Comparison of Electric-Field-Gradient Distributions between Ferromagnetic hcp and fcc Cobalt

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The high-resolution hyperfine spectroscopy, modulated adiabatic passage of oriented nuclei (MAPON), has been applied for the first time to high-purity, elemental systems. Detailed comparisons between the electric-field gradients (efg's) and, in particular, their distributions are obtained for ^{60}Co*Co* where the hosts are a single crystal of hcp cobalt and a polycrystalline cobalt foil of predominantly fcc character. Further comparisons between these MAPON data and earlier ^{59}Co NMR data on hcp cobalt metal strongly support additivity of efg's between lattice and local ion contributions.

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During the course of the extensive and systematic experimental studies on magnetic hyperfine fields in crystallographic cubic ferromagnet metals [1] it was discovered that, quite generally, there is a substantial electric-field gradient (efg) acting on the impurity nuclei [2]. The source of the efg has been attributed to the unquenched orbital angular momentum on the impurity atom, providing, through the relativistic spin-orbit coupling on that atom, an electric quadrupole hyperfine interaction (EQI) for nonspherical nuclei. This interaction is nominally isotropic with respect to an applied magnetic field [3] and may be several hundred kilohertz in strength for heavy mass ($A > 180$) impurity nuclei, but rapidly diminishes to a few kilohertz for lighter impurity nuclei. Recently it has been shown [4] that cobalt metal in its hexagonal-close-packed (hcp) form is a superior host to Fe or Ni for the observation of frequency-resolved quadrupolar splittings of heavy radioactive impurity atoms in implanted source experiments employing continuous-wave nuclear magnetic resonance on oriented nuclei (NMRON). In these experiments the primary aim is to obtain excited-state nuclear quadrupole moments for comparison with nuclear model calculations. The high-temperature fcc cobalt lattice is a desirable recoil implantation host, which has not yet achieved prominence in the study of excited-state nuclear magnetic dipole moments, nor for that matter, impurity magnetic hyperfine fields. A major difficulty is the preparation of reliable single-phase fcc foils. Unlike the hcp phase of pure Co the efg of the fcc phase is sufficiently small that its EQI (and hence efg) has not been well studied with conventional NMR, nor cw NMRON. Modulated adiabatic passage on oriented nuclei (MAPON) [5] spectra provide in a very direct way, the finer features of the EQI distribution, and hence efg distribution, in those cases where the EQI is a perturbation to a dominant magnetic hyperfine interaction (MHFI). From the solid-state physics viewpoint the significance of high-resolution efg distribution measurements in metals is that they provide a sensitive indicator for what are the primary causes of deviations from perfect cubic symmetry and ultimately provide a benchmark for testing fundamental theories, e.g., *ab initio* band-structure modifications to local impurity wave functions. Prior to this work, MAPON has been applied only to impurity NMRON probes in the ferromagnets Fe and Ni [6–12]. EQI distributions are extremely sensitive to the presence of near-neighbor impurity point defects. The truly isolated-impurity concentration limit is not yet unambiguously established in the ferromagnetic metal hosts, due to the NMRON signal-to-statistical noise requirement of confining the radioactive probe within the radio frequency (rf) skin depth, leading to relatively high ($\sim$0.05–0.5 at.%) local impurity concentrations for reasonable experimental count rates. These additional impurity contributions to the EQI distribution obscure the more intrinsic host and local moment deviations [13–16] from cubic symmetry which may be better studied in the pure elements. The MAPON technique, possessing frequency resolution down to a few hundred hertz, is ideally suited to compare and contrast the two stable low-temperature phases, hcp and fcc, of elemental cobalt, via their respective EQI, and hence efg, distributions. In particular, it is capable of extracting details of the much smaller EQI associated with the fcc coordination. Furthermore, these two martensitic phases of cobalt metal provide an excellent case for the experimental testing of the hitherto assumed additivity of the efg lattice contribution and the local ion contribution.

It is known from earlier studies [17,18] of elemental hcp cobalt using conventional ^{59}Co NMR, that the EQI, as well as the MHFI, is anisotropic. Also, the MHFI's of fcc and hcp cobalt are very similar in strength, the mean hcp magnetic hyperfine field being only $\sim$1.5% higher than the fcc value. In this paper, as well as providing quantitative verification of the new MAPON spectroscopy via comparison with conventional ^{59}Co NMR, the independent study of the hcp single crystal assumes added significance when assigning sites in the more difficult mixed-phase fcc foil. Also, it provides a useful figure of merit to compare with the efg distribution widths of the impurity–cubic-host systems. Altogether, four hcp single crystals of various thicknesses (9, 5, 4.5, and 3 μm) and two fcc foils (both 2 μm) of differing quench history have been studied. Details of sample preparation and of the precursor cw NMRON spectra, single-passage data, and the applied-field variations of the hcp EQI mode values will be published elsewhere [19]. In this Letter we provide only the MAPON spectra for (i) the case of the electronic magnetization **M** parallel to the *c* axis for one hcp crystal, and (ii) the case of one fcc foil for two rf field strengths.

Figure 1(a) shows the raw MAPON spectra for two of the cobalt samples, a mechanically thinned, then electropolished, neutron-irradiated, 5-μm hcp crystal with the *c* axis perpendicular to the plane of the disk, and a neutron-irradiated, annealed, then quenched, 2-μm polycrystalline foil of predominant fcc coordination. These data were obtained for positive dv/dt. Figure 1(b) provides the analytical derivative and hence the relative efg distributions directly. For the sharper distributions studied on the hcp single crystals it was necessary to modify the analytical derivative technique compared with past practice on the broader impurity systems. Instead of differentiating the raw MAPON data directly, differentiation of best-fit smooth curves to the integral data were

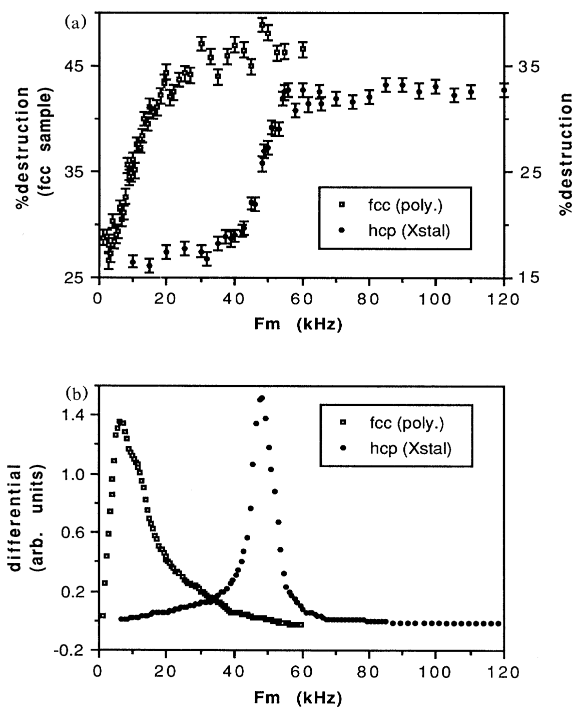

FIG. 1. (a) Raw MAPON data for a 2-μm-thick polycrystalline fcc cobalt foil in 0.2-T applied magnetic field, and a 5-μm hcp single crystal in zero field, with the detector parallel to the *c* axis. For the fcc specimen the rf voltage was 8.2 V p.p. and for the hcp specimen 30 V p.p. In both cases the rf sweep, dv/dt, was positive and the sweep duration was 147 ms. (b) The analytical differentials of these spectra.

obtained, at much higher data density. The abscissas are labeled in terms of the modulation frequency which equates directly to $P/h = 3e^2qQ/4I(2I-1)h$. The mode EQI for ^{60}Co in the hcp single-crystal cobalt is $-48.5(5)$ kHz with FWHM 7.4(7) kHz, and using the value for the quadrupole moment of $Q_{60} = +0.44(5)$ b [20] yields an efg of $V_{zz}(=eq) = -27.3(32)\times 10^{19}\,\mathrm{V\,m^{-2}}$. This agrees with the value of $-27.7(28)\times 10^{19}\,\mathrm{V\,m^{-2}}$ [$Q_{59} = +0.404(40)$ b [20]] obtained using conventional ^{59}Co*Co* NMR, wherein the EQI information is derived to a typical accuracy of $\pm 0.6\%$ from fitting the amplitude modulation of the spin-echo T_2 decay [18]. This ^{60}Co*Co* EQI value is also in accord with the less accurate measurement by Hagn and Zech [21] using 0°-90° differential cw NMRON. Defining a nuclear-parameter-free figure of merit for sharpness of the efg distribution as $F = |\bar{P}|/\Delta P$, where ΔP is the FWHM of the EQI distribution, it is found that the hcp Co sample yields an F value of 6.6(7), i.e., 2.1(4) times greater than the most dilute impurity system studied so far in crystallographically cubic ferromagnetic hosts, viz. ^{57}Co in codiffused ^{60,57}Co*Fe* [9] for which $F = 3.1(4)$ was obtained using the same differentiation procedure as above. Although the hcp Co result is the sharpest efg distribution so far measured in a metal the mode efg in hcp Co is, for $\mathbf{B}_{\mathrm{app}} \| c$ axis, approximately 8–12 times the mode efg for impurities in bcc iron, due to the lattice contribution. It therefore appears that with appropriate care in sample preparation, the impurity cubic host systems are providing close to the intrinsic isolated-impurity efg average or mode value. Note that this simple comparison does not take into account the fundamental, low mode asymmetric Poisson-like nature of the impurity efg distribution (which would increase ΔP), wherein impurity near neighbors, and also dislocations and other crystal defects, contribute to a *high-frequency* tail [22], and in extreme cases of higher impurity doping, elevation of the mode value to higher frequencies [8]. The almost symmetric EQI [Fig. 1(b), hcp] and hence efg distribution of the hcp Co sample is, to date, unique in MAPON studies. There is no significant high-frequency tailing, reflecting the high quality of the single-crystal sample and, as expected, the absence of impurity point-defect contributions to the efg. However, additional experiments [19] provide, in striking contrast to the impurity systems, marked *low-frequency* asymmetry when the detector is orthogonal to the *c* axis, but the applied field is not quite strong enough (< 1.7 T) [17,18] to turn all the components of **M** into the detector direction—i.e., reflecting the incomplete alignment of **M** components with the detector and external magnetic-field direction.

Low-field (≤ 0.2 T) cw NMRON spectra on both fcc foil samples gave no evidence for the presence of parasitic hcp phase; however, higher-field ($B_0 \sim 0.6$–0.7 T) cw NMRON spectra did provide NMRON intensity in the hcp magnetic frequency domain. Despite an improved quench procedure on the second foil, with the aim of removing the parasitic hcp phase, it was found that there still remained a significant but slightly reduced hcp shoulder in the high-field (0.6–0.7 T) cw NMRON spectra; this difficulty to completely remove the more stable low-temperature hcp phase is in accord with the observations of others [23,24]. The MAPON sweeps were carefully restricted to eliminate contributions from the parasitic hcp phase. The low mode, Poisson-like asymmetry of the fcc cobalt EQI distribution shown in Fig. 1(b) is very similar to that for impurity systems. Figure 2(a) provides the integral MAPON spectra for the fcc cobalt foil for two rf voltages, the low-power 8.2-V-p.p. run of Fig. 1(a), and a high-power 30-V-p.p. run for comparison. Their analytic differentials, using the same technique as for the hcp specimen, are shown in Fig. 2(b). From Fig. 2(b) the smaller and more intrinsic mode value for the fcc cobalt is $\bar{P}/h=-6.2(4)$ kHz with a FWHM of 12.0(7) kHz, yielding a mode efg of $V_{zz}=-3.5(5)\times10^{19}\ \mathrm{V\,m^{-2}}$. Also from Fig. 2(b), for the higher-power run, the mode value is seen to be 13.8(5) kHz with a FWHM of 20.1(5) kHz. We believe these marked increases in mode value and distribution FWHM are indicative of sampling fcc sites of greater imperfection, deeper within the foil, rather than reflecting only rf power broadening. Similar rf power increases applied to the

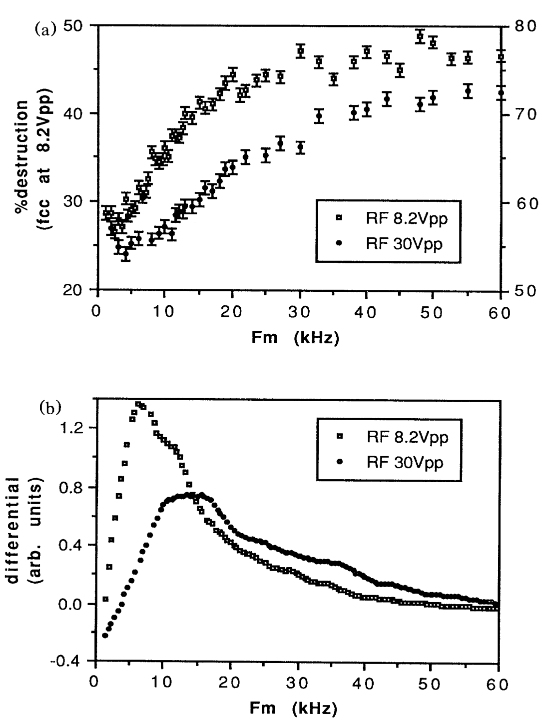

FIG. 2. (a) Raw MAPON data for a fcc cobalt polycrystalline foil of 2-μm thickness in 0.2-T applied magnetic field, for two different rf power levels. In both cases the rf sweep, dv/dt, was positive and the rf sweep duration was 147 ms. (b) The analytical differentials of these spectra.

4.5-μm hcp sample were far less dramatic in producing broadening and there was no shift in the mode value. MAPON theory [5] predicts a reduction in the apparent mode value as the rf field increases. This was carefully searched for on the sharper efg hcp sample, but was not discerned despite the excellent signal-to-noise ratio. This result implies that the internally enhanced rf frequency, $\omega_1=\gamma B_1$, in these relatively thick NMRON samples remains well below the EQI, in common angular frequency units.

The F value for the lower-rf-power fcc sample is 0.52(5), about 6 times lower than the ^{60,57}Co*Fe* single-crystal result of Back [9], whose cw NMRON spectra yielded satellite evidence of the ^{59}Co carrier in the sample, and about 3 times lower than that of the polycrystalline ^{60}Co*Fe* thin-foil result of Yazidjoglou [25]. It is clear, therefore, that the fcc ^{60}Co*Co* foils under study here are dominated in their efg distribution by stacking faults and strain, associated either with the established coexistence of the minor hcp phase, or quenched induced. Whereas more extended anneals and more violent quenches may produce a pure fcc phase at room temperature, such is the propensity for Co to martensitically transform that it is highly likely that during cooldown of the thin polycrystalline foils some hcp, and certainly additional stacking faults, will appear. We believe that the evidence for the minor hcp phase in our samples was made apparent because of the stability of the dilution refrigerator, and the lower temperatures and higher magnetic fields employed, in comparison with earlier cw NMRON studies [21,26] on thin ^{60}Co*Co* foils. Further experiments are required to determine if the hcp phase can be removed completely. The negative sign of the efg, as measured by single-passage NMRON sweep asymmetry, agrees with that for hcp Co. The post-passage sweep asymmetry was pronounced and not characteristic of the much weaker asymmetry of a perfectly randomly distributed efg (of apparent opposing sign [27]) as might occur if the efg principal axis was tied solely to the crystal axes, as for magnetostriction or crystal defect origin only. Detailed MAPON studies of single-crystal Co*Fe* have previously shown [7] that the efg is not isotropic but remains of common sign (in this case, positive) along all three principal cubic axes, [100], [111], and [110], and that this sign is reproduced in a single-passage NMRON measurement on the polycrystalline host. We therefore believe that the negative sign is intrinsic to the fcc Co*Co* system, in accord with theoretical predictions [18]. Having first tested quantitatively the MAPON hcp cobalt V_{zz} mode value against the conventional ^{59}Co NMR result at 0° (and at 90°, see Ref. [19]) we next proceed to test the algebraic additivity of the lattice and local ion efg contributions in cobalt metal, by comparing the ratio of the relativistic EQI contribution and lattice contribution as deduced from conventional ^{59}Co NMR [18] with the ratio of the fcc and hcp ^{60}Co MAPON EQI results. In this comparison we are assuming that the lowest-rf-power

MAPON spectrum on the fcc Co sample [Fig. 2(b)] reflects the intrinsic mode efg result, and that reduction to even lower rf powers, or complete removal of hcp cobalt, if it can be achieved, will not lower this value further. From studies of even lower-mode-value impurity systems, e.g., ^{54}Mn*Ni* [8], ^{60}Co*Fe* [7], as a function of rf power, we are confident that there is no complication from ω_1 being of comparable magnitude to the EQI splitting.

The results, using the 4.2-K data from Fekete *et al.* [18], are

$$P_{\rm rel}/P_{\rm total}(^{59}{\rm Co}) = V_{zz}({\rm rel})/V_{zz}({\rm total}) = 0.126(3)$$

(note that the relevant number for $P_{\rm lattice}/h$ from the text of Ref. [18] is incorrectly transcribed to the abstract) and, using the data from this work,

$$P_{\rm fcc}/P_{\rm hcp}(^{60}{\rm Co}) = V_{zz}({\rm fcc})/V_{zz}({\rm hcp}) = 0.128(9)\,.$$

The larger error in the MAPON result is not due to an inherent weakness in MAPON spectroscopy; rather, it reflects (predominantly) the relatively broad efg distribution in the fcc Co sample. This concurrence, pessimistically to within 10% but with indications of far better agreement, is extremely encouraging that the long-assumed additivity of lattice and local ion efg contributions in noncubic elemental metals is indeed appropriate. We stress, however, that this result is not necessarily transferable to impurities in noncubic metals. MAPON studies on impurities in crystallographically cubic metals have already proceeded to the point where it is clear that it is the impurity-host combination that is important, there being no simple connection with lattice or impurity in isolation. Accordingly, we are in agreement with Hagn [28], who has stressed that perceived "universal correlations" of efg's of *impurities* in noncubic metals [29], as opposed to pure noncubic metals, are unrealistic.

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