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Hyperfine Fields in Dilute Alloys of Co in Fe

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Spin-echo NMR spectra of ^{57}Fe and ^{59}Co in Fe alloys with 0.8, 2.6, 3.3, and 6 at.% Co have been decomposed to determine the influence of Co atoms on nearby Fe and Co hyperfine fields as a function of radial separation. Of the possible alternatives, the preferable solution of this long-standing question is similar, for the Fe sites, to that of Wertheim, Buchanan, and Wernick, but with second-nearest-neighbor effects only one-half as great. The model is interpreted in terms of an oscillatory radial variation affecting all sites, combined at Fe sites with changes in local moments to yield an over-all monotonic variation in hyperfine field with distance from Co atoms.

The distribution of Fe hyperfine fields in dilute alloys of cobalt in iron has been the subject of numerous NMR and Mössbauer-effect studies. While the experimental results are in substantial agreement, the interpretations have not been, despite reliance on a common model.[1] This paper is a further attempt to rectify this situation using NMR data for higher Co concentrations than reported elsewhere,[1,2] and with greater resolution than is available in Mössbauer studies.[3] The effects of Co impurities on Fe hyperfine fields are found to be about the same as those given by the more recent interpretations, although second-nearest-neighbor effects come out significantly smaller. A connection is also made with the Co hyperfine fields in the same alloy system.

In the generally used model, the effects of Co impurities are taken to depend only on distance (i.e., all Co impurities on a given spherical shell of neighboring sites are equivalent), and the effects of impurities are additive. With the further assumption that the Co atoms are distributed at random, one identifies observable features of the spectra using intensities calculated from the probabilities of occurrence of various near-neighbor configurations. Only a few neighbor shells, on the order of four, appear to be important in accounting for the main features of the hyperfine field spectra of dilute Fe alloys, in agreement with the range of perturbations established by neutron diffraction.[4]

Early pulsed-NMR studies[5] attributed the single distinct Fe satellite line found with low Co concentrations to an impurity in the nearest-neighbor shell and assumed that farther shells caused small perturbations. Analyses of unresolved Mössbauer spectra found larger shifts,[6] and Wertheim[3] pointed out that the change of Mössbauer peak position with concentration also implies that there must be hyperfine field shifts of greater magnitude. The cw NMR work of Mendis and Anderson[2] with very low Co concentrations suggests that the observed satellite is the result of a more distant neighbor, identified as the third neighbor. The first- and second-shell effects were presumed to be greater, but broadened beyond observability, a limitation not shared by the Mössbauer work. Recent spin-echo traces of a 1% sample by Budnick *et al.*[1] show evidence of these greater shifts, while Mössbauer work by Wertheim *et al.*,[3] analyzed for the effects of four shells of neighbors, agrees with the assignments by Mendis and Anderson. In all of these interpretations auxiliary conditions are imposed to obtain unique solutions. It has generally been assumed that the effects decrease monotonically with distance; this is particularly important for Mössbauer studies where no features are resolved.

This paper reports an examination of zero-field, 4.2 °K, spin-echo NMR spectra of Fe:Co alloys without the above constraint. Both ^{57}Fe and ^{59}Co spectra of samples containing 0.8, 2.6, and 3.3 at.% Co were studied. The Co resonance of a 6 at.% sample was also used; the corresponding Fe signal was unusable. These traces were the basis for an earlier report,[5] but have been reexamined in light of later developments.

The experimental results for ^{57}Fe are shown as points in Fig. 1, as are the corresponding spectra for ^{59}Co in Fig. 2. Corrections for relaxation-time variations were unnecessary and frequency-dependent amplitude variations are small enough

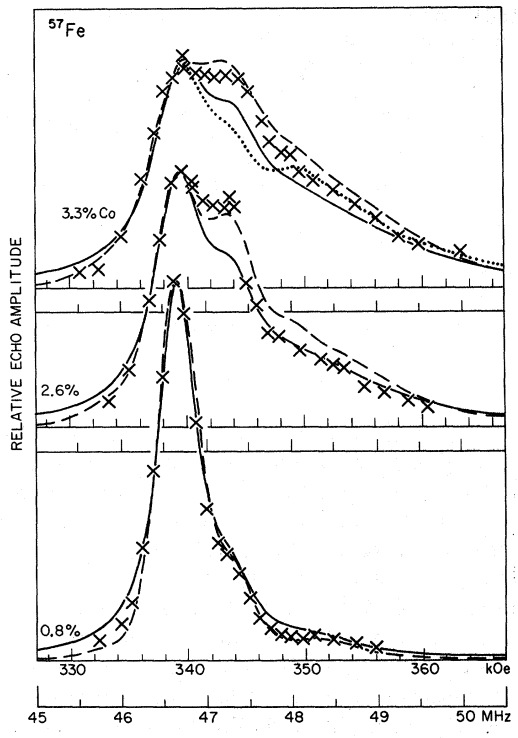

FIG. 1. Spin-echo spectra of ^{57}Fe in alloys of Fe with 0.8, 2.6, and 3.3 at.% Co (4.2 °K, zero external field). Crosses indicate experimental data. Solid curves were calculated with model A (see text). Model B gives the dashed curves and model C (for 3.3 at.%), the dotted curve.

that they also were not corrected. The instrumental conditions introduced more broadening than obtained by Budnick *et al.*,[1] but the results are quite compatible. Evaluation of the ^{57}Fe centroid shifts with concentration c yields substantial agreement with Wertheim[3]: $\Delta H/H_0 = 0.54c$.

A search was made for parameters with which a computer using the model described above could systematically generate shapes in agreement both with our spectra and with those of Budnick *et al.* To this end alternative decompositions of the traces which are possible with reasonable allowance for experimental error were tested, together with the solution given by Wertheim *et al.*[3]

Initial decomposition of a spectrum was accomplished graphically. The additivity model implies that one can single out any particular shell of neighbors for consideration. Neglecting additional broadening due to Co in that shell, the entire spectrum represents a set of several component spectra, all of the same shape, one for each possible number n_i of Co atoms in the chosen shell i. Each component is displaced relatively by the amount $n_i \Delta H_i$, where ΔH_i is the shift produced by one Co atom in shell i, and has a relative amplitude given by the probability of n_i Co atoms being in the shell when the Co concentration of the alloy is c. For each tentative assignment of a prominent feature in the spectrum to the effect of a particular neighbor shell, one can thus readily find graphically the shape of the corresponding components. The shape of the component is caused by the effects of Co atoms in other shells and can be decomposed in turn; one continues until only a simple basic line shape remains.

Restricting the basic lines to either Gaussian or Lorentzian shapes, alternative decompositions of the Fe spectra were found which were acceptable, in the sense that at each stage it was possible to use component amplitudes given by probabilities suitable to the total number of sites d_i in some near-neighbor shell. These alternatives were used as initial models for computer-generated shapes. After refinement, including the addition of line broadening from nearest-neighbor impurities, based on comparisons with the experimental results, two distinct models were found to reproduce

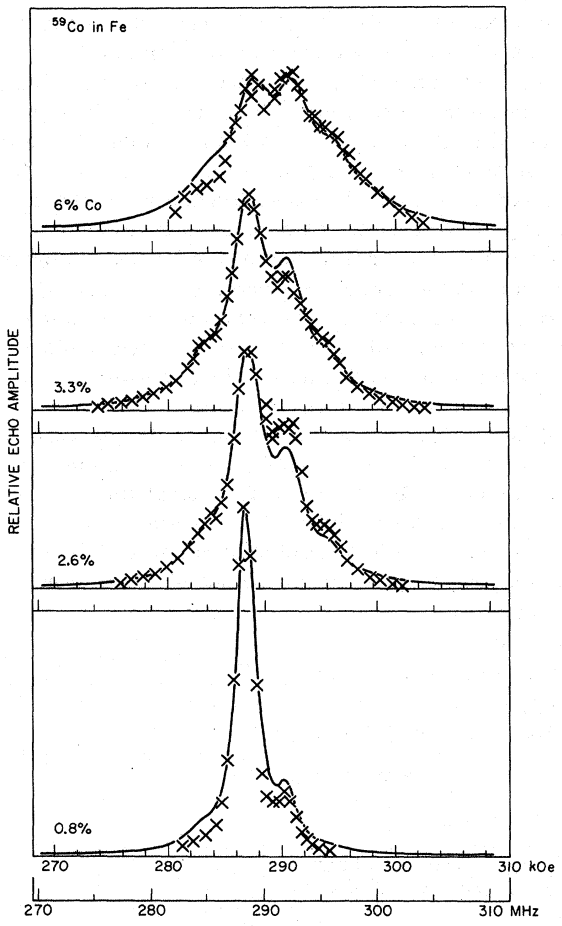

FIG. 2. Spin-echo spectra of ^{59}Co in Fe alloys containing 0.8, 2.6, 3.3, and 6 at.% Co. The smooth curve was computed using the parameters in Tables I and II. Crosses are experimental points.

TABLE I. Hyperfine fields at ^{57}Fe and ^{59}Co in dilute bcc alloys of Co in Fe (4.2 °K). Shift per neighboring Co atom in different near shells. Positive signs signify increases in NMR frequencies.

Shell	(Distance)^2 (a_0^2)	Number of sites in shell, d_i	ΔH at Fe (kOe) Model A	Model B	Model C[a]	ΔH at Co (kOe)
$N1$	$\frac{3}{4}$	8	12.35	12.7	11.9	−4.0
$N2$	1	6	5.3	−5.1	10.2	3.6
$N3$	2	12	4.4	0.65	4.4	3.6
$N4$	$\frac{11}{4}$	24	~0.65	4.4	0.65	~0.6
$N5$	3	8	...	5.5	...	...
$N6$	4	6		...		
$N7$–$N9$		24 each				

[a]Wertheim *et al.*, Ref. 3.

adequately the ^{57}Fe spectra. A reasonable fit to the ^{59}Co spectra was also obtained. The parameters of these models, as well as the model of Wertheim *et al.*[3] (model C), are given in Tables I and II, and the curves which they generate are illustrated by the smooth curves in Figs. 1–3.

The difference between the Fe models A and B is related to the shapes used for the basic components. Model A, like the model for Co, is composed of Lorentzian shapes throughout; whereas model B matches the spectra of Budnick *et al.*[1] with Lorentzian lines, but used Gaussian shapes to describe the instrumental broadening in our spectra. The general widths of these shapes (Table II) were chosen to fit, and are seen to increase with Co concentration. In order to conform to the experimental results, it was necessary to assign considerable additional widths to the $N1$ and $N2$ (nearest and next-nearest) contributions. These widths are in agreement with those postulated by Mendis and Anderson.[2] It is not possible to distinguish whether such broadening is actually symmetric, because of the instrumental width.

The simpler model A, which, as discussed below, seems to be the better choice, is quite similar to that given by Wertheim *et al.*[3] except for the assignment of the $N2$ shift. The parameters of model C are found to yield spectra deficient in intensity at the first major satellite position, as illustrated in the 3.3 at.% case of Fig. 1. In comparing the other two Fe models, one sees that model A also underestimates the intensity at that satellite position, while model B overestimates other regions, but probably within the range of experimental uncertainty. The shapes given by model A in Fig. 3 generally reproduce better the spectra of Budnick *et al.*, although the main satellite amplitude is observed to fall between those of the two models.

The assignment of the shifts ΔH_i shown in Table I to individual neighbor shells is, of course, a matter of interpretation. What a successful fit actually determines is a set of shifts correlated with weighting factors which are possible for near-neighbor shells. Since they contain equal numbers of sites d_i, as shown in Table I, shells $N1$ and $N5$ are indistinquishable and are not readily separated from $N2$ and $N6$. The criteria of choice must involve other considerations. In both Fe models, the nearest-neighbor $N1$ shell is assigned the largest shift ΔH. Since it seems unnecessary to go beyond $N6$ to identify resolvable structure, $N3$ and $N4$ are unique. $N2$ is identified by its need for additional broadening, and $N5$, by causing a shift comparable to that of $N4$. $N4$ in model A and $N3$ in model B were assigned to account for the asymmetry of the main line noted both by Mendis and Anderson[2] and by Budnick *et al.*[1] Assignment of Co shifts was made following the arguments presented below for

TABLE II. Linewidths used to compute spectra. Half-width at half-maximum (kOe).

General widths: Co concentration c%	0.25[a]	0.5[a]	1.0[a]	0.78	2.6	3.3	6
For Fe model A (and C)	0.2	0.4	0.8	1.9	2.4	2.7	...
model B	0.2	0.4	0.8	2.0	2.2	2.6	...
For Co	...	...	...	0.95	1.3	1.4	1.5
Additional natural widths associated with individual neighbors:	$N1$	$N2$					
For Fe model A (and C)	1.7	0.2					
model B	1.9	1.9					
For Co	0.5	...					

[a]To match data of Budnick *et al.*, Ref. 1.

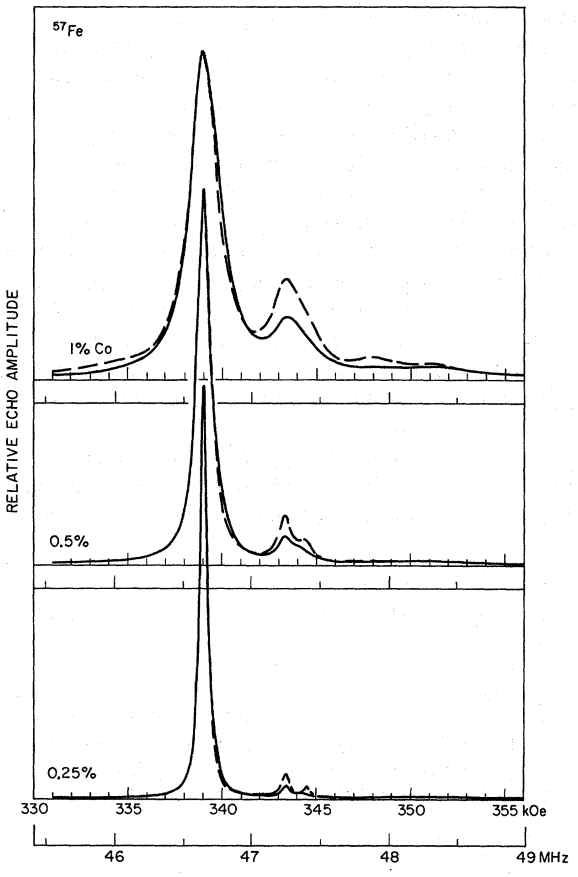

FIG. 3. Spin-echo spectra computed from model A (solid curves) and model B (dashed curves) for comparison with the experimental data of Budnick *et al.* (Ref. 1).

making a correspondence between the Co and Fe spectra. The same considerations reinforce the $N1$ assignment in model A for Fe.

Our experimental NMR spectra, in agreement with Wertheim's Mössbauer results, give $\Delta H = 183c$ (kOe) $= c\sum d_i H_i$ for the shift of centroid position with Co concentration c in the Fe spectra at 4.2 °K; here a positive sign means increasing frequency. The above summation, using the parameters for model A, gives 199 kOe, for model B, 228 kOe, and for model C, 225 kOe. The residual differences can be attributed to negative shifts caused by farther shells, especially the populous $N7$ to $N9$. Budnick *et al.*[1] observed that the main peak shifts by about $-22c$ (kOe) and broadens with concentration, as one would expect from these farther neighbors.

In contrast to the behavior of the Fe spectra, the Co spectra show much smaller centroid shifts. The mean value obtained from the four traces is $\Delta H = 55c$ (kOe). The assignments shown in the table for Co shifts give $50c$ (kOe). Since both Co and Fe sites should be affected approximately equally by the polarization of conduction electrons scattered from impurity sites, it is proposed that the difference between the Fe and Co spectra is the result of changes in the localized Fe moments near Co impurities. This picture relaxes the requirement for a monotonic decrease in hyperfine field shift with radial distance, although over-all model A for Fe does display such behavior.

The magnetization of Fe: Co is known[7] to increase initially at the rate of $1.1\mu_B$ per substituted Co atom. Since the Co moment itself in dilute concentrations has a moment in the range 0 to $0.5\mu_B$ less than Fe,[4] the implication is that the nearby Fe moments must increase by 1.1 to $1.6\mu_B$ *in toto*, however this is distributed. The Co moment appears to be considerably more constant.[4] The extra centroid shift of the Fe spectra, 128 kOe per added Co, is of suitable magnitude for the amount of Fe moment change assumed.

On the assumption that nearest-neighbor interactions dominate the transfer of this added moment and that a constant fraction f of excess moment at any Fe site is transferred to each $N1$ Fe neighbor to that site, one obtains a distribution as follows. From a count of the number of linkage paths available, if an increment $\Delta\mu$ appears on each $N1$ Fe to a Co impurity, there should be $4f\Delta\mu$ at each $N2$, $2f\Delta\mu$ at $N3$, $1f\Delta\mu$ at $N5$, $9f^2\Delta\mu$ at $N4$, and smaller amounts at farther neighbors. The useful point here is the 2:1 ratio between the $N2$ and $N3$ moment changes. Using the differences in shifts ΔH_i between corresponding Fe and Co sites, one can evaluate the relative moment changes for each possible assignment of shifts. The only assignments which give this 2:1 ratio are model A for the Fe spectra and the model given in Table I for the Co spectra. These preferred assignments give the radial variations at Fe and Co sites indicated schematically in Fig. 4. They yield a value of $\Delta\mu$

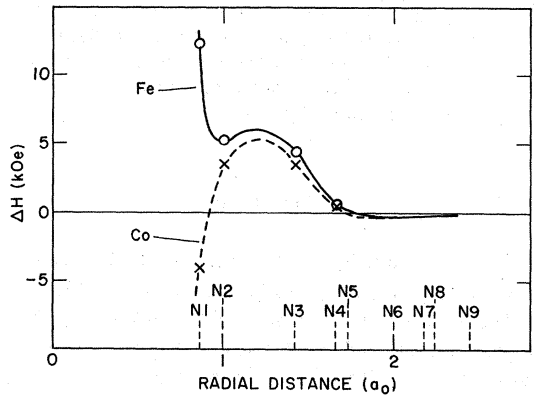

FIG. 4. Variations in hyperfine field shifts with radial distance from a Co impurity according to the Co and Fe (A) models of Table I. The smooth curves are schematic.

($\sim 0.16\mu_B$) which produces a field increase at Fe nuclei of 16.4 kOe, and give f the value 0.025, so that the moments transferred to $N2$, $N3$, $N4$, and $N5$ should cause additional shifts at Fe of 1.64, 0.82, 0.09, and 0.41 kOe, respectively, about as observed. The $N4$ shift shown in Table I for Co, which was included in computing the spectra, was assigned on the assumption that it approximated the Fe shift.

As discussed above, this interpretation suggests that the Co spectra display mainly the effects of Co impurities on the polarization of delocalized electrons, with an oscillatory behavior having zeros between the first and second shells and at about the fifth shell as shown in Fig. 4. This is not unlike the radial variation about nonmagnetic impurities.[8] Small moment changes could occur on the Co atoms without seriously affecting this conclusion, although such changes would foreshadow the eventual breakdown of the assumed additivity picture.

In summary, two possible schemes are capable of explaining the Fe spectra within the additivity model. One of these, model A above, is similar to that proposed elsewhere,[2,3] although next-nearest-neighbor Co effects are only one-half as large. Both Fe models imply that oscillatory conduction-electron polarization effects exist here similar to those found with nonmagnetic impurities, but they are augmented by local moment changes on Fe atoms near Co impurities. The model A is preferable in that, by simple arguments, it can be correlated with the Co resonance behavior, which appears mainly to be the results of conduction-electron polarization.

I am happy to acknowledge that the experimental data were obtained in collaboration with M. Rubinstein, using samples prepared by M. B. Stearns and G. F. Day.

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Low-Temperature Heat Capacity of the Metamagnet $Ni(NO_3)_2 \cdot 2H_2O$†

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The heat capacity C_p of Ni $(No_3)_2 \cdot 2H_2O$ has been measured in the range $1.5\ K \leq T \leq 10\ K$, revealing a sharp λ anomaly characteristic of the transition to a magnetically ordered state at $T_N = 4.105 \pm 0.005$ K. The magnetic contribution to C_p has been separated from the lattice part and the temperature variation of the magnetic entropy has been calculated. The magnetic entropy at T_N is found to be only $0.546R$, suggesting a two-dimensional character to the ordering which is compatible with the picture of this system as an antiferromagnetically coupled array of alternating sheets of ferromagnetically aligned Ni^{++} spins. This interpretation, however, is complicated by the effect of anisotropy on C_p.

INTRODUCTION

Nickel nitrate dihydrate forms monoclinic crystals belonging[1] to the space group $P2_1/c$. The bimolecular unit cell has the dimensions $a = 5.79$ Å, $b = 5.90$ Å, and $c = 8.51$ Å with $\beta = 91.1°$. The crystals are needlelike with the a axis parallel to the needle axis and exhibit good cleavage along the bc plane. Ni^{++} ions at the two nonequivalent sites in the unit cell are surrounded by octahedra composed of four oxygens (from four NO_3^- groups) and two water molecules. Within bc sheets, every Ni^{++} ion is connected by a NO_3^- group to each of four neighboring Ni^{++} ions. Intersheet linkages are presumably rather weak. The path between Ni^{++} ions on adjacent sheets traverses at least two NO_3^- ions.

The magnetic susceptibilities of powdered and single-crystal $Ni(NO_3)_2 \cdot 2H_2O$, measured at low temperatures by Berger and Friedberg,[2] reflect