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Hyperfine-field spectrum of epitaxially grown bcc cobalt

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The hyperfine-field spectrum of the bcc phase of a 357-Å-thick metallic cobalt film, epitaxially grown on a GaAs substrate, has been determined by spin-echo nuclear magnetic resonance. The peak of the distribution of hyperfine fields in bcc Co occurs at 167 MHz, much lower than the value found for fcc Co (217 MHz), suggesting that the moment in the bcc phase is lower than that of the fcc phase, in agreement with the measurements of Prinz, but in disagreement with recent theoretical calculations (assuming that no significant structural differences exist between theory and experiment). The full width of the distribution is 75 MHz, seven times greater than that found in thin fcc Co films. X-ray rocking-curve measurements yield a linewidth of 118 arc seconds, implying too low a dislocation density to explain the observed NMR line broadening.

I. INTRODUCTION

Cobalt exists in nature with two crystal structures. At temperatures below 698 K the hexagonal-close-packed (hcp) structure has the lower energy while above this temperature the stable structure is face-centered cubic (fcc). There is, however, little difference between the energies of the two forms at 0 K. The hcp and fcc phases can coexist at room temperature. A recent calculation suggests that the energy of the hcp phase is only 2 mRy lower than that of the fcc phase, and also only 3 mRy lower than that of the bcc phase (which does not occur in nature.) Prinz[1] stabilized the bcc phase of Co for the first time by growing a film on a GaAs substrate. The match between the lattice spacing of bcc Co and the (110) GaAs substrate was found to be sufficiently close to enable single-crystal films to be epitaxially grown with thicknesses up to 375 Å.

The magnetic moment per atom of Co in each of the three crystal structures has been calculated by a number of groups.[2–4] While there is some discrepancy between them, they all predict that the bcc phase has the largest moment. In contradiction to theory, the magnetization measurements on bcc Co films indicate that the Co moment in the bcc phase is much lower than in the hcp or fcc phases. It has been suggested that the discrepancy arises because of defects in the bcc film.[5]

In order to investigate this possibility we have made the first measurements of the hyperfine field of bcc Co. The peak value of the magnitude of the hyperfine field is found to be lower than that of the fcc or hcp phases of Co and to be consistent with the magnetization measurements. The width of the distribution of the hyperfine fields is, however, some seven times greater than that typically found in fcc Co films.

II. EXPERIMENTAL

The growth of the bcc Co films has been described in detail.[1] The growth was carried out in a conventional molecular-beam-epitaxy (MBE) system, modified with high-temperature ovens, by evaporating cobalt metal on a polished (110) GaAs substrate. The growth process is monitored by continual observation of the reflection high-energy electron diffraction (RHEED) patterns. The epitaxial growth of bcc cobalt on GaAs is possible because the predicted value of the lattice constant of bcc cobalt is only 0.2% less than that of a $c(\frac{1}{2}\times 1)$ construction upon a GaAs lattice.

At cobalt metal thicknesses of less than 50 Å, the RHEED growth patterns display bcc symmetry. Above this thickness, the bcc structure of Co usually collapses, and a bifurcation of the diffraction pattern is observed. The thickness at which this transformation occurs depends on substrate conditions and growth conditions. The thickest bcc sample obtained to date is 357 Å. This film was the only film studied in detail by techniques including vibrating-sample magnetometry, ferromagnetic resonance, and (in the present publication) nuclear magnetic resonance.

Superconducting quantum-interference device (SQUID) magnetometer measurements recently made by Krebs[6] showed that $4\pi M = 14.4$ kOe/cm^3 for this 357-Å-thick sample of bcc Co at 4.2 K, where M is the magnetic moment per unit volume. (This value can be compared to that of hcp Co, where $4\pi M = 17.87$ kOe at 4 K.) Ferromagnetic-resonance experiments were also performed on this film,[6] and the g value was determined by measuring the resonant magnetic field with applied field perpendicular to the plane of the film. A g value of this magnitude $g = 2.16$ implies that a small portion of the measured magnetic moment is orbital in nature, and that the spin-only magnetic moment is reduced from a measured spin-plus-orbital moment of $1.39\mu_B$ per atom to a spin-only value of $1.29\mu_B$ per atom. (The present value differs slightly from the value of $1.41\mu_B$ total moment measured by Prinz[1] using a vibrating-sample magnetometer.)

The zero-field NMR of pieces of the 357-Å bcc film which was used for the magnetization measurements was measured using a coherent swept-frequency spin-echo spectrometer[7] at the University of St. Andrews, Scotland. Initial measurements were made at 1.5 K using an untuned broadband delay-line sample holder and computer control of the spectrometer.[8] The signal from the small amount of material available was not visible on an oscilloscope but was easily detected by signal averaging. A series of checks at spot frequencies was made using tuned circuits to confirm the great width of the distribution of hyperfine fields revealed by the initial measurements. The measured values of echo height were corrected for the frequency dependence of the gain of the amplifiers and the sensitivity of the sample holders and then divided by the square of the frequency to give the final distribution of hyperfine fields in the sample, Fig. 1.

In multidomain samples of fcc Co, the NMR signal at low power arises from nuclei within domain walls. Walls are not thought to exist in the bcc film, but the easy axis is in the plane of the films and the anisotropy field is low, so there is appreciable enhancement of the applied rf field due to domain rotation. The transverse relaxation time

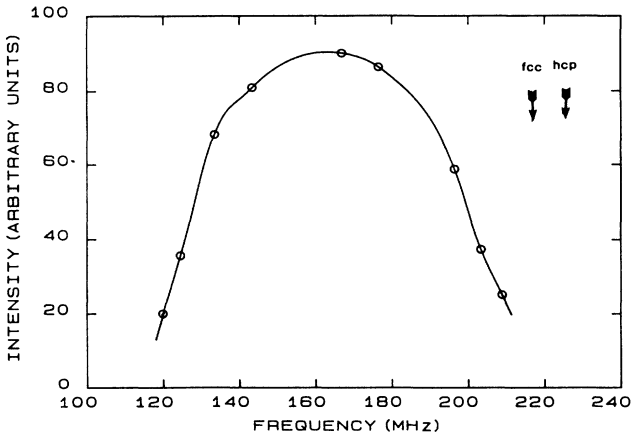

FIG. 1. The distribution of hyperfine fields in a 357-Å-thick film of bcc Co at 1.5 K. The hyperfine fields of fcc and hcp Co are also indicated.

T_2 was found to be 180 ± 10 μs in the bcc film, much longer than in multidomain fcc Co, where $T_2 \approx 25$ μs, which supports the view that there are few domain walls in the film.

The peak of the distribution of hyperfine fields shown in Fig. 1 occurs at 167 MHz, much lower than the value found for fcc Co (217 MHz), suggesting, as discussed below, that the moment per atom in the bcc phase is lower than that of the fcc phase. The full width of the bcc Co spectrum at half maximum is 75 MHz.

III. DISCUSSION

The main contributions to the hyperfine field in a $3d$ ferromagnetic material may be written

$$H = H_c + H_v + H_{\text{orb}} , \tag{1}$$

where H_c is the contact interaction with core electrons, H_v the contact interaction with valence electrons, and H_{orb} the contribution due to any unquenched angular momentum. The core electrons are those in the filled argon shell, and the valence electrons include both the $3d$ and $4s$ electrons. Small terms such as the Lorentz field ($+6$ kG) will be neglected in this discussion. The hyperfine field in hcp Co is anisotropic[9] (-219 to -227 kG) but only the isotropic part (-224 kG) will be considered since we wish to compare it with the hyperfine fields in the fcc and bcc systems. The magnetic data for hcp, fcc and bcc cobalt are compiled in Table I.[2–4,6,9–14]

The most important contribution to the hyperfine field in ferromagnetic $3d$ systems[14] has been found to be H_c, and it has become common practice[15] to estimate magnetic moments from hyperfine-field measurements by ignoring the other terms in Eq. (1) and writing

$$H_c = -130\mu_s , \tag{2}$$

where H_c is in kG and μ_s is the spin moment per atom in Bohr magnetons. It has recently been shown that this rule of thumb is incorrect for the top atomic layer of an Fe film, where both computation[2] and experiment[16] find an increased moment over the bulk value with a reduction in the magnitude of the hyperfine field, but it may reasonably be used for layers away from the surface. Since the present film is 357 Å thick, and the rf field at 200 MHz will excite all the nuclei, the surface layer will make a negligible contribution to the NMR signal.

There is no prescription for finding H_v but computer calculations on Fe (Refs. 2 and 17) and fcc Co (Ref. 17) suggest that in bulk material H_v is negative and between one-third and one-quarter of the magnitude of H_c. Only in the surface layer of Fe has H_v been found to be positive.[2]

The total hyperfine field in both hcp and fcc Co is negative due to the dominant contribution of the contact interaction, and will be assumed to be negative in bcc Co, although this has not yet been established by experiment.

On the basis of the contact interaction alone it is clear that the value found for the hyperfine field of bcc Co (-166 kG) supports the low value of the magnetic moment found experimentally. Indeed a simple scaling of

TABLE I. Magnetic data for cobalt at 0 K.

	hcp	fcc	bcc
μ	1.72[a]	1.75[b]	1.4[c]
g	2.18[d]	2.06–2.10[e]	2.16[f]
μ_s $(2\mu/g)$	1.58	1.67–1.70	1.3
μ_s (theory)	1.63,[g] 1.59[h]	1.56[i]	1.73,[g] 1.72,[h] 1.68[i]
ν (MHz)	225[j]	217[k]	167[l]
H (kG) $(-\nu/1.005)$	−224	−216	−166

[a]Reference 10.
[b]Reference 11.
[c]Reference 6.
[d]Reference 12.
[e]Reference 13.
[f]Reference 6.
[g]Reference 2.
[h]Reference 4.
[i]Reference 3.
[j]Reference 9 (isotropic term).
[k]Reference 14.
[l]Present work.

the form

$$H_{\rm bcc}=H_{\rm fcc}(\mu^s_{\rm bcc}/\mu_{\rm fcc})=216(\mu^s_{\rm bcc}/\mu^s_{\rm fcc}) \quad (3)$$

using the values of Table I gives a value of −167 kG, in agreement with the peak of the distribution in Fig. 1.

The orbital term in metallic Co is probably not negligible, but its magnitude is difficult to establish accurately. In the free atom[14]

$$H_{\rm orb}=(g-2)\mu_s\langle r^{-3}\rangle=325(g-2)\mu_s \ , \quad (4)$$

where $H_{\rm orb}$ is in kG and μ_s is the number of Bohr magnetons per Co atom, but an accurate calculation of $\langle r^{-3}\rangle$ does not seem to have been made for the metal. The orbital contribution to the hyperfine field has a positive sign, and in some intermetallic Co compounds, e.g., $GdCo_5$,[18] is large enough to overcome the negative contribution of the contact interaction to give a net positive hyperfine field.

Values of H_c and $H_{\rm orb}$ calculated from Eqs. (2) and (4) are given in Table II for each Co crystal structure, and H_v is found using the experimental value of H and Eq. (1). It will be seen that, after allowing for $H_{\rm orb}$, the value of H_v is negative and of reasonable magnitude for the bcc Co structure. On balance, then, the measured value of the hyperfine field tends to support the low experimental value of the magnetic moment of the bcc phase of Co, although the issue is complicated by our poor understanding of the orbital contribution to the hyperfine field.

The width of the distribution of hyperfine fields for the bcc Co film is, however, difficult to understand. Dislocations, domain walls, or voids in a single-crystal, cubic, ferromagnetic film with the magnetization in the plane would be expected to produce a width less than the maximum demagnetizing field (18 kG); in fcc films 10 kG has been observed,[19] while the full width at half maximum for the bcc film is 75 kG.

TABLE II. The magnetic data for cobalt, see Table I, used to calculate the core and orbital contributions to the hyperfine field, Eqs. (2) and (4), and the deduced valence contribution.

	hcp	fcc	bcc	Theory bcc
μ	1.72	1.75	1.4	
g	2.18	2.08	2.16	
μ_s	1.58	1.68	1.3	1.73
H_c	−205	−218	−169	−225
$H_{\rm orb}$	+92	+43	+68	+90
$H_{\rm expt}$	−224	−216	−166	
H_v	−109	−41	−65	−31

A stress gradient through the film, due to differential expansion between the Co film and the GaAs substrate, would act to increase the width of the distribution, because in fcc Co the NMR frequency changes[20] by +128 kHz/kbar. (The value for bcc Co is not known but would not be expected to be very different.) Using thermal expansion data for Ni, since bulk fcc Co does not exist at low temperature and no measurements are available for bcc Co, we estimate that the Co film would be under tension at a plane interface with the GaAs ∼−8 kbar at 4.2 K, resulting in a frequency shift of ∼−1 MHz, far too small to explain the measured width of the distribution of hyperfine fields.

Another source of line broadening, inclusion of substrate atoms in the metallic film, has been ruled out by high-resolution synchrotron-radiation photoemission studies of bcc Co epitaxially grown on GaAs.[21] This study showed that the amount of dissociated Ga and As in the overlayer decays exponentially away from the Co/GaAs interface with a decay length of 2 Å. The As solubility in the Co film far from either boundary is only 0.26 at. %, far too dilute to be a significant source of broadening.

Perhaps more relevant to the problem at hand is the discovery of Xu *et al.*[21] by low-energy electron diffraction (LEED) that a weakly ordered bcc phase of Co forms of a GaAs substrate; i.e., bcc Co/GaAs is a mosaic characterized by many dislocations and grain boundaries. These results are in contrast to analogous data for the Fe/GaAs system which indicated the formation of a well-ordered bcc Fe overlayer. The dislocation density is not given, so no estimate of the line broadening from this source can be made from this study. Furthermore, the structural regularity of the Co layer grown on a (100) face of GaAs investigated by Xu *et al.* is not as high as that reported by Prinz[22] on the present samples grown on the (110) surface of GaA.

IV. X-RAY CHARACTERIZATION

We have characterized two epitaxially grown thin Co films by x-ray diffraction. The first is a sample with a

thickness of 3100 Å which underwent a conversion early in its growth to hcp cobalt. The second film is the 357-Å bcc sample examined by zero-field NMR.

Oscillation photographs, similar to those described in Ref. 23, were obtained on a Weissenberg Camera. The 3100-Å sample was indexed based on hcp Co. The spots corresponding to different planes were very elongated and smeared out indicating a mosaic distribution in the Co film. Furthermore, these spots appear at different film coordinates than those for the GaAs substrate. X-ray results were consistent with RHEED patterns obtained for the same film, which also showed hexagonal symmetry.

An oscillation photograph for the 357-Å Co film was taken for 72 h. No spots corresponding to hexagonal structure, nor any additional spots other than GaAs, were detected on the x-ray film. In contrast to the 3100-Å thick film of Co, single-crystal diffractometer scans did not show the peaks corresponding to hexagonal structure, nor were the scans able to resolve any peaks that would be expected for bcc or fcc structures, implying an almost perfect match between the substrate and the Co film. Glancing-angle Read Camera x-ray photographs were taken to determine the structure of the 357-Å Co film. No spots resolvable from GaAs were seen on the film. Based on these results we infer that the structure of the thinner Co film is not hexagonal but it is cubic, with a lattice parameter so close to GaAs that peaks corresponding to Co films are not resolvable on oscillation and Read photographs. In order to resolve the peaks corresponding to the Co film, rocking curves on a double-crystal spectrometer were measured. In this double-crystal spectrometer arrangement the monochromating crystal was InSb(001) oriented for a (400) diffraction with a FWHM (full width at half maximum) of 9 arc seconds. Figure 2 shows the rocking curves for the 357-Å-thick film sample thus obtained. In addition to the GaAs substrate (220) peak, an additional satellite peak, on the low-angle side as indicated by the arrow in the figure, is attributed to the Co film. Based on the separation between substrate and the shoulder peaks, a d spacing of 1.997 Å has been calculated. Assuming the Co structure to be bcc and the peak to diffract from (110) diffraction planes, one obtains a lattice parameter for bcc Co of 2.825 Å. This is in good agreement with total energy calculations for bcc Co which predict 2.81 Å.[3] The dislocation density ρ can be obtained roughly from the formula[24]

$$\rho=\beta^2/4.35b^2 , \tag{5}$$

where β is the FWHM and b is the Burgers vector which in this case is taken equal to the d spacing. We estimate the dislocation density $\rho\approx 2\times 10^8$ lines/cm^2. For comparison, well-annealed metals have dislocation densities of 10^5–10^6 lines/cm^2 while cold-worked metals can have as many as 10^{12} lines/cm^2.

Assuming that a dislocation line will only perturb the NMR frequencies of nuclei which are its nearest and next-nearest neighbors in cobalt metal,[25] we find that the defect density deduced from x-ray diffraction does not explain the NMR linewidth. For a dislocation density of

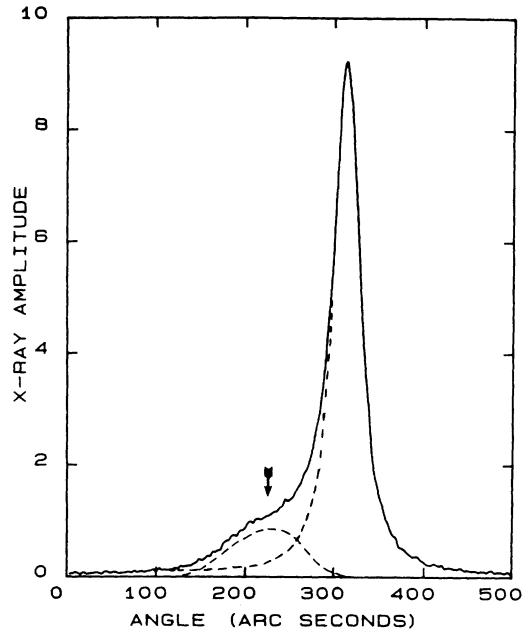

FIG. 2. Double-crystal x-ray rocking curve for a 357-Å Co film on a GaAs substrate. The arrow indicates the position of the Co(110) peak on the shoulder of the GaAs(220) peak.

$\sim 10^8$ lines/cm^2, only one in 10^5 nuclei is shifted by the fault. This is far too small an effect to be a significant broadening mechanism.

The width of the distribution of hyperfine fields, 75 MHz, indicates a not yet understood source of magnetic disorder. Thin cobalt films typically display large resonance linewidths of the order of 10–20 MHz.[26] Previous authors have attributed the enhanced linewidths of thin films to the effects of anisotropic hyperfine interactions (in hcp Co), the presence of stacking faults, or a distribution of magnetic moments.

V. CONCLUSION

Magnetization and nuclear-magnetic-resonance investigations are complementary studies. The former is a macroscopic probe which yields spatially averaged information, whereas the latter is a microscopic probe which yields the distribution of hyperfine fields. NMR can distinguish anamolous surface layers from the bulk. Both the average magnetic moment and the average hyperfine field are significantly lower in bcc Co/GaAs than in the stable fcc and hcp phases of cobalt metal. Although the hyperfine field is not necessarily proportional to the magnetic moment, our best estimates indicate that the hyperfine field scales with the moment in the case of the three phases of cobalt metal. In Table II, it can be seen that the orbital and valence electron nearly cancel each other out, leaving the core polarization contribution as the dominant contribution to the hyperfine field. Since this contribution is directly proportional to the spin moment, we conclude that the hyperfine-field measurement

confirms the fact that magnetic moment in bcc Co is significantly lower than that of fcc and hcp Co. Assuming there exist no significant structural differences between theory and experiment, the low moment disagrees with theoretical predictions which have been calculated for bcc Co. Strain, stacking faults, and inclusion of substrate atoms have been discussed, and their effect on the NMR line appears to be negligible.

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