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Hyperfine Field Spectra of Binary Fe-Co Alloys: Nuclear Magnetic Resonance of ^{57}Fe and ^{59}Co

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The distribution of hyperfine fields in iron-rich *Fe*Co binary alloys has been investigated by spin-echo and continuous-wave nuclear-magnetic-resonance techniques. Both the ^{57}Fe and the ^{59}Co hyperfine field spectra have been examined. The spin-echo technique is found to give an accurate spectral line shape, without the appearance of extraneous instrumental effects. The anomalously large relative intensity of the prominent satellite line observed in alloys containing a low concentration of cobalt atoms is shown to be the result of a near degeneracy of two distinct resonances; these resonance lines originate at nuclear sites which are nearest neighbors and next nearest neighbors to a cobalt impurity atom. Other lines in the ^{57}Fe and ^{59}Co spectra which have previously been observed by other workers have been reinterpreted. The distribution of hyperfine fields in this alloy system is believed to result primarily from changes in the core-polarization contribution to the hyperfine field, the changes in the conduction-electron-polarization contribution being substantially smaller.

INTRODUCTION

THE nuclear-magnetic-resonance (NMR) frequency of ^{57}Fe in pure iron metal when measured at 4.2°K occurs at 46.65 Mc/sec,[1] corresponding to a nuclear hyperfine field of 339 kOe. When a small percentage of cobalt impurity is substitutionally introduced into the iron lattice by the process of alloying, the ^{57}Fe resonance line is observed to broaden, though its peak remains unshifted to first order, and small satellite lines appear in the high-frequency wing of the central resonance.[2] The ^{59}Co resonance has also been observed in these iron-rich binary Fe-Co alloys at 289.2 Mc/sec (286.3 kOe),[3] where similar line broadening effects and the appearance of satellite lines can also be discerned.[4] The structure appearing in the Fe and Co resonances of this alloy system are both due to the influence of nearby cobalt impurities on the hyperfine fields of the two constituents. Those Fe or Co nuclei which have a cobalt atom in their immediate vicinity have hyperfine fields which are sufficiently perturbed so as to give rise to well-resolved satellite lines. The hyperfine fields at Fe (or Co) nuclei without a cobalt neighbor in their near proximity are perturbed to a lesser extent; the changes in their hyperfine fields are too small to be completely resolved, which causes the central resonance line to broaden.

Although the above statements have been abstracted from the literature, there is a controversy over the origin (and even the very existence) of the aforementioned satellite lines. This is so, despite (or, perhaps, because of) the numerous and diverse investigations of the hyperfine field spectra in the Fe-Co system. The ^{59}Co resonance in these alloys has been studied by measurements of specific-heat anomalies,[5] continuous-wave (cw) NMR,[3,4,6,7] and pulsed NMR.[8] The ^{57}Fe resonance in Fe-Co has been examined by the Mössbauer effect,[9–11] cw NMR,[12–14] and pulsed NMR.[14,15] The recent publications of Mendis and Anderson[13] and Stearns[15] are of particular relevance to the present article.

As an example of the disagreement among the various authors who have studied the ^{57}Fe hyperfine field spectrum of Fe–Co, we quote the following disparate results they have reported, typically in a $Fe_{99}Co_{01}$ alloy. Budnick *et al.*,[2] Rubinstein *et al.*,[14] and Mendis and Anderson[13] report a single satellite line occurring at a frequency $\sim$1.3% above the central resonance; the latter authors attribute this to the effects of a third-neighbor cobalt impurity. Wilson[12] reports no observable satellite lines; Wertheim *et al.*[10] report a satellite due to a nearest-neighbor (nn) cobalt atom at +4.3% and a second satellite line at +2.1% due to the presence of a next-nearest-neighbor (nnn) cobalt impurity atom. Stearns, in her Mössbauer-effect study,[11] reports that no resolved structure exists, and in her pulsed NMR study,[15] she attributes the observed structure purely to instrumental effects. Finally, Johnson *et al.*[9] report lines for Fe–Co alloys not much broader

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[1] J. I. Budnick, L. J. Bruner, R. J. Blume, and E. L. Boyd, J. Appl. Phys. **32**, 120S (1961).

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[3] Y. Koi, A. Tzujimura, T. Hihara, and T. Kushida, J. Phys. Soc. Japan **16**, 1040 (1961).

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[6] E. Simanek and Z. Sroubek, Czech. J. Phys. **B12**, 202 (1962).

[7] G. H. Day, Ph.D. thesis, University of California, 1964 (unpublished).

[8] R. F. Jackson, R. G. Scurlock, D. B. Utton, and T. H. Wilmshurst, Phys. Letters **12**, 168 (1964).

[9] C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, Proc. Phys. Soc. (London) **81**, 1079 (1963).

[10] G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. Letters **12**, 24 (1964).

[11] M. B. Stearns, Phys. Rev. **146**, 439 (1966).

[12] G. V. Wilson, Proc. Phys. Soc. (London) **84**, 689 (1964).

[13] E. F. Mendis and L. W. Anderson, Phys. Rev. Letters **19**, 1434 (1967).

[14] M. Rubinstein, G. H. Stauss, and M. B. Stearns, J. Appl. Phys. **37**, 1334 (1966).

[15] M. B. Stearns, Phys. Rev. **162**, 496 (1967).

than those of pure iron. There is a similar lack of accord in the reported results on the ^{59}Co hyperfine field spectra of these alloys.

The purpose of the present paper is to present new data on the nuclear resonance spectra of iron-rich FeCo alloys which will clarify the existing uncertain situation. Our results show unambiguously that the ^{57}Fe satellite structure reported by Mendis and Anderson[13] (and by Budnick *et al.*[2]) are indeed correct, as is the satellite structure on the Co^{59} resonance reported by LaForce *et al.*[4,7] However, we disagree with both of these authors on their analysis concerning the origin of these additional resolved lines, and present what is believed to be the correct configuration of nearby cobalt impurities which are responsible for the appearance of these satellite resonances. In addition, we show that Stearns has been unduly pessimistic concerning the ability of the spin-echo technique to correctly resolve hyperfine structure in Fe-Co alloys. Further, we show that there is a quite accurate scaling between the ^{59}Co and the ^{57}Fe resonance spectra. Finally we confirm the remarkable additivity of impurity effects on the hyperfine field of both constituents of this alloy system which has been observed by other workers.

EXPERIMENTAL TECHNIQUE

Both cw and transient excitation of ^{59}Co and ^{57}Fe nuclear spins have been utilized in this study. A frequency-swept, frequency-modulated rf oscillator and a variable-frequency spin-echo spectrometer were used, respectively, for these two types of excitation.

An article describing the construction of the rf oscillator has recently appeared.[16] This oscillator-spectrometer is recommended as being exceedingly simple to construct, and as being reliable as well as versatile in operation. It is built by coupling the oscillator head of Measurements Corporation's Model 59 "Megacycle Meter" grid dip meter to a ripple-free power supply, and adding a source of frequency modulation. Lock-in techniques are used to amplify and display the nuclear resonance signals. While the ^{59}Co resonance in these *Fe*Co alloys could be observed with the oscillator operating in its marginal mode of detection, it was necessary to employ super-regenerative detection to trace the ^{57}Fe resonance, due to this nucleus' low natural abundance and small gyromagnetic ratio. When using super-regenerative detection for line-shape investigations, it is essential to avoid the spurious sidebands which can occur in the resonance spectrum, spaced at integral multiples of the quench frequency. This becomes a formidable task when super-regenerative detection is used to investigate line shapes of narrow signals, e.g., of pure nuclear quadrupole resonances. It is, however, easily accomplished when the nuclear resonance line is wide and inhomogeneously broadened, as is the case of the resonances investigated in this paper. The essential requirement is the use of sufficiently slow quench rates, so that the quenching frequency is substantially lower than the NMR linewidth. With the quench frequency so adjusted, the individual sidebands in the spectrum collapse, becoming unresolvable from one another. This results in an instrumental broadening of the resonance spectrum, usually negligible compared to the natural linewidth of the sample, and in the complete elimination of spurious structure. For typical quench frequencies used in this study, we estimate the super-regenerative instrumental linewidth to be about 100 kc. The procedure for accomplishing this is to trace the resonance through, using a relatively high quench frequency. The quench rate is then lowered, the amplitude of the quenching signal is adjusted to maintain the oscillator's sensitivity, and the spectrum is traced again. This process is repeated until lowering the quench rate has no further effect upon the details of the resonance spectrum. In this work, we used the lowest quenching rates consistent with maintaining the requisite sensitivity, about 30 kc for the ^{57}Fe resonance.

The technique of transient excitation of nuclear spins in ferromagnetic alloys is by now well established, and has been fully described by Streever and Uriano.[17] It consists of creating a spin-echo by applying to the sample two consecutive pulses of rf excitation, and measuring the amplitude of the spin-echo signal as a function of frequency across the inhomogeneously broadened nuclear resonance line. This procedure has been criticized in a recent paper of Stearns.[15] Stearns has contended that the large rf enhancement factor in iron produces extraneous and complex structure when the spin-echo technique is used to examine the resonance line shape of ferromagnetic alloys. In particular, Stearns has performed a spin-echo study on a sample of $Fe_{0.99}Co_{0.01}$, and finds gross structure periodic in $1/\tau$ (τ is the duration of the applied rf pulse) due entirely to high turning angle effects. She concludes that such effects render the spin-echo technique useless in determining the distribution of hyperfine fields in *Fe*Co alloys. We wish to take exception to these conclusions concerning the applicability of the spin-echo technique to iron alloys. Budnick and Skalski[18] have found, and we concur with this finding, that by using applied rf pulses of long duration and small amplitude the resonance spectrum can be accurately and reproducibly traced. For narrow lines with high enhancement factors, turning angle effects are quite serious; but their effect can be completely eliminated, except for a residual instrumental broadening which are estimate to be about 400 kc, for the broad resonances which these iron alloys display. The situation is analogous to the elimination of the spurious sideband re-

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[16] M. Rubinstein and S. Shtrikman, Am. J. Phys. **35**, 945 (1967).

[17] R. C. Streever and G. A. Uriano, Phys. Rev. **139**, 135 (1965).

[18] J. I. Budnick and S. Skalski, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967), p. 724.

sponses in the super-regenerative detection technique which we have discussed above. A convenient pulse length is chosen for the spin-echo spectrometer, and the resonance spectrum is traced. The pulse length is then increased, the amplitude of rf excitation adjusted, and the resonance spectrum is traced again. The process is repeated until further lengthening of the pulse length has a negligible effect on the spectrum. In this work we have used pulse lengths of the order of 50-μsec duration.

In Fig. 1 we compare the super-regenerative and the spin-echo traces obtained in an iron alloy containing 1% cobalt impurity at 4.2°K. Both the ^{57}Fe and the ^{59}Co resonance spectra are shown. When allowance is made for the difference in the inherent resolution of the two techniques, there is good agreement between super-regenerative and spin-echo spectra obtained for each alloy constituent. Equally important, researchers elsewhere have published spectra of $Fe_{0.99}Co_{0.01}$ using the marginal oscillator technique; LaForce *et al.*[4] have examined the ^{59}Co spectrum (Fig. 2 of their paper), and Mendis and Anderson[13] have studied the ^{57}Fe spectrum [Fig. 1(c) of their paper]. Excellent agreement is obtained by comparing these spectra to our own. We conclude, therefore, that the use of the spin-echo method to investigate the hyperfine field distribution is justified, at least in the case of *Fe*Co alloys.

EXPERIMENTAL RESULTS

The similarity between the ^{57}Fe and the ^{59}Co resonance spectra shown in Fig. 1 is quite evident. Both resonances show a prominent satellite line occurring on the high-frequency side of the central, unshifted peak. This satellite is displaced from the central component by +4.7 kOe (0.65 Mc/sec) in the ^{57}Fe spectrum and +3.5 kOe (3.5 Mc/sec) in the ^{59}Co spectrum; these displacements are designated, respectively, as ΔH^{Fe} and ΔH^{Co}. When alloys with both higher and lower cobalt concentrations are examined, additional satellite lines appear in both spectra. For these lines, too, a one-to-one correspondence exists between the Co and the Fe spectra. With suitable scaling of the horizontal frequency axis and vertical amplitude axis, the ^{59}Co resonance and the ^{57}Fe resonance can be made to coincide. Using the same scaling factor for alloys of different cobalt concentration, the positions of the other (corresponding) resolved lines are also found to coincide. Moreover, when instrumental broadening corrections are made, the linewidths of the individual resonances are found to scale with this same constant of proportionality. We may thus define a scaling factor which characterizes the *Fe*Co alloy system as the ratio of the hyperfine field shift of the prominent ^{59}Co satellite line (from the central ^{59}Co resonance) to the corresponding field shift of the ^{57}Fe; we obtain $\Delta H^{\mathrm{Co}}/\Delta H^{\mathrm{Fe}}=0.74$. Such a detailed scaling of the solute and solvent hyperfine spectra has been previously noted in the *Fe*Mn system,[19] where a scaling factor $\Delta H^{\mathrm{Mn}}/\Delta H^{\mathrm{Fe}}=1.26$ was obtained. Scaling is to be expected when only one of the two competing causes of hyperfine field shifts (spin polarization of 4*s* conduction electrons, or charge screening by itinerant 3*d* electrons) is dominant. A vital part of the interpretation of these spectra consists in assigning to each satellite line a nucleus, or group of nuclei, that resides on a fixed shell about a cobalt site. If this can be done properly, a mapping of the magnetic disturbance emanating from the cobalt impurity is obtained. We shall find the detailed correspondence between the ^{59}Co and the ^{57}Fe resonances very helpful in this regard.

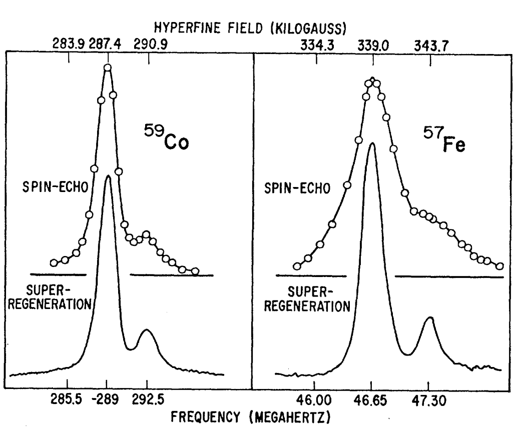

FIG. 1. ^{59}Co and ^{57}Fe hyperfine field spectra in a $Fe_{99}Co_{01}$ alloy at 4.2°K.

Surrounding each substitutional cobalt impurity in the bcc iron lattice is a nn shell consisting of eight sites, a nnn shell containing six sites, a third- and fourth-neighbor shell containing 12 and 24 sites, respectively, etc. The hyperfine field at a ^{57}Fe or a ^{59}Co nucleus which resides in one of these near-neighbor sites will be altered somewhat because of the short-ranged influence of the central Co impurity. However, it is expected that the hyperfine field shifts of atoms beyond third or fourth nn are too small to be resolved from each other. Each resolved satellite line in the experimental spectrum is assigned to a given configuration of nearby cobalt impurities by comparing the measured intensity to the theoretical intensity, computed by assuming the alloy contains a purely random distribution of cobalt atoms. When the resonance spectra consist of a main line and a single resolved satellite line, the ratio of the intensity of the satellite line to the intensity of the main line in a perfectly random alloy is given by $nc/(1-c)$, where c is the impurity concentration and n is the number of equivalent sites on the shell associated with the satellite line. For the 1% *Fe*Co alloy whose spectra are shown in Fig. 1 we would anticipate an intensity ratio of 0.08 if the satellite line is caused by nearest neighbors to the cobalt impurity, 0.06 if second nearest neighbors are suspected, 0.12 if third nearest neighbors, etc. The obvi-

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[19] M. Rubinstein, G. H. Stauss, and J. Dweck, Phys. Rev. Letters **17**, 1001 (1966).

ous choice is, of course, the nn shell, since nuclei in this shell would be expected to be perturbed most by the impurity. Unfortunately, the measured ratio of the amplitude of the satellite line to the amplitude of the principal line (or the ratio of their respective integrated intensities) is approximately twice the theoretical value of 0.08, for the 1% random alloy. From the data in Fig. 1, we obtain an intensity ratio of 0.15 for both the ^{59}Co and the ^{57}Fe resonances. LaForce, Day, and Ravitz observe an intensity ratio of the satellite to the main line for a 1% Co alloy of 0.13 in their study of the ^{59}Co resonance, while Mendis and Anderson report a ratio of 0.12 in the ^{57}Fe resonance of iron containing 1% cobalt impurity. Day[7] has attributed the anomalously high satellite line intensity on the ^{59}Co resonance to a tendency of the Co atoms to cluster together, creating more nn cobalt atoms than would result from a purely random distribution of cobalt atoms. This argument is negated by the finding that the ^{57}Fe resonance scales with the ^{59}Co resonance, and that the iron satellite is also anomalously intense. Only in a random alloy will we obtain the same statistical distribution of atoms around a cobalt site as around an iron site; and only in such a random alloy will the two resonances be expected to scale as exactly as they are observed to do. Mendis and Anderson sought to explain the satellite line on the ^{57}Fe resonance as due to iron atoms with a cobalt atom as a *third* nearest neighbor. As there are 12 third nearest neighbors in the iron lattice, as compared to 8 first nearest neighbors, the additional intensity on the satellite line can be explained by this hypothesis. Mendis and Anderson further assumed that the satellite lines due to iron atoms with either a first- or a second-nn cobalt atom are too broad to be observed.

In this paper evidence is presented which favors a third, and different, explanation of the spectra. We shall show that difficulties in interpreting the resonance spectra are due to a rather unexpected occurrence. The hyperfine field shift at a Co (or Fe) site which is a first nearest neighbor to a Co impurity is almost exactly equal in magnitude and sign to the hyperfine field shift at a second-nn site. The prominent satellite line observed in Fig. 1 is actually composed of two unresolved lines, a nn and a nnn resonance. As there are eight nn sites and six nnn sites, the amplitude of the satellite line is enhanced considerably by the "accidental" degeneracy of the two resonances. Assuming complete coincidence of the two lines, an intensity ratio of satellite to main line of 0.14 is predicted for a 1% alloy. This is in agreement with the value of 0.15 found in this paper, the value of 0.13 found by LaForce, Day, and Ravitz, and the value of 0.12 reported by Mendis and Anderson.

In order to resolve the two components of the satellite line, the ^{59}Co resonance in a sample of alloy containing $\frac{1}{2}$% cobalt impurity was investigated. After grinding, this alloy was annealed under argon at 600°C for 30 min to remove strains induced by the powdering procedure, whereas the 1% alloy did not receive an anneal after it was filed. The instrumental broadening of the spectrometer was minimized by using the rf oscillator in its marginal mode of operation. (Superregenerative detection was employed in the 1% alloy.) The inhomogeneous linewidth and relaxation time of this resonance was such that fast-passage techniques could easily be employed. This enabled the resonance to be detected in phase-quadrature with the applied modulation, eliminating frequency-dependent background from the spectrum and displaying the inhomogenously broadened absorption line shape directly.[20] The combination of lower impurity concentration, strain-annealing, and marginal detection enabled the satellite line on the ^{59}Co resonance to be resolved into two components. This resonance spectrum is displayed in Fig. 2, where a splitting of the satellite line is evident. This line can be graphically resolved into two distinct components separated by 400 kc, whose amplitudes are very nearly in the ratio of 8 to 6, in agreement with the numerical ratio of nn to nnn sites,

The splitting of the ^{59}Co satellite line has been observed previously by LaForce *et al.*,[4] but it was misinterpreted as a dipolar splitting of the nn line. The sloping baseline on their spectra mistakenly led these authors to believe that the two components had equal intensity. The use of the fast-passage effect eliminates the sloping baseline and shows that the amplitudes are actually in the ratio of 8 to 6. This fact indicates that the splitting is not dipolar in origin, but results from a small difference in isotropic hyperfine field between the first- and the second-nn sites.

It has been implicit in our argument that an explanation of the anomalous intensity of the ^{59}Co satellite line is also applicable to the ^{57}Fe line. Thus, the 400-kc splitting on the cobalt line should, by simple scaling, result in a 75-kc splitting between the nn and nnn resonances on the iron spectrum. This is too small a splitting to resolve by spin-echo or super-regeneration,

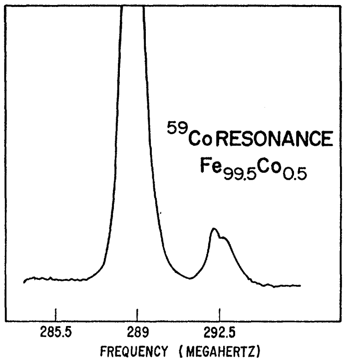

FIG. 2. ^{59}Co hyperfine field spectra in an iron alloy containing $\frac{1}{2}$% cobalt. The satellite line at 292.5 Mc/sec is split by 400 kc.

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[20] D. L. Cowan and L. W. Anderson, Phys. Rev. **135**, A1046 (1964).

TABLE I. Summary of the positions of satellite lines and the corresponding occupational configuration of atoms about a cobalt impurity, as discussed in the text. Data are taken partly from LaForce *et al.*,[a] partly from Mendis and Anderson,[b] and partly from confirmatory measurements of our own in *Fe*Co alloys containing up to 6% cobalt.

Configuration	Single nn	Single nnn	Two nn's and/or nnn's	Three nn's and/or nnn's	Single $N3$ and/or $N4$
Shift of ^{59}Co satellite (kOe)	+3.3	+3.7	+7.0	+10.5	+0.6
Shift of ^{57}Fe satellite (kOe)	+4.4	+5.0	+9.4	+14.1	+0.8

[a] References 4 and 7. [b] Reference 13.

and probably too small to resolve by marginal oscillator detection.

Besides the lines discussed above, it is possible to resolve other lines in the spectra of this alloy system. (Much of what we have to say concerning these lines relies on a synthesis of the results of LaForce *et al.*[4,7] and Mendis and Anderson[13] with our own confirmatory data. The reader is referred to their papers for the spectra.) As the concentration of cobalt atoms is increased, additional satellite lines appear in the high-frequency wings of both the ^{59}Co and the ^{57}Fe resonance. These additional lines are displaced from the central resonance by hyperfine field shifts which are, within experimental error, exactly two times, three times, and four times the shift of the satellite line due to a single nn (or nnn) cobalt impurity. From this fact, and from measurements of relative intensity, we can identify these additional lines as arising from ^{59}Co or ^{57}Fe nuclei with two, three, and four nn or nnn cobalt impurities, respectively. (The splitting of these lines is not observed in cobalt concentrations exceeding 1% due to the large line-broadening effects.) The additivity of these impurity effects, which are remarkably accurate in *Fe*Co, has been previously observed by both LaForce[4] and Mendis[13] in their investigations.

It is possible to infer the existence of yet another satellite line by the spectral examination of alloys containing less than 1% cobalt. This satellite line is only partially resolvable from the central resonance, and is due to nuclei with a single cobalt impurity as either a third or fourth nearest neighbor. The lack of resolution of this line from the central peak prevents us from being more specific. This line is displaced to the high-frequency side of the central iron line by 0.8 kOe and to the high-frequency side of the central cobalt line by a proportional amount, 0.6 kOe. The experimental findings are summarized in Table I. It should be noted that the satellite line caused by nuclei with a single nnn impurity is displaced to a higher field than the corresponding line caused by nuclei with a single nn impurity.

DISCUSSION

It seems to be generally agreed that the Fermi surface in iron intersects both a narrow $3d$-like band and a broad $4s$-like band of electrons. The $3d$ band, at least, is split by the exchange interaction into two subbands of opposite spin, resulting in a net magnetization of 2.2 μ_B per iron atom. When a cobalt impurity atom is introduced into the iron lattice, itinerant electrons are obliged to shield the excess nuclear charge of the cobalt locally, in order to maintain over-all charge neutrality. This shielding is accomplished primarily by the $3d$ electrons, owing to their larger density of states. Because the $3d$ band is initially magnetized, this screening results in a concomitant magnetic disturbance which emanates from the cobalt impurity atom. It is the spatial distribution of this magnetic moment disturbance which Low and his collaborators seek to quantify with their neutron diffuse-scattering technique.[21] The $4s$ electrons sense this localized magnetic disturbance through the s-d exchange interaction, and undergo exchange scattering. This exchange scattering produces a spatially varying magnetization in the $4s$ band, extending outward from the impurity site. Although the induced magnetization in the $4s$ band is an order of magnitude weaker than the induced magnetization in the $3d$ band, its hyperfine interaction with the nuclear moments is an order of magnitude stronger. Thus, the impurity-induced changes in the hyperfine fields of transition-metal alloys are, in general, due to two competing mechanisms of roughly equal strength; although for some alloys (e.g., *Fe*Al and *Fe*Mn) it is possible to show that $4s$ spin-polarization effects are dominant.

To date, the various theories which attempt to describe the magnetic disturbance of the $3d$ band electrons in transition-metal alloys have relied on a coupling of phase-shift analysis with a δ-function potential,[22] or with the Friedel sum rule,[23] use of the Green's function method,[24] and the random-phase approximation to the dielectric function.[25,26] The response of the $4s$ conduction electrons to the impurity potential has been treated by the use of some refinement of the Ruderman-Kittel-

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[21] M. F. Collins and G. G. Low, Proc. Phys. Soc. (London) **86**, 535 (1965).

[22] F. Gautier, in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (W. A. Benjamin, Inc., New York, 1963).

[23] A. Blandin and J. Friedel, J. Phys. Radium **20**, 160 (1959).

[24] A. M. Clogston, Phys. Rev. **125**, 439 (1962).

[25] G. G. Low, Proc. Phys. Soc. (London) **92**, 938 (1967).

[26] D. J. Kim and B. B. Schwartz, Phys. Rev. Letters **20**, 201 (1968).

Yosida interaction.[27] Unfortunately, these theories are only moderately successful in predicting the observed properties of the simplest alloy systems, e.g., those involving noble metals as solvents, and a discussion from first principles of hyperfine fields in ferromagnetic transition-metal alloys seems hardly feasible at present. We, therefore, adopt a phenomenological approach, using the experimental results primarily obtained in neutron diffraction and magnetization studies of this, and similar, iron alloys.

The observed radial distribution of hyperfine fields at sites surrounding the impurity atom can be decomposed into two factors: a contribution that is proportional to the induced magnetic disturbance in the "localized" $3d$ moment at atoms situated near the impurity site, and a second contribution that is proportional to the spatial fluctuations of the $4s$ conduction-electron spin polarization about the impurity atom. The $3d$ magnetic disturbance interacts with the nuclei by core polarization of the inner s shells while the $4s$ contribution interacts directly by Fermi-Segre "contact" interaction. The radial distribution of the hyperfine field shifts at iron nuclei at a distance r from a cobalt impurity, $\Delta H^{\mathrm{Fe}}(r)$, may be given by the formula

$$\Delta H^{\mathrm{Fe}}(r)=a\Delta\mu^{\mathrm{Fe}}(r)+b\Delta\sigma(r). \qquad (1)$$

Here, $\Delta\sigma(r)$ is a function describing the radial dependence of the $4s$ conduction-electron spin polarization produced by the interaction of the $4s$ electrons with the magnetic moment residing on the impurity site, $\Delta\mu^{\mathrm{Fe}}(r)$ is the induced change in the localized $3d$ magnetic moment at iron sites displaced a distance r from the impurity site, b is the Fermi-Segre contact interaction constant $(8\pi/3)\,|\Psi(0)|^2$, equal to about 1.5–2 MG/μ_B, and a is the constant of proportionality appropriate to the core-polarization mechanism in transition metals, typically -100 to -150 kG/μ_B.

When the ^{59}Co hyperfine field distribution is being considered, we are then concerned with the shift in hyperfine field at a cobalt nucleus which is located at a small distance r from another cobalt impurity, $\Delta H^{\mathrm{Co}}(r)$. An analogous formula to Eq. (1) may be written, with the induced change in the cobalt moment substituted for the change in the iron moment. It is assumed that the constants of proportionality a and b and the conduction-electron spin polarization $\Delta\sigma(r)$ are unchanged in going from an iron atom to an equivalently positioned cobalt atom, since both solute and solvent are transition-metal atoms with similar nuclear charges.

$$\Delta H^{\mathrm{Co}}(r)=a\Delta\mu^{\mathrm{Co}}(r)+b\Delta\sigma(r). \qquad (2)$$

In order to proceed further, it is necessary to make use of the neutron diffraction data of Collins and Low.[21] By measurements of the diffuse scattering of slow neutrons impinging on samples of dilute iron alloys, these authors were able to obtain information on the value of the localized moment residing on the impurity atom, and on the spatial distribution of magnetic moment disturbance around the impurity [the function $\Delta\mu^{\mathrm{Fe}}(r)$ in Eq. (1)]. The most probable value of the magnetic moment on the cobalt atom obtained by this technique is 2.1 μ_B. Since the value of the moment residing on the iron atoms is 2.2 μ_B, there is only a very small difference, 0.1 μ_B, between the moment on the host and the moment on the impurity atom in these *Fe*Co alloys. The magnitude of the exchange interaction between a localized impurity moment and the $4s$ conduction electrons is proportional to the *difference* between the impurity and the host moment; consequently, we may expect the $4s$ conduction-electron contribution to the hyperfine field shifts [the quantity $a\Delta\sigma(r)$ in Eqs. (1) and (2)] to be small. We therefore hypothesize that the $4s$ conduction-electron contribution can be neglected to first order, and that the distribution of hyperfine fields in *Fe*Co measures predominantly the distribution of $3d$ magnetic moment present in this alloy system.

The neutron scattering data of Collins and Low have been analyzed by these authors, and also by Campbell,[28] using a different approach, to yield quantitative values for the moment distribution around the cobalt impurity site. They find that the magnetic moment disturbance created by a cobalt impurity outside the impurity site to be everywhere positive, rather than oscillatory. The average moment on the first and second neighbors to the cobalt impurity is found to be increased by $+1\%$ ($+0.02$ μ_B) relative to the pure iron value. (The error bars on this value are substantial.) We have found the average hyperfine field shift on first and second ^{57}Fe neighbors to the cobalt impurity to be $+4.7$ kOe; this represents an increase of $+1.4\%$ over the pure iron value of 339 kOe. Considering the poor resolution of the neutron scattering experiments, this does not appear to represent any real disagreement between the two measurements. If we assume that each Bohr magneton of moment on the iron site increases the (absolute value of the) hyperfine field by 150 kOe,[29] we obtain the result that the moment on iron atoms which are nearest neighbors and next nearest neighbors to a cobalt impurity are increased by 0.03 μ_B over their unperturbed value of 2.2 μ_B. The fact that the second-nn line is shifted slightly higher than the first-nn line may be due to oscillatory $4s$ conduction-electron effects; more likely, it is caused by the change in sign of the hyperfine field from the negative (with respect to pure iron) magnetic moment increment on the cobalt site

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[27] K. Yosida, Phys. Rev. **106,** 893 (1957); A. W. Overhauser and M. B. Stearns, Phys. Rev. Letters **13,** 316 (1964); T. A. Kaplan, *ibid.* **14,** 499 (1965); R. E. Watson and A. J. Freeman, Phys. Rev. **152,** 566 (1966).

[28] I. A. Campbell, Proc. Phys. Soc. (London) **89,** 71 (1966).

[29] A. J. Freeman and R. E. Watson, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. II A, p. 270.

to the positive and decreasing moment increments on the neighboring iron sites. Such a picture has been sketched by Low[25] to represent the trends indicated by his neutron scattering data.

A somewhat different analysis has been used by Bernas and Campbell[30] to correlate the iron hyperfine field distribution with the magnetic moment distribution determined by neutron scattering. These authors have proposed an empirical relationship between the *average* hyperfine field shift of nn and nnn iron sites to an impurity and the change in the average moment on these sites relative to pure iron. This relationship involves two terms: a contribution induced by a direct core-polarization term proportional to the change in the moment on the iron site in question, and a conduction-electron-polarization term depending on the changes in the moments on the surrounding sites. The relationship is

$$\Delta H = a\Delta\mu_1 + b \sum_{\mathrm{nn,nnn}} \Delta\mu_n, \tag{3}$$

where ΔH is the experimentally observed change in the average field on nearest and next-nearest neighbors to an impurity, $\Delta\mu_1$ is the average change in moment at the iron site in question, $\Delta\mu_n$ is the change in moment, relative to pure iron, of the surrounding sites (including the impurity moment), and the sum is over nn and nnn sites only, with further terms ignored. The value for a is given as 90 kOe/μ_B, and the value for b is taken as 6 kOe/μ_B, irrespective of whether the neighboring site is occupied by a host atom or an impurity. The reason for considering the *average* of the shifts of nearest and next nearest neighbors is that the sum of the moments on the first and second neighbors is much better defined from the neutron scattering results than the values of the two sites individually. In the case of *Fe*Co, where the field shifts are almost equal on the two sites, this expression would appear to be particularly well suited.

Using Eq. (3), Bernas and Campbell have obtained good agreement concerning both magnitude and sign between the calculated and the experimentally determined hyperfine field shifts on a variety of iron alloys. The notable exception listed in their paper is *Fe*Co, where the calculated value is less than half the experimental value, compared to discrepancies of 10–15% for all the other iron alloys. Part of the trouble results from using Mössbauer-effect results of Wertheim *et al.*[10] as the experimental input; their value for the field shifts in *Fe*Co are larger by a factor of 2 than the results reported in the present paper. Judging from the preceding discussion, there is also some reason to question the accuracy of the neutron diffraction analysis concerning the value of the change in the moment on iron atoms surrounding a cobalt impurity. We will, therefore, reverse the procedure of Bernas and Campbell; we accept as given both the value of the cobalt moment (2.1 μ_B) and the value of the average hyperfine field shifts of the nearest and next nearest iron neighbors to a cobalt impurity (4.7 kOe or +1.4%), and use Eq. (3) to calculate the change in the moment induced by the cobalt impurity on neighboring iron sites, $\Delta\mu^{\mathrm{Fe}}$. An iron atom which is a nearest neighbor to a cobalt impurity will be a nearest neighbor or a next nearest neighbor to six other iron atoms (in addition to the cobalt) which are also nearest neighbors or next nearest neighbors to the cobalt; similarly, an iron atom which is a next nearest neighbor to a cobalt is adjacent to four other iron atoms (in addition to the cobalt) which are also nearest neighbors or next nearest neighbors to the same cobalt. Thus, an average perturbed iron atom is adjacent to 1 cobalt impurity and 5.1 perturbed iron atoms. Using Eq. (3), we obtain for the weighted average change in an iron atom with a nn or a nnn cobalt impurity, $\Delta\mu^{\mathrm{Fe}} = +0.044\ \mu_B$, a +2% shift in the value of the unperturbed iron moment. This is to be compared to the value of +1% deduced by Campbell from the neutron diffraction data. Nevertheless, we may estimate the individual contributions made by the core polarization [the first term in Eq. (3)] and by conduction-electron polarization [the second term in Eq. (3)] by accepting the 2% value. We find that the core-polarization term is responsible for 84% of the total field shift, in agreement with the conclusions reached in the preceding discussion.

SUMMARY

We have sought to demonstrate that the spin-echo technique can yield reliable information on the hyperfine field distribution in ferromagnetic alloys. New data are presented on the ^{57}Fe and the ^{59}Co nuclear resonance spectra in *Fe*Co alloys which show that there exists a detailed scaling of the two constituent resonances. A new interpretation on the origin of the individual spectral lines is offered, which is in accord with the experimentally observed intensities. We have also suggested that the hyperfine field distribution in this alloy system arises predominantly from core-polarization effects.

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[30] H. Bernas and I. A. Campbell, Solid State Commun. **4**, 577 (1966).