, 128.8, 128.7, . . . , 125.3, 125.2 MHz. During the ing periods of 40 sec the center frequency ν_c was kept stable. After completion of the counting periods, ν_c was swept rapidly to the next nominal frequency within ~0.1 sec. During that time the rf power was switched off in order to avoid the occurrence of adiabatic-fast-passage changes of the γ anisotropies. Always two successively measured spectra with opposite sweep direction were added together.

For the spectra shown in Fig. 1 a total of five 125.2−128.8−125.2 MHz cycles were added. The solid lines in Fig. 1 represent the results of least-squares fits for which a Gaussian line shape and a linear background have been assumed as theoretical curves. It is evident that the centers of the 0° and 90° resonances are displaced by ~60 kHz. Similar measurements have been performed for a total of

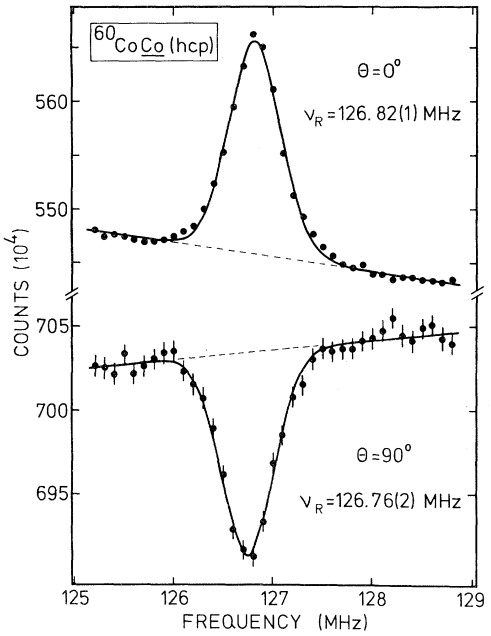

FIG. 1. NMR-ON spectra of ^{60}Co in a hcp single crystal measured at $T=10(1)$ mK for $\theta=0°$ (top) and (bottom). The displacement of the resonance centers is statistically significant.

six different values of the rf power P_{rf}. The resulting 0°−90° differential resonance displacement $\overline{\Delta\nu}=\overline{\nu(0)}-\overline{\nu(90)}$ versus P_{rf} is illustrated in Fig. 2. The shaded area is the result of a least-squares fit for which a linear dependence of $\overline{\Delta\nu}$ on P_{rf} has been assumed. The result $d\overline{\Delta\nu}/dP_{rf}=0.09(70)$ kHz/dBm, demonstrates that the dependence of $\overline{\Delta\nu}$ on P_{rf} is weak. This is in agreement with the theoretical expectation as has been shown in part I. Three independent experiments have been performed, yielding $\overline{\Delta\nu}=60(10)$, 58(8), and 51(12)

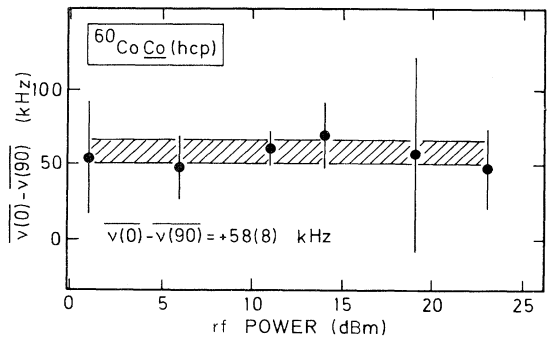

FIG. 2. Differential resonance displacement $\overline{\Delta\nu}=\overline{\nu(0)}-\overline{\nu(90)}$ for ^{60}Co in hcp Co measured at $T=10(1)$ mK a a function of the applied rf power (30 dBm $\hat{=}$1 W).

kHz. The mean value

$$\overline{\Delta\nu}=\overline{\nu(0)}-\overline{\nu(90)}=+57(6)\ \text{kHz}$$

is adopted as the final result. For the average 0° resonance center,

$$\overline{\nu(0)}=126.82(2)\ \text{MHz}$$

has been obtained.

B. ^{60}Co*Co* (fcc)

Figure 3 shows NMR-ON spectra versus frequency and time measured in sweep-mode technique for $B_0=1.06(1)$ kG at $\theta=0°$ (top) and $\theta=90°$ (bottom). The following parameters were chosen: frequency range 122.4–126.4 MHz; frequency resolution 0.1 MHz per channel; counting time 20 sec/100 kHz; rf power $P_{\text{rf}}=1$ dBm; rf modulation width $\Delta f_t=200$ kHz. Normally all resonance spectra measured in sweep-mode technique are somewhat "delayed" in sweep direction; i.e., symmetric in time but asymmetric in frequency. This is due to the finite spin-lattice relaxation time which causes an exponential return of the γ anisotropy to the thermal equilibrium value if the resonance region is passed by the rf. In this way the effective resonance center (the rf frequency for which the resonance amplitude has its maximum value) is shifted in sweep direction. This effect is normally compensated for by adding always two successively measured spectra with opposite sweep direction.

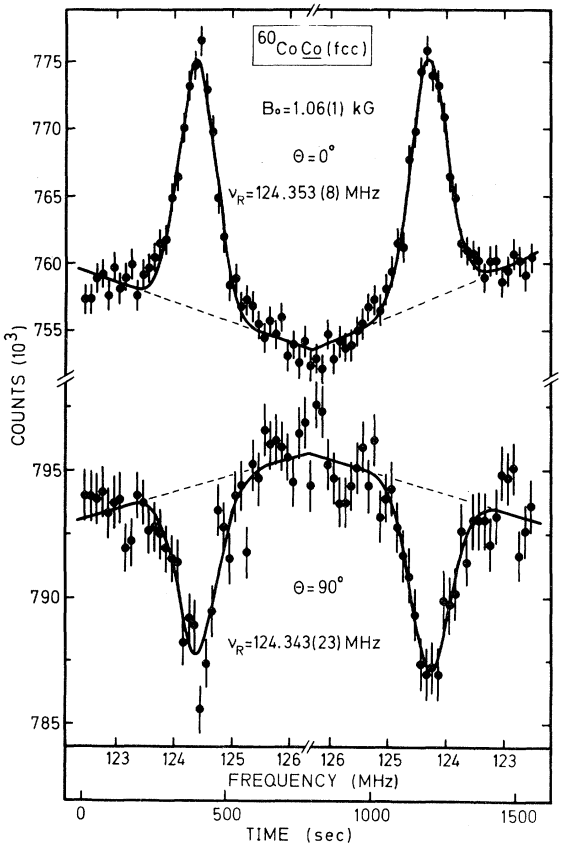

FIG. 3. NMR-ON spectra of ^{60}Co in fcc Co measured in sweep-mode technique versus frequency and time.

An analysis of the time dependence of such sweep-NMR-ON spectra yields information on the resonance center ν_R and the spin-lattice relaxation time T_1' simultaneously. This has been discussed in detail in Ref. 8. The solid line in Fig. 3 is the result of a least-squares fit using the relation[8]

$$R(\nu)=R_a(\nu)+\int_{\nu_1}^{\nu} R_a(\nu')\exp[-(\nu-\nu')/(T_1'\rho)]d\nu' \quad (1a)$$

for the sweep-up and

$$R(\nu)=R_a(\nu)-r\int_{\nu_2}^{\nu} R_a(\nu')\times\exp[-(\nu'-\nu)/(T_1'\rho)]d\nu' \quad (1b)$$

for the sweep-down. Here $R_a(\nu)$ is the "adiabatic" resonance with center ν_R which would be obtained in the limiting case that all spin-lattice relaxation effects can be neglected. $R_a(\nu)$ depends on the distribution of the hyperfine field for which a Gaussian line has been assumed. In Eqs. (1a) and (1b) ρ is the sweep rate, $\nu_{1,2}$ are the lower and upper frequency boundaries, and r is a parameter which takes into account that the resonance amplitudes for both sweep directions may be different. For the decay of the γ anistropy a single-exponential function with time constant T_1' is assumed. This is justified for moderate rf powers, as has been shown by model calculations in part I.

Similar measurements have been performed for a total of 17 different values of the external magnetic field B_0. The center frequencies ν_R of the 0° and 180° data as a function of B_0 are shown in the upper part of Fig. 4. Assuming a linear dependence of ν_R on B_0 the least-squares fit (solid line in Fig. 4) yields

$$\nu(B_0=0)=124.98(1)\ \text{MHz},$$

$$d\nu/dB_0=-0.583(6)\ \text{MHz/kG}.$$

The main uncertainty of dv/dB_0 results from the calibration of our polarizing field which has been performed with the resonance shift of $^{60}CoFe$, which was found to be reproducible to an accuracy of 1%, assuming $K(^{60}CoFe)=0$ for the Knight-shift parameter. Using the relation

$$|dv/dB_0| = |g(1+K)\mu_N/h| \ , \tag{2}$$

and taking $g(^{60}Co)=0.759\,80(16)$ (Ref.9), we find $K(^{60}CoCo)=0.006(10)$. As the assumption $K(^{60}CoFe)=0$ is possibly not justified,[10] only the difference of the Knight-shift parameters can be quoted reliably:

$$K(^{60}CoCo)-K(^{60}CoFe)=0.006(10) \ .$$

The lower part of Fig. 4 shows the deviation of the measured resonance centers from the fitted straight line. It is a remarkable fact that the resonance centers are well described by a linear behavior on B_0 even for such small polarizing fields $B_0<1$ kG, for which the samples are only partly magnetized.

Figure 5 illustrates $\overline{\Delta\nu}$ versus B_0, $\overline{\nu(0)}-\overline{\nu(180)}$ (top) and $\overline{\nu(0)}-\overline{\nu(90)}$ (bottom). Assuming $\overline{\Delta\nu}$ to be independent of B_0, we find $\overline{\nu(0)}-\overline{\nu(180)}$ $=-1(4)$ kHz which is in agreement with the expectation $\overline{\nu(0)}-\overline{\nu(180)}=0$ and $\overline{\nu(0)}-\overline{\nu(90)}$ $=-15(6)$ kHz. Taking into account the data for $\overline{\nu(180)}-\overline{\nu(90)}$,

$$\overline{\Delta\nu}=\overline{\nu(0)}-\overline{\nu(90)}=-15(5) \text{ kHz}$$

is adopted as final result.

The ratio of resonance amplitudes for both sweep directions [parameter r in Eq (1b)] was found to be in agreement with unity for all spectra. This means that no adiabatic-fast-passage effects for the γ anisotropies have to be considered and that a conventional analysis, neglecting the time dependence of the γ anisotropies, should yield the same results. We have performed such an analysis, i.e., of adding always two successively measured spectra with opposite sweep direction and performing least-squares fits with Gaussian line shapes. All results quoted above were confirmed.

IV. DISCUSSION

In part I it has been shown that the relations

$$\overline{\nu(0)}=\nu_M+\overline{c(0)}\Delta\nu_Q \tag{3}$$

and

$$\overline{\Delta\nu}=\overline{\nu(0)}-\overline{\nu(90)}=\overline{\Delta c}\,\Delta\nu_Q \tag{4}$$

hold. Here $\overline{\nu(0)},\overline{\nu(90)}$ are the effective resonance centers measured for $\theta=0°$ and 90°, ν_M is the mag-

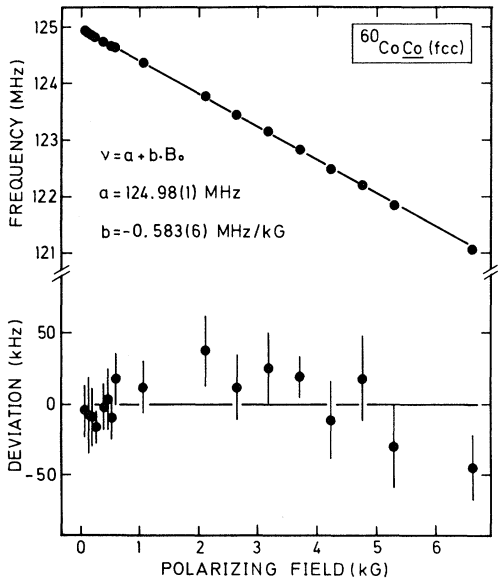

FIG. 4. Resonance centers ν_R of ^{60}Co in fcc Co versus external magnetic field B_0 (top) and deviation of these frequencies from the linear best fit (bottom). Although the sample is not saturated magnetically for $B_0<1$ kG, the resonance centers are well described by the linear behavior on B_0.

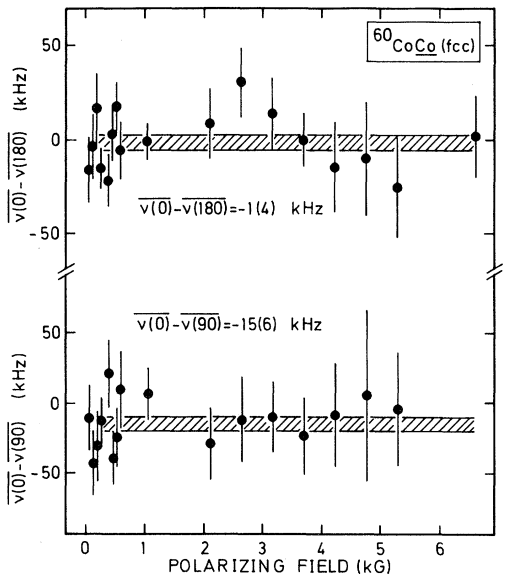

FIG. 5. Differential resonance displacement $\overline{\Delta\nu}$ for $^{60}CoCo$ (fcc) versus B_0. Top: $\overline{\nu(0)}-\overline{\nu(180)}$. Bottom: $\overline{\nu(0)}-\overline{\nu(90)}$. The shaded areas represent the average values plus-minus one standard deviation as obtained from the least-squares fits.

netic hyperfine splitting, and $\Delta\nu_Q$ is the quadrupole subresonance separation. The calculation of the constants $\overline{c(0)}$ and $\overline{\Delta c}$ has been outlined in detail in part I; for $1/T=100(10)$ K^{-1} and $\Delta t=40$ sec one finds $\overline{c(0)}=-3.1(1)$ and $\overline{\Delta c}=-0.61(7)$. [The dependence of $\overline{c(0)}$ and $\overline{\Delta c}$ on the rf power is extremely weak; the corresponding uncertainty is included in the quoted errors.]

From our experimental 0°—90° differential resonance displacement $\overline{\Delta\nu}=+57(6)$ kHz, we find

$$\Delta\nu_Q=-93(16)\text{ kHz}\ .$$

From the experimental 0° resonance displacement we can deduce a second independent value for $\Delta\nu_Q$. With $\nu_M=219.9(1)$ MHz for the magnetic hyperfine splitting in the direction of the c axis of stable ^{59}Co in hcp Co (Ref.2) and the ratio of g factors, $g(^{60}\text{Co})/g(^{59}\text{Co})=0.5747$,[11] one expects $\nu_M=126.38(7)$ MHz for ^{60}Co in hcp Co. Taking $\overline{\nu(0)}=126.82(2)$ MHz as quoted in Sec. III A, we find $\overline{\nu(0)}-\nu_M=0.44(9)$ MHz, from which

$$\Delta\nu_Q=-142(29)\text{ kHz}$$

is deduced. The mean value

$$\Delta\nu_Q=-104(14)\text{ kHz}$$

is adopted as final result, from which the quadrupole interaction frequency

$$\nu_Q=-3.1(4)\text{ MHz}$$

is obtained. For ^{59}Co*Co* Kawakami *et al.*[2] found $|\nu_Q|=2.90(7)$ MHz. The ratio $|\nu_Q(^{60}\text{Co})/\nu_Q(^{59}\text{Co})|=1.07(14)$ is in good agreement with the ratio of quadrupole moments $Q(^{60}\text{Co})/Q(^{59}\text{Co})=+1.11(6)$.[11] Combining the results for ^{59}Co and ^{60}Co, the EFG of Co in hcp Co is deduced to be

$$eq=-0.30(3)\times10^{-17}\text{ V/cm}^2\ .$$

The negative sign fits well into the systematics of EFG's in hexagonal transition metals as proposed by Raghavan *et al.*[3,4] and extended by Ernst *et al.*[5,6] For ^{60}Co*Co* (fcc) the interpretation of the 0°—90° differential resonance displacement $\overline{\Delta\nu}=-15(5)$ kHz, is more difficult, since, in order to get a statistically significant resonance effect in a resonable measurement time, the modulation width Δf_t had to be chosen relatively large in comparison to $|\Delta\nu_Q|$. This means that not only one quadrupole subresonance can be affected simultaneously by the rf. In this way a stronger dependence of $\overline{\Delta c}$ on the rf power is introduced. Estimating $\overline{\Delta c}=-0.60(25)$— the negative sign is unique —

$$\Delta\nu_Q=+25(13)\text{ kHz}\ ,$$

and hence

$$\nu_Q=+0.75(39)\text{ MHz}$$

is obtained. Assuming the direction of the EFG being collinear with the direction of the hyperfine field, the EFG is deduced to be

$$eq=+0.07(4)\times10^{17}\text{ V/cm}^2\ .$$

From Mössbauer-effect measurements on ^{57}Fe in Fe, Spijkerman *et al.*[12] also found positive quadrupole splittings, $\nu_Q=+52(14)$ and $+102(81)$ kHz for $T=298$ K and 4.3 K, respectively, which leads to a similar positive EFG taking into account the ratio of quadrupole moments $Q(^{60}\text{Co})/Q(^{57}\text{Fe};\ 3/2^+)\sim+2.2$. From theoretical calculations,[13—15] the unquenched orbital momentum of the 3*d* electrons should cause a negative EFG; our experimental results are in contradiction with this expectation.

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