

SPIN-ECHO STUDIES OF CONDUCTION-ELECTRON POLARIZATION
ABOUT THE IMPURITY ATOM IN Fe-RICH ALLOYS*

J. I. Budnick, T. J. Burch,† S. Skalski, and K. Raj
Fordham University, The Bronx, New York 10458
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In this Letter some of the disagreement between previous NMR investigations of transition-metal impurities in Fe is clarified. A clear analysis of the experimental data is presented and its relation to the average unpaired spin density in several Fe alloys as measured by neutron scattering is pointed out.

There has been considerable interest in the effect of impurity atoms in a ferromagnetic transition metal, especially on the electronic structure at host atoms which are near neighbors to an impurity.¹⁻⁵ Changes in the local electronic structure about a particular atom due to alloying produce changes in the hyperfine field at its nucleus. In particular, if the impurity disturbs the conduction-electron polarization (CEP), it will affect the hyperfine field at atoms which are quite distant from the impurity.² Numerous measurements of the hyperfine field have been made in a variety of alloys by continuous-wave⁶ (cw) and spin-echo nuclear magnetic resonance studies^{4,7} as well as by application of the Mössbauer effect.^{1,2} The conclusions that are drawn from these works about the spatial distribution of the measured hyperfine fields and consequently about the role of CEP effects appear to be in conflict.

In this paper we present new experimental results with which we clarify and resolve conflicts^{6,7} in the existing experimental situation for Fe-rich alloys. In addition we draw conclusions from this data about CEP and point out relationships between the NMR data and the spin-density distribution about an impurity in Fe as determined by neutron scattering.⁸ In particular, we discuss in detail the NMR spectra for Fe:Co—a system extensively discussed in the literature—and we compare the behavior of this system and several other similar systems (Fe:Ni, Fe:Rh, Fe:Pt, Fe:Pd).

The NMR spectra of most Fe-rich alloys show at least one clearly resolved satellite line. Reported measurements of the intensity of this resolved satellite relative to the intensity of the main line for Fe:Co^{4,6,7} are not in agreement and, therefore, the explanations of the origin of this satellite have differed significantly. The cw experiments of Mendis and Anderson on an alloy Fe_{0.99}Co_{0.01} give a value of this ratio of 0.12, while the spin-echo result of Rubinstein gives a value of 0.15. This satellite has been assigned to Fe atoms with an impurity in the third-neigh-

bor shell by Mendis and Anderson, while Rubinstein associates this line with Fe atoms having a single Co impurity as a first or second near neighbor. The latter assignment implies that the field shift is the same at Fe atoms which are first and second near neighbors of an impurity. Clearly any deductions about CEP effects would differ drastically depending on the assignment chosen. Furthermore, the early Mössbauer-effect work¹ indicated appreciable intensity at higher fields which is not observed in the cw experiment and not emphasized by Rubinstein in his analysis.

We will make the analysis of all our alloys in this paper on the basis of new spin-echo data taken at 1.35°K. The resolution of these data is better than that of the previously reported spin-echo NMR data⁷ because the echo signal is stronger at the lower temperature, permitting the use of longer rf pulses which have fewer Fourier components. Spectra⁹ for several concentrations of Fe:Co alloys are shown in Fig. 1. The repetition rate and pulse-separation times of the experiment were chosen so that there was no distortion of the spectra from T_1 or T_2 relaxation effects.

On comparing our spectra with the previously published results we find that the integrated intensity of the resolved satellite relative to the main line is 1.5 to 2.0 times larger in our spectra than either of the results of Refs. 6 and 7. This difference is understandable if we note that the relative intensity of the resolved lines in the spectra of Ref. 7 were obtained by measuring only the relative amplitudes of the resolved lines. One must assume that the lines due to Fe atoms with various near-neighbor configurations are symmetric and have the same width in order for the data to be treated in this way; this is apparently not the case for the spectra of Ref. 7. The spectra are, however, very similar to ours, and if the integrated intensity rather than the amplitude is calculated for Rubinstein's spectra, the agreement with our result is quite good. On the other hand, the experiments reported in Ref. 6

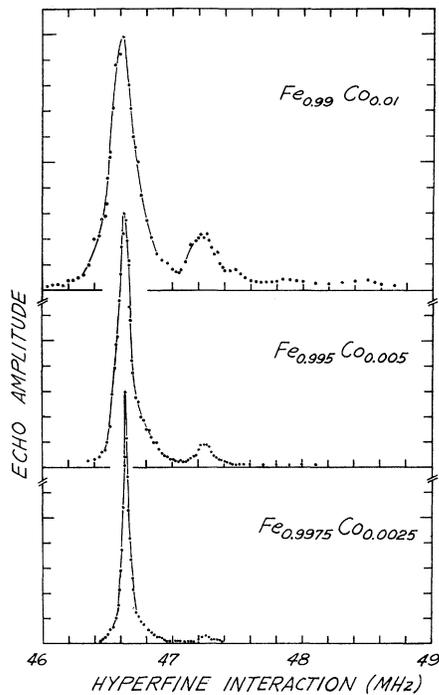


FIG. 1. Spin-echo spectra of ^{57}Fe in Fe:Co alloys at 1.35°K .

are cw experiments. Data are, therefore, obtained as the derivative of an absorption rather than the absorption itself. Only relatively large changes in the slope of the absorption are seen. As mentioned by Mendis and Anderson, broad slowly varying contributions to the intensity would not be observed. If we draw what we believe to be a reasonable base line for a cw experiment on our spin-echo spectra, thus excluding the weak and broad contributions, the integrated intensities of the upper portions of our spin-echo spectra and the cw spectra of Ref. 6 are in good agreement. Finally, the earliest Mössbauer work indicated significant intensity corresponding to field shifts 2 or 3 times as high as the shifts reported in either Ref. 6 or 7 for the resolved satellite. Our spectra (taken at low temperature with an increased signal-to-noise ratio) clearly show a low-intensity broad contribution in this region. This intensity is too large to be explained by Fe atoms with more than one impurity in their nearest-neighbor shells.

To assign various parts of a spin-echo spectrum to sites with specific neighbor configurations is very difficult. Indeed, in view of the fact that the spectral lines due to nuclei in sites with different neighbor configurations almost certainly have different widths and different degrees

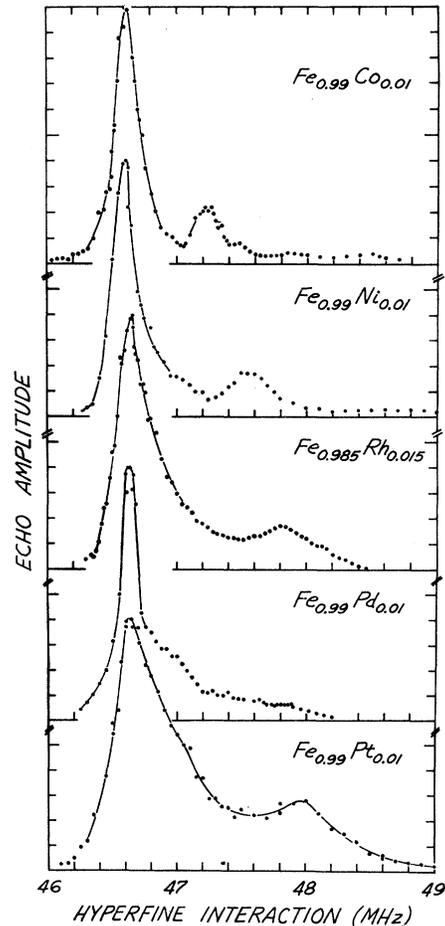


FIG. 2. Spin-echo spectra of ^{57}Fe in some Fe alloys containing elements to the right of Fe in the periodic table at 1.35°K .

of asymmetry, a unique solution to this problem is probably impossible unless assumptions are made concerning broadening, asymmetry, and the positions of the lines to reduce the number of parameters.

At this stage a more fruitful approach may be to determine the total number of atoms affected by the impurity and thus obtain an approximate range for the spin perturbation. Some results of our spin-echo data on several systems are presented in Fig. 2. Our spin-echo data do show the following characteristics which any explanation of the hyperfine fields in these alloys must take into consideration: (1) A large intensity on the high-frequency side of the main line. The number of neighbor shells required to explain this intensity decreases slightly with increasing alloy concentration. (2) A clearly resolvable satellite line. The separation of this line from the main line does not depend on the concentra-

tion in a given alloy system but does vary between different alloy systems. The width of the satellite is concentration dependent. (3) A small but definite concentration-dependent shift of the main line. (4) A concentration-dependent broadening of the main line.

These characteristics of the spectra are consistent with the following observations. The large total intensity outside the symmetrized main line argues for a perturbation of the matrix spin density which extends out to about 4 to 6 neighbor shells for Co or Ni in Fe, the systems most extensively studied by us. The fact that most of this intensity is on the high-frequency side of the main line agrees well with the neutron-scattering experiments⁸ which show that, for the systems studied here, the perturbed spin density is definitely positive. The apparent decrease in the number of shells required to fit the data may be a consequence of the increased broadening occurring at higher concentrations. This would effectively place more intensity in the main line.

The separation of the clearly resolved satellite from the main line increases as we go through the Co-Ni-Rh-Pd-Pt impurity series. This behavior is remarkably similar to the variation of the perturbed matrix spin density⁸ for the more distant regions of the disturbance, and suggests that part of this satellite may arise from Fe atoms which are third neighbors to the impurity.

The definite shift in the peak of the main line, while difficult to accurately describe quantitatively, may arise from small but uniform changes in one part of the spin density. A variety of causes exist for such changes, e.g., density-of-states changes, changes in the *s-d* admixture on alloying, and repopulation effects between the *s* and *d* bands.

The fairly symmetric broadening of the main line with increased concentration suggests oscillation in the perturbed hyperfine interaction at Fe sites far from an impurity. This could be due to oscillations in the CEP at the distant sites. The spin-density perturbation about an impurity in the Fe lattice, for the impurities studied in this paper, does not show any clear oscillations. However, any oscillations in the CEP consistent with the NMR data are on too small a scale to be detected by neutron scattering.

Although we have discussed the NMR results for a class of Fe-alloy systems for which the impurity is to the right of Fe in the periodic table (class *R*), there is also a strong correla-

tion of NMR and neutron-scattering results for the alloy systems for which the impurity lies to the left of Fe (class *L*). In particular we might mention that in Fe:Mn and Fe:V¹⁰ as well as Fe:Cr, one observes a satellite with a negative field shift. This is entirely consistent with the neutron-scattering result that in class-*L* systems there is a negative spin-polarization perturbation of the matrix at the nearest-neighbor distance whereas with the class-*R* systems, the perturbation is positive. The case of Fe:Ru is somewhat anomalous. In this system one observes well-resolved satellites with both positive and negative frequency shifts.¹¹ One thus cannot escape the conclusion that the spin-polarization perturbation observed in the neutron-scattering experiments, whatever the source (CEP or otherwise), largely determines the hyperfine-field distributions observed by NMR.

In conclusion, we would like to stress that there is more apparent than real disagreement between the various NMR studies of dilute Fe alloys. Furthermore, the NMR results for a large class of Fe alloys are quite consistent with the neutron-scattering results and increase our confidence that it should be possible to understand the gross features of the spatial dependence of both the hyperfine field and spin polarization in dilute solid solutions in terms of a fairly simple theoretical model.

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†Present address: St. Joseph's College, Philadelphia, Pa.

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quencies, a correction must be introduced to obtain a spectrum proportional to the number of nuclei at a given frequency. We have determined that, for our method of measurement, the ratio of the echo amplitude and the frequency is the appropriate quantity to be used in the analysis of spectra. Our conclusion is based on results obtained for the relative intensities of the two separated Fe resonances in Fe₃Si [T. J. Burch, thesis, Fordham University, 1968 (unpublished)] and the relative intensities of the two Ru-isotope resonanc-

es in Ni-rich Ni:Ru alloys (J. J. Murphy, unpublished). We have made no frequency correction to the data reported here since the error introduced is only a few percent over the frequency range in question and would not affect our conclusions.

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TEMPERATURE DEPENDENCE OF THE LINEWIDTH IN CRITICAL SPIN FLUCTUATION

P. Résibois and C. Piette

Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium

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Starting from the kinetic equations obeyed by the time-dependent spin-correlation functions, we have calculated the homogeneous function which appears in the dynamical scaling expression for the linewidth of critical fluctuations in ferromagnets and antiferromagnets. In agreement with recent experimental findings, this function shows a minimum for $\kappa/q \equiv$ inverse correlation length/wave number $\neq 0$.

A series of recent experiments¹⁻⁴ on magnetic substances has provided a remarkable confirmation of the dynamical scaling assumptions (DSA) of Halperin and Hohenberg.^{5,6} Moreover, DSA have also received strong theoretical support from the work of Kadanoff and Swift,⁷ Kawasaki,⁸ and Mori.⁹

Nevertheless the only formulation leading to a fully microscopic understanding of DSA is based on the kinetic equations obtained independently by De Leener and one of the authors (P.R.)^{10,11} (Ref. 11 is hereafter referred to as RDL IV) and by Kawasaki.^{12,13} Unfortunately, these equations have only been justified in the Weiss limit, where the number of neighbors is taken large (see Ref. 10).

Although the Weiss condition is a severe limitation (it is known at equilibrium to lead to erroneous critical indices), the simplest dimensional predictions of this kinetic theory are well verified.

For example, let us consider the spectral function for the spin autocorrelation function, $\Gamma_q(\omega)$ (q is wave number, ω is frequency), and let us denote by $\omega_0(q)$ and $\omega_0^\tau(q)$, respectively, the linewidths of this function at T_c for ferromagnets ($q \simeq 0$) and antiferromagnets ($q \simeq \tau$, where τ is the vector characterizing the staggered magnetization); one finds

$$\omega_0(q) \propto q^{5/2}, \quad \omega_0^\tau(q) \propto (q-\tau)^{3/2} \equiv q^{*3/2}. \quad (1)$$

These results are in remarkable agreement with experiments.

It is thus very tempting to explore further the consequences of this kinetic theory which, in principle, allows us to go beyond DSA. For instance, DSA predicts that, at a temperature $T \neq T_c$ (characterized by a correlation length κ^{-1}), the following results replace Eqs. (1):

$$\begin{aligned} \omega_\kappa(q) &= \omega_0(q)f(\kappa/q), \\ \omega_\kappa^\tau(q) &= \omega_0^\tau(q)f^\tau(\kappa/q^*), \end{aligned} \quad (2)$$

where f and f^τ are homogeneous functions of κ/q ; they are unknown except for their asymptotic behavior:

$$\begin{aligned} f(x) &\rightarrow 1, \quad f^\tau(x) \rightarrow 1, \quad \text{when } x \rightarrow 0; \\ f(x) &\propto x^{1/2}, \quad f^\tau(x) \propto x^{3/2}, \quad \text{when } x \rightarrow \infty. \end{aligned} \quad (3)$$

On the contrary, kinetic theory allows us to compute f and f^τ explicitly for all values of x . We have performed such a calculation which we now summarize briefly.

The starting point is the kinetic equation obeyed by the time-dependent spin-correlation function $\tilde{\Gamma}_q(t)$ [normalized in such a way that $\tilde{\Gamma}_q(t=0) = 1$]: It reads [see RDL IV, Eq. (I.5)]

$$\partial_t \tilde{\Gamma}_q(t) = \int_0^t \tilde{G}_q(\tau | \tilde{\Gamma}_q) \tilde{\Gamma}_q(t-\tau) d\tau, \quad (4)$$

where the non-Markoffian kernel \tilde{G}_q is a functional of $\tilde{\Gamma}_q$, and can be expanded according to rules given in RDL IV:

$$\tilde{G}_q(\tau | \tilde{\Gamma}_q) = \tilde{G}_q^{(2)}(\tau | \tilde{\Gamma}_q) + \tilde{G}_q^{(4)}(\tau | \tilde{\Gamma}_q) + \dots \quad (5)$$

The explicit form of $\tilde{G}_q^{(2)}$ is given in RDL IV, Eq. (3.1). In a ferromagnet close to T_c , it re-