Experimental Evidence for a Large Collinear Electric Field Gradient of Ir in hcp-Co

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Measurements of quadrupole-interaction-resolved NMR on oriented nuclei were performed on ^{188}Ir in a hcp-Co single crystal. The magnetic and electric hyperfine interaction frequencies were determined as function of the angle θ between the electronic magnetization $\vec{M}$ and the single crystal c axis. A large collinear electric field gradient (CEFG) (principal axis parallel $\vec{M}$) was found, $eq^{(c)} = -0.378(7) \times 10^{17}$ V/cm^2. Within the series of the 5d elements Ir, Pt, Au, and Hg this is exceptional: The experimental CEFG's of Pt, Au, and Hg in hcp-Co are at least ~2 orders of magnitude smaller and consistent with $eq^{(c)} = 0$. [S0031-9007(98)05894-3]

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It is well known that an electric field gradient (EFG) exists at the nuclear site of atoms dissolved as dilute impurities in the cubic ferromagnetic hosts Fe, Ni, and fcc-Co [1–10]. The existence of an EFG in a cubic ferromagnetic host lattice has been attributed to an unquenched orbital momentum caused by the spin-orbit interaction of the nd electrons [4,8,9]. The principal axes system of this EFG is given by the direction of the magnetization; the electric and magnetic hyperfine interactions are thus collinear. Especially for 5d elements the collinear EFG (CEFG) $eq^{(c)}$ is relatively large. Experimental data exist for IrFe [1,4,10], IrNi [1,4], AuFe [5], AuNi [6], Au$Co^{(\mathrm{fcc})}$ [7], PtFe [6], and Pt$Co^{(\mathrm{fcc})}$ [6]. As the CEFG originates from the spin-orbit interaction of the nd electrons at the impurity site, such a CEFG could exist also for nd elements as dilute impurities in hcp-Co. In hcp-Co, however, a relatively large EFG exists because of the noncubic lattice structure, which we denote in the following as lattice EFG (LEFG) $eq^{(L)}$. Both contributions can be separated due to the different transformation properties against rotation of the magnetization $\vec{M}$ with respect to the crystal axis c. Whereas the CEFG is (to first approximation) invariant against rotation of the magnetization, the LEFG has second-order-tensor transformation properties. Actually, for ^{59}Co$Co^{(\mathrm{hcp})}$ the existence of a small rotation-invariant EFG has been reported in the literature [11,12]. Thus, taking into account that the CEFG's of 5d elements in Fe and Ni are by ~2 orders of magnitude larger than those of the 3d elements, a moderately large CEFG was to be expected for 5d elements in hcp-Co. First experiments on ^{198}Au$Co^{(\mathrm{hcp})}$, however, gave evidence that the CEFG for Au in hcp-Co is extremely small and consistent with zero, $eq^{(c)}(\mathrm{Au}Co^{(\mathrm{hcp})}) = -0.002(3) \times 10^{17}$ V/cm^2 [13]. Comparing this with the CEFG of Au in Fe and fcc-Co, $eq^{(c)}(\mathrm{Au}Fe) = -0.113(5) \times 10^{17}$ V/cm^2 [5], $eq^{(c)}(\mathrm{Au}Co^{(\mathrm{fcc})}) = (-)0.11(3) \times 10^{17}$ V/cm^2 [7], one might conclude that the CEFG of Au in hcp-Co is zero because of a symmetry of the local electronic wave function. In order to clarify whether the CEFG's are comparably small for all 5d elements, we performed measurements on Pt, Hg, and Ir in hcp-Co. Actually, for Pt and Hg in hcp-Co a similar behavior was found as for Au: The CEFG is—if at all existent—extremely small and consistent with zero, too: $|eq^{(c)}(\mathrm{Pt}Co^{(\mathrm{hcp})})| \leq 0.008 \times 10^{17}$ V/cm^2, $|eq^{(c)}(\mathrm{Hg}Co^{(\mathrm{hcp})})| \leq 0.013 \times 10^{17}$ V/cm^2 [6]. For Ir in hcp-Co, however, now completely unexpected, a very large CEFG was found. These experiments are presented here.

The hyperfine interaction of radioactive isotopes at substitutional lattice sites in ferromagnetic hcp-Co consists of a magnetic-dipole and an electric-quadrupole contribution:

(i) The magnetic hyperfine field B_{HF} is parallel (antiparallel) to the electronic magnetization $\vec{M}$, the absolute magnitude depending (slightly) on the angle between $\vec{M}$ and the single-crystal c axis. The magnetic interaction frequency is given by

$$\nu_{\mathrm{mag}} = |g\mu_N/h|\,|\vec{B}_{\mathrm{HF}} + \vec{B}_0|\,, \tag{1}$$

$$\vec{B}_0 = \vec{B}_{\mathrm{ext}} - \vec{B}_{\mathrm{dem}}\,, \tag{2}$$

where B_{ext} is the applied external magnetic field, B_0 is the (effective) external magnetic field at the nuclear site, and B_{dem} is a demagnetization field, which depends on the geometry of the sample.

(ii) Because of the hexagonal symmetry of hcp-Co, an axially symmetric lattice electric field gradient (LEFG) $eq^{(L)}$ exists, the principal axis being given by the single-crystal c axis. In addition, a CEFG $eq^{(c)}$ may exist, the

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principal axis being given by the direction of $\vec{B}_{\mathrm{HF}}$. The strength of the electric interaction is described by the quadrupole interaction frequencies $\nu_Q^{(c,L)}$

$$\nu_Q^{(c,L)} = e^2 q^{(c,L)} Q/h\,, \tag{3}$$

where eQ is the nuclear spectroscopic quadrupole moment. For IrFe, it was found recently that the CEFG depends on the direction of magnetization with respect to the crystallographic axes [10]. Such a directional dependence of the CEFG might also occur for hcp-Co; it is—if existent—in first order described by

$$\nu_Q^{(c)} = \nu_Q^{(c,\mathrm{iso})} + \nu_Q^{(c,\mathrm{anis})} P_2(\cos\theta)\,, \tag{4}$$

where θ is the angle between the electronic magnetization $\vec{M}$ and the single crystal c axis.

In the absence of an external magnetic field B_{ext}, or if B_{ext} is applied parallel c, $\vec{M}$ and $\vec{B}_{\mathrm{HF}}$ are parallel to the c axis, which is the direction of spontaneous magnetization. We denote this as "0° geometry." By applying an external magnetic field B_{ext} perpendicular to the c axis ("90° geometry"), the direction of the magnetization can be turned away from the c axis ($B_{\mathrm{ext}} = 0$) towards the direction of the external magnetic field, which is reached for $B_0 \geq B_A^{\perp}$ ($B_{\mathrm{ext}} \geq B_A^{\perp} + B_{\mathrm{dem}}$), where $B_A^{\perp} =$ 13.5 kG is the perpendicular anisotropy field. The angle θ between $\vec{M}$ and c can be adjusted between 0° and 90° via B_{ext}: It is obtained from the minimum of the total energy

$$E_{\mathrm{tot}} = K_1 \sin^2\theta + K_2 \sin^4\theta - \vec{M}(\theta)\vec{B}_0\,, \tag{5}$$

where K_1 and K_2 are the known anisotropy constants for Co.

The energy eigenvalues E_m of the nuclear spin system are calculated by diagonalization of the Hamiltonian,

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_M + \mathcal{H}_Q^{(c)} + \mathcal{D}(\theta)\mathcal{H}_Q^{(L)}\mathcal{D}^{-1}(\theta)\,, \\ \mathcal{H}_M &= -h\nu_{\mathrm{mag}} I_z\,, \\ \mathcal{H}_Q^{(c,L)} &= h\nu_Q^{(c,L)} \frac{3I_z^2 - I(I+1)}{4I(2I-1)}\,, \end{aligned} \tag{6}$$

where $\mathcal{D}(\theta)$ is the normally used rotation matrix and I is the nuclear spin. A set of $2I$ subresonance frequencies $\nu_{m\to m+1} = |E_{m+1} - E_m|/h$ is obtained.

In the following we confine ourselves to $I = 1$ (^{188}Ir). Then two subresonances with frequencies ν_1 and ν_2 exist. Let us, for a simplified discussion, first assume that the lattice quadrupole interaction is small compared to the magnetic interaction, i.e., $|\nu_Q^{(L)}| \ll \nu_{\mathrm{mag}}$. Then, first-order perturbation theory yields that the effective lattice quadrupole interaction follows a $P_2(\cos\theta)$ dependence:

$$\nu_1 = \nu_{\mathrm{mag}}(\theta) - \frac{1}{2}\Delta\nu_Q(\theta)\,, \tag{7}$$

$$\nu_2 - \nu_1 = \Delta\nu_Q(\theta) = \frac{3}{2}[\nu_Q^{(\mathrm{iso})} + \nu_Q^{(\mathrm{anis})} P_2(\cos\theta)]\,, \tag{8}$$

$$\nu_Q^{(\mathrm{iso})} = \nu_Q^{(c,\mathrm{iso})}\,, \tag{9}$$

$$\nu_Q^{(\mathrm{anis})} = \nu_Q^{(L)} + \nu_Q^{(c,\mathrm{anis})}\,. \tag{10}$$

Experimentally, $\nu_Q^{(\mathrm{iso})}$ and $\nu_Q^{(\mathrm{anis})}$ are best obtained from measurements of $\Delta\nu_Q(\theta)$ for $\theta = 0°$ ($\Delta\nu_Q^{\parallel}$) and 90° ($\Delta\nu_Q^{\perp}$). Actually, as $|\nu_Q^{(L)}| \ll \nu_{\mathrm{mag}}$ is not fulfilled here, there is a *small* deviation from the $P_2(\cos\theta)$ dependence of the effective lattice quadrupole interaction. In the data analysis this has been taken into account properly. In the absence of a CEFG, $\Delta\nu_Q^{\parallel}/\Delta\nu_Q^{\perp} = -2$ is expected.

In the NMR-ON method the resonant absorption of an applied radio frequency (rf) field is detected via nuclear radiation [14]. The angular distribution $W(\vartheta)$ of γ rays emitted in the decay of oriented nuclei at the temperature T is given by

$$W(\vartheta) = 1 + \sum_{k\ \mathrm{even}} A_k B_k(a_m) P_k(\cos\vartheta) Q_k\,, \tag{11}$$

where all parameters have their conventional meaning [15]. In the present work the "anisotropy"

$$\epsilon = W(0°)/W(90°) - 1 \tag{12}$$

has been analyzed.

Samples of ^{188}Ir$Co^{(\mathrm{hcp})}$ were prepared at the mass-separator ISOLDE/CERN. ^{188}Hg, obtained from the spallation reaction of 1 GeV protons on a liquid Pb target, was implanted with $E = 60$ keV into a hcp-Co single crystal disk ($\Phi = 10$ mm; thickness 0.25 mm; c axis parallel to the surface). The following decay chain is relevant:

$$^{188}\mathrm{Hg}(T_{1/2} = 3\ \mathrm{min}) \to {}^{188}\mathrm{Au}(T_{1/2} = 9\ \mathrm{min})$$
$$\to {}^{188}\mathrm{Pt}(T_{1/2} = 10.2d) \to {}^{188}\mathrm{Ir}(T_{1/2} = 41.5h) \to {}^{188}\mathrm{Os}\,.$$

Using a ^{3}He-^{4}He-dilution refrigerator with a top-loading facility, the samples were cooled to temperatures near 10 mK.

For 0° geometry, measurements were performed for ten different values of B_{ext} between 0 and 20 kG. Figure 1 shows both subresonances ν_1 and ν_2 as measured at $B_{\mathrm{ext}} = 10$ kG. The resonance shift of both resonances was in perfect agreement with the expectation according to the known g factor. The subresonance separation was—as expected—independent on B_{ext}; the final average value is

$$\Delta\nu_Q^{\parallel} = -38.08(1)\ \mathrm{MHz}\,.$$

The top part of Fig. 2 shows the result of a 90°-geometry measurement for $B_{\mathrm{ext}} = 18$ kG, from which $\Delta\nu_Q^{\perp} = +9.06(12)$ MHz is obtained. Thus $\Delta\nu_Q^{\parallel}/\Delta\nu_Q^{\perp} = -4.20(6)$, which is strongly different from -2 as expected for a pure lattice quadrupole interaction.

In principle, a deviation of $\Delta\nu_Q^{\parallel}/\Delta\nu_Q^{\perp}$ from -2 could be due to an angular dependence of the principal component of the LEFG. This could be due to an angular dependence of the Sternheimer effect. (The Sternheimer

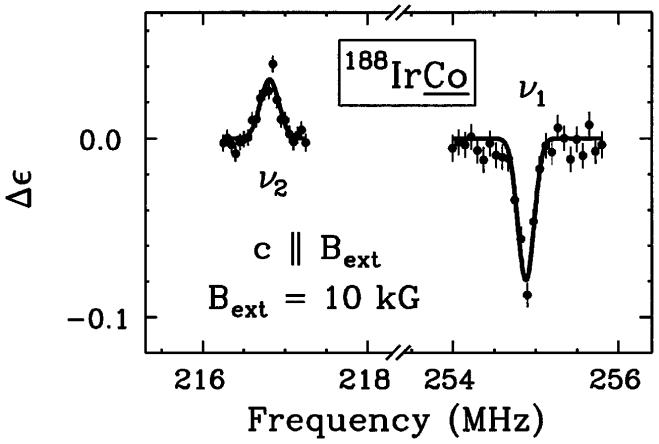

FIG. 1. NMR-ON spectra of $^{188}\mathrm{Ir}Co^{(\mathrm{hcp})}$ measured in 0° geometry. For ν_1 the γ anisotropy is reduced, whereas it is enhanced for ν_2. The latter is due to the population transfer from the $m = 0$ sublevel to the energetically higher $m = 1$ sublevel. Thus, with respect to thermal equilibrium, the sum of populations of the $m = +1$ and -1 states is enhanced by the resonance absorption at ν_2, which is accompanied by an increase of the γ anisotropy.

factor takes into account the (anti)shielding of an external EFG—here the LEFG—by the *local* electrons at the impurity site.) Then, $\nu_Q^{(L)}$ in Eq. (10) has to be replaced by

$$\nu_Q^{(L)}(\theta) = \nu_Q^{(L)}[1 + a_2^{(L)} P_2(\cos\theta)], \qquad (13)$$

where $a_2^{(L)}$ is an anisotropy constant for the LEFG.

Thus, there are two extreme scenarios within which a deviation of $\Delta\nu_Q^{\parallel}/\Delta\nu_Q^{\perp}$ from -2 can be explained, the existence of a large CEFG or an angular dependence of $\nu_Q^{(L)}$. These can be distinguished by a measurement of $\Delta\nu_Q(\theta)$ as a function of θ. Whereas the zero passage of $\Delta\nu_Q(\theta)$ occurs at $\theta = 54.7°$ for the scenario of a pure angular-dependent $\nu_Q^{(L)}$, it is expected at $\theta = 64.0(1)°$ for the scenario of the large CEFG.

Therefore we measured the angular dependence of the subresonance frequencies in 90° geometry. Several spectra are shown in Fig. 2. The resonance centers ν_1 and ν_2 vs B_{ext} are shown in Fig. 3. All data of the 0°- and 90°-geometry measurement together were analyzed with a *least-squares* fit, in which the isotropic and anisotropic parts of the magnetic and the electric hyperfine interaction were free parameters, as well as the demagnetization field and the exact angle α between c and B_{ext}. For each value of B_{ext} the angle θ was determined via Eq. (5). Figure 4 shows $\Delta\nu_Q$ as function of θ. It is evident that the theoretical curves as obtained from the *least-squares* fit (full lines in Figs. 3 and 4) describe the experimental data perfectly. The zero passage of $\Delta\nu_Q$ occurs at 64.4(1.2)°. The *least-squares* fit result for the anisotropy constant of the LEFG is $a_2^{(L)} = -0.02(7)$. Thus the scenario of an angular-dependent $\nu_Q^{(L)}$ can definitely be ruled out, and it

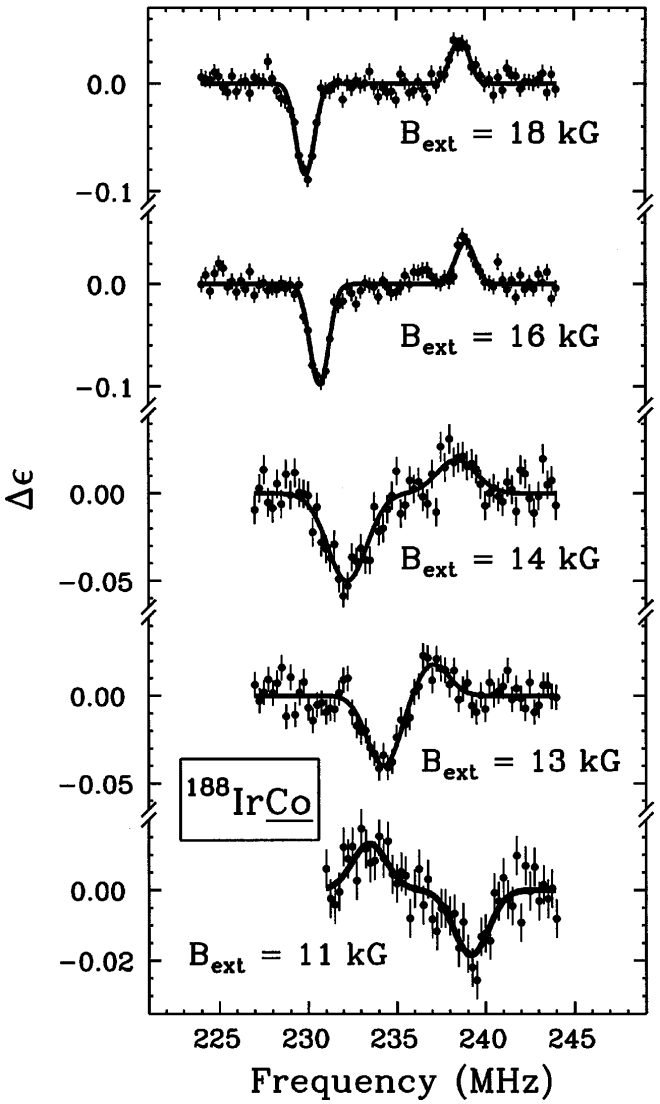

FIG. 2. NMR-ON spectra of $^{188}\mathrm{Ir}Co^{(\mathrm{hcp})}$ measured in 90° geometry for different values of B_{ext}. It is obvious that the effective quadrupole interaction changes sign between $B_{\mathrm{ext}} =$ 13 and 11 kG.

is proven that the strong deviation of $\Delta\nu_Q^{\parallel}/\Delta\nu_Q^{\perp}$ from -2 must be due to the existence of a large CEFG.

Taking $Q(^{188}\mathrm{Ir}) = +0.484(6)$ b [16] and $a_2^{(L)} = 0$, the final values for the EFG's of Ir in hcp-Co are

$$eq^{(L)} + eq^{(c,\mathrm{anis})} = -1.790(23) \times 10^{17}\ \mathrm{V/cm^2},$$
$$eq^{(c,\mathrm{iso})} = -0.378(7) \times 10^{17}\ \mathrm{V/cm^2}.$$

The anisotropic part of the CEFG—if existent—cannot be separated experimentally from the LEFG. The result for the isotropic part is, however, unique. In comparison to all known CEFG's of $3d$, $4d$, and $5d$ elements in Fe, Ni, fcc-Co, and hcp-Co the CEFG of $\mathrm{Ir}Co^{(\mathrm{hcp})}$ is exceptionally large.

Summarizing, we have investigated the quadrupole interaction of $5d$ elements in hcp-Co to answer the

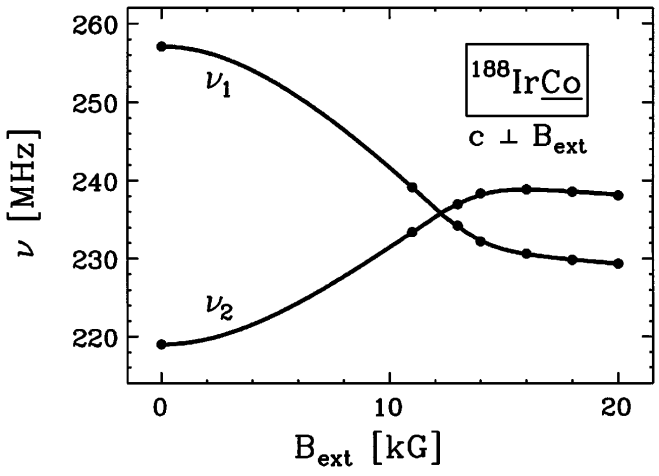

FIG. 3. Dependence on the external magnetic field of the subresonances ν_1 and ν_2 in 90° geometry. The solid lines are the result of a *least-squares* fit. The resonance crossing ($\Delta\nu_Q = 0$) occurs at $B_{\text{ext}} = 12.2$ kG.

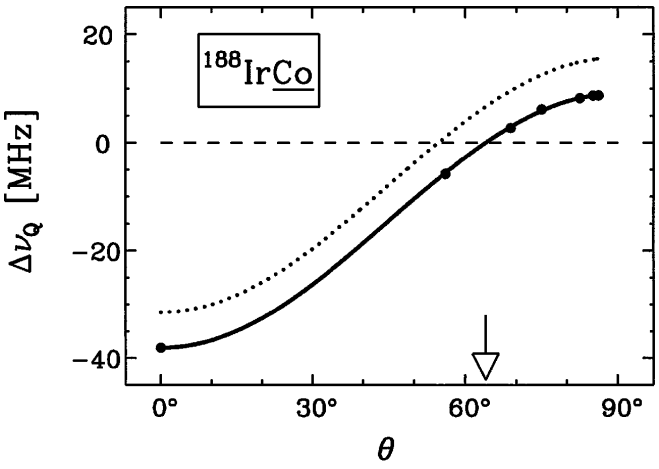

FIG. 4. Dependence of the effective quadrupole splitting on the angle θ between the electronic magnetization $\vec{M}$ and the single-crystal c axis. The zero passage occurs at 64.4(1.2)° which proves the existence of a collinear EFG of Ir in hcp-Co. The dotted curve represents the lattice contribution to the effective quadrupole splitting (zero passage at 54.7°).

question whether a collinear EFG acts, similar to those known for the 5*d* elements in Fe, Ni, and fcc-Co. The situation for hcp-Co was found to be completely different: Whereas the CEFG of Pt, Au, and Hg is very small—the experimental results are consistent with zero—a very large CEFG was found for Ir in hcp-Co. These findings should stimulate theoretical work on this subject.

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