Determination of moment distributions and hyperfine fields at and surrounding transition-element solute atoms in Fe

Mary Beth Stearns

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121 (Received 26 September 1973)

A new method is developed which uses the hyperfine spectra of the Fe atoms in dilute Fe alloys to obtain (i) the moment on a transition-metal-solute atom in Fe, (ii) the moment perturbations in the Fe matrix, and (iii) the hyperfine-field shifts at the Fe atoms in the four-nearest-neighbor shells to the solute atom. We find that this method has much more sensitivity than the comparable technique using elastic diffuse neutron scattering. A moment perturbation varying as $1/r^3$ is found to best fit the spectra. For Co and Ni solute atoms we obtain moments of $(1.9 \pm 0.1)\mu_B$ and $(1.4 \pm 0.1)\mu_B$, respectively. These agree with the neutron-scattering results but are much more accurately determined. The moments at Rh and Pd in Fe are found to be $(1.1 \pm 0.2)\mu_B$ and $(0.7 \pm 0.2)\mu_B$, in agreement with neutron-scattering results on more concentrated alloys. The hyperfine-field shifts are obtained in a much more fundamental way than the previous analyses of FeCo spectra. This results in very different hyperfine-field shifts than the previous determination. The average-moment and moment-perturbation behavior is discussed from the point of view that the magnetic behavior of the 3d transition series is determined by the coupling via exchange and interband mixing of mainly localized moments through a small fraction of itinerant d electrons. This is in contrast to a charge-perturbation-type model where the moment behavior is attributed to arise from the different screening of the spin-up and spin-down delectrons. The latter is not believed to be significant in determining the moment behavior. Using the results of this analysis we derive from only hyperfine-field data the value of the core-polarization hyperfine field in Fe. We find indications that this term may be larger than the values previously obtained by band calculations. From the derived moments of Rh and Pd we can obtain a value for the hyperfine field per μ_B due to core polarization for the 4d transition series. We find reasonable agreement with the calculated value. Earlier derivations of the moments of 4d and 5d solute atoms in Fe, as obtained from their measured hyperfine fields, omitted the large self-polarization conduction-electron term. This is considered here and corrected moment values are obtained.

I. INTRODUCTION

The moment distributions on the solute and solvent atoms in binary alloys of transition metals have been mainly investigated by elastic-diffuseneutron-scattering experiments. The early experiments¹ were done on nondilute disordered alloys and their interpretation were very model dependent. Next experiments on dilute binary alloys were performed.² These had the advantage that they were easier to interpret since at sufficient dilution each solute atom disturbs the magnetic moments of the solvent atoms only in its neighborhood and the solute atoms can be regarded as isolated from one another. The neutron experiments, however, have inherent disadvantages in that they measure only the Fourier transform of the magnetic-moment density and so far have only been carried out with long-wavelength neutrons and thus low spatial resolution.

Since hyperfine fields (hff) in Fe alloys originate from the moments, the hyperfine spectra also contain information about the moment distributions. Thus having a model for the origin of the hyperfine field³ it should be possible to drive the moment distribution from the hyperfine-field spectra. We proceed to do this here and find that we can determine the moment on the solute atom and the form of the moment perturbation in the Fe matrix very accurately. This method appears to be much more sensitive to the moment distributions than the present neutron-scattering technique. At present the method is limited to only Fe alloys.

One of the most thoroughly investigated transition-metal-alloy systems is FeCo. We give a brief review of the history of hff measurements for this alloy in Sec. II. We then discuss and indicate the method on this system in Sec. III. In this section we also apply the method to the dilute alloys FeNi, FeRh, and FePd. In Sec. IV we discuss the origin of the moment variations. In Sec. V we use the results of this analysis to derive the core-polarization hff from experimental data only. We find indications that it may be somewhat larger than that obtained from band calculations. In Sec. VI we evaluate the hyperfine-field contribution from the core polarization of 4d-transition-series moments. In Sec. VII we give a corrected derivation of the moments on other 4d- and 5d-transitionseries elements in Fe as obtained from the hyperfine field at the 4d or 5d solute atom.

II. HISTORY OF HYPERFINE SPECTRA OF THE FeCo SYSTEM

The spectra of Fe-rich Co alloys has been measured by $M\ddot{o}ssbauer^{4-6}$ and continuous-wave-⁷⁻¹⁰

9

2311

and pulsed-¹¹⁻¹⁵ NMR experiments. The resolution is inherently very poor (~16 kG) for the Mössbauer technique and nothing much more than a broadening and shifting of the outer lines can be seen. However, by careful computer analysis the centroid of the outer lines can be accurately measured and from this the variation of the average hyperfine field $\overline{H}(x)$ as a function of the atomic percent Co, x, can be obtained. These measurements show that⁴⁻⁶

$$\overline{H}(x)/H_{\rm Fe} = 1 + 0.51x$$
,

as shown in the Appendix A. For dilute alloys this average hyperfine field is given by

$$\overline{H}(\chi) = H_{\rm Fe} + \left(\sum_{n=1}^{\infty} M_n \Delta H_{\rm Fe}^{Nn}\right) \chi ,$$

where M_n are the number of sites in the *n*th shell surrounding a solute atom and ΔH_{Fe}^{Nn} is the change in the hyperfine field at the nth shell due to a solute atom. Both the Co and Fe resonances have been studied by NMR measurements^{13,15} and they show very similar behavior. Since the hyperfine field at an iron atom is much better understood than that of Co we will here concern ourselves only with the Fe spectra. Part of the original difficulty in the interpretation arose because the NMR Fe spectrum consists of a main peak and one well-resolved satellite at about 0.6 MHz above the main peak. Since the hyperfine field in Fe is negative, this satellite corresponds to a -4.4-kG hyperfinefield shift due to a Co solute atom. This satellite was shown to have further structure in Refs. 13 and 14 and from intensity considerations was interpreted by Rubinstein¹³ to be due to Co atoms in the first (N1) and second (N2) nearest-neighbor shells, while Mendis and Anderson¹⁰ interpreted it as due to N3. For these measurements the observed intensity agreed with either interpretation since there are 14(8+6) atoms in the first two shells and 12 in the N3 shell and the experiments were not accurate enough to distinguish between them. In fact, the early NMR experiments were sadly lacking in intensity in the satellites.^{14,16} The cw-NMR spectra only gave 1+0.25x for H(x)/ $H_{\rm Fe}$. In Ref. 10 Mendis and Anderson discussed the fact the cw-NMR experiments seem incapable of detecting hyperfine-field shifts $\Delta H_{\rm Fe}^{Nn}/H_{\rm Fe}$ greater than 2.4%. (However, Rubinstein et al.¹⁷ did see the N1 satellite in FeMn; it has a 6% shift.) The excellent resolution of these cw experiments seems to be obtained at the cost of sensitivity. Mendis et al.¹⁰ never saw the satellites due to N1interactions in FeAl and FeSi alloys. They attribute this to some unknown field anisotropy which is presumed to be especially bad for the N1 shell. Therefore for some unknown reason the cw-NMR technique as used so far does not give reliable intensity measurements.

In the earlier spin-echo measurements the full complexities^{3,18} of the ferromagnetic NMR were not understood and the spin-echo spectra were not as reliable as possible. However, the technique has improved with understanding and the method is now reliable. Thus the more recent very careful experiments of Budnick *et al.*¹⁴ gave integrated intensities for the resolved satellite in the FeCo spectra which are 1.5-2 times greater than the earlier experiments^{10,13} and agree with the slope of the Mössbauer experiments.

As will become clear in this analysis, we should not necessarily expect the satellites in an alloy like FeCo to be resolvable. It is more likely that the shifts due to the first few near-neighbor shells are very close in magnitude and that with the inherent linewidths of the ferromagnetic alloys used in these experiments it is not possible to clearly resolve the satellites.

III. PROCEDURE FOR DETERMINING HYPERFINE-FIELD SHIFTS

The Co atom should be a rather ideal case of a solute atom which develops a moment in Fe. The Co moment is expected to be mainly localized^{3b} and the magnitude of the Co moment is about the same magnitude as that of the Fe moment. Thus a Co atom should perturb the Fe matrix very little We will consider only dilute alloys so that we can assume that there are no interference effects between solute atoms. In practice we shall use alloys with about 1% of a solute atom in Fe so this is a fairly valid assumption.

The procedure for determining the hyperfinefield shifts due to a solute atom in the nth shell fundamentally assumes that we know the conduction-electron polarization (CEP) surrounding a moment in an Fe matrix. We then proceed as follows:

(i) Neutron-scattering experiments² indicate that the moments on Fe atoms surrounding a Co or Ni atom increase. We therefore assume for the moment perturbation surrounding a solute atom an increase in the moment in shell m having a radial variation of $1/r^m$.

(ii) Using the measured average-saturationmoment data we can obtain a relation between the moment on a Co atom in Fe, μ_{Co} , and the perturbed Fe moments (thus the power m).

(iii) The CEP surrounding an Fe moment in an Fe matrix has been measured.^{3,19} Using these values and the known hyperfine field in pure Fe we can derive expressions for the hyperfine-field shifts due to a Co atom being in the near-neighbor shells to an Fe atom. These expressions have only two unknown parameters, μ_{Co} and m. We thus have two independent relations between μ_{Co}

TABLE I. Values of quantities used in the evaluation of the hyperfine-field shifts of an Fe atom near a solute atom.

Shell	N1	N2	N3	N4	N5	N6
M _N	8	6	12	24	8	6
$(r_1/r_n)^3$	1	0,65	0.23	0.14	0,125	0.08
$\Delta H_{m{\eta}}^{Fe}$ (kG/ μ_B)	- 12.1	-2.7	+2.4	+0.6	+ 0.3	+0.6

and m.

(iv) Using the derived hyperfine-field shifts we calculate on a computer the hyperfine-field spectra of the Fe atoms and compare then to the measured spectra. We find the analysis is very sensitive to value of μ_{C_0} and the radial fall-off power of the matrix perturbation, m. Each of these parameters is uniquely determined by the Fe spectra and the average saturation magnetization.

(v) Finally, we have another check on the hyperfine-field shifts obtained by taking the sum $\sum_{\sigma} M_n \Delta H_{Fe}^{N}/H_{Fe}$.

A. FeCo spectra

1. Perturbation of Fe moments surrounding a Co atom

We assume a functional variation of the Fe moments which varies as $\Delta \mu_1 (r_1/r_n)^m$, where $\Delta \mu_1$ is the moment increase of Fe atoms in the firstneighbor shell (N1) to a Co atom and r_n is the distance of the *n*th neighbor shell from the Co atom. The values of $(r_1/r_n)^3$ through N6 are given in Table I for a $1/r^3$ falloff of the moment perturbation.

2. Relation between μ_{C_0} and $\Delta \mu_1$ from average saturation magnetization

The average saturation moment of dilute FeCo alloys has been measured by Weiss and Forrer and by Bardos.²⁰ The data of Weiss and Forrer has a slope of 0.43 and of Bardos a slope of 0.52; we will thus take

$$\overline{\mu}(x) = (1 + 0.47x)\mu_{\rm Fe}$$
,

where x is the concentration of Co in atomic percent. If an alloy contains N sites it has N(1-x)Fe atoms and Nx Co atoms. Thus for a moment perturbation extending through the six-nearestneighbor shells $(\sum_{n=1}^{6} M_n = 64)$,

$$(1+0.47x)N\mu_{\rm Fe} = N(1-65x)\mu_{\rm Fe} + N\sum_{n=1}^{6} M_n x(\mu_{\rm Fe} + \Delta\mu_n) + Nx\mu_{\rm Co} ,$$
(1)

where M_n is the number of sites in the *n*th shell and $\Delta \mu_n$ is the increased moment in the *n*th shell surrounding a Co atom. This reduces to

$$0.47\,\mu_{\rm Fe} = -\,\mu_{\rm Fe} + \sum_{n=1}^{6} M_n \Delta \mu_n + \mu_{\rm Co} \,\,. \tag{2}$$

For a $1/r^3$ moment perturbation this becomes

$$\mu_{\rm C_0} = 3.26 - 19.6\Delta\mu_1 , \qquad (3)$$

where μ_{C_0} and $\Delta \mu_1$ are given in Bohr magnetons μ_B and μ_{F_e} was taken as 2.22 μ_B . It is easy to evaluate Eq. (2) for any power of r using $\Delta \mu_n = \Delta \mu_1 (r_1/r_n)^m$. The values for $1/r^2$ and $1/r^4$ moment perturbation are listed in Appendix B.

3. Hyperfine-field shifts

To calculate the hyperfine-field shifts we assume that each atom in the lattice causes a CEP oscillation surrounding it. We will assume that in dilute alloys (~1% solute) these oscillations can be linearly superimposed. This is really only valid when the moment on the solute atom is close to that of Fe since we know that saturation effects do exist³ and are quite large for N1. Thus this assumption is not too accurate when the solute atom's moment is appreciably different from that of Fe. We further assume that the solute atom goes into the Fe matrix with a perturbation which can be represented by only an increase in the moment of the Fe atoms surrounding the solute atom. Since the band structures (or atomic structures) of Co and Ni are very similar to that of Fe, we expect this assumption to be best for these. The more the transition series of the solute atom varies from that of the host, the less valid we expect this assumption to be. We will see that this becomes apparent for Pt in the 5d transition series.

The CEP hyperfine-field shifts in the *n*th shell, ΔH_n , surrounding an Fe atom in *pure* Fe have been obtained³ from measuring the shifts in FeSi and FeAl alloys out to N6. The shifts in kg/ μ_B are listed in Table I. In order to obtain the hyperfinefield shift at an Fe atom located in the nth shell from a solute atom, we first determine the occupational distribution surrounding this Fe atom. For example, let us consider an Fe atom which is a nearest neighbor (N1) to a Co atom as shown in Fig. 1, call this Fe^{1} . We see that besides having a nearest neighbor Co, three of its Fe nearest neighbors are N2 to the Co atom and three are N3to the Co atom, while the other is N5 to the Co atom. The moments and thus the core polarization and CEP hyperfine field from each of the other Fe near neighbors to an Fe¹ will thus be altered by the Co atom. In Table II we list the environment of each Fe atom in the first four shells surrounding a Co atom. We give the positions with respect to a Co atom Nn(Co) of the Fe atoms surrounding an Fe^n atom which is in the *n*th neighbor shell to the Co atom. We assume that within the vicinity

2313



FIG. 1. Fe lattice containing one Co atom (O). The numbers given on each site indicate the shell, with respect to the Co atom, of that Fe atom (\bullet). To obtain the positions with respect to the Co atom of the Fe atoms surrounding a nearest-neighbor Fe atom to Co focus attention on the atom labeled Fe and read off its near-neighbor shells. These positions are given in Table II.

of each Feⁿ atom we have only one Co atom, i.e., dilute alloys. We consider only four shells because by this distance the CEP is small and the number of atoms in N5 and N6 are only eight and six and thus much less important than N3 and N4. However, in reality these outer shells do contribute small shifts whose effects can clearly be seen in the spectra of the 4*d*-transition-series alloys.

We will now calculate the shifts in hyperfine field at an Fe atom due to the moment changes in the four nearest-neighbor shells surrounding the Fe atom. The hyperfine field at an Fe atom in these dilute alloys is given by

$$H_{\mathbf{F}\mathbf{e}} = H_{\mathbf{c}\mathbf{p}} + H_{\mathbf{c}\mathbf{e}} ,$$

where H_{cp} is the field due to the core polarization and H_{ce} is due to the 4s-like conduction-electron polarization. There is, of course, no volume overlap contribution H_v for Fe, Co, or Ni atoms in each other since they are all closely the same size.³ The 4d- and 5d-transition-series atoms are also small enough that there is no H_v term. As usual let us break up the H_{ce} term into two terms, one due to the Fe atom itself, H_s , and the other due to the surrounding neighbors, H_{Σ} ; we get

TABLE II. Occupational distribution of the atoms surrounding an Fe^n atom that is in the *n*th nearest-neighbor shell to a Co atom.

<i>N</i> 1 (Fe ⁿ)	Nn (Co)	N2 (F e ⁿ)	Nn(Co)	N3(Fe ⁿ)	Nn(Co)	<i>N</i> 4(Fe ^{<i>n</i>})	Nn(Co)
		$Fe^n = 1st r$	nearest nei	ghbor to C	0		
1Co		3Fe	<i>N</i> 1	3Fe	N1	3Fe	N2
3Fe	N2	3Fe	N4	6Fe	N4	6Fe	N3
3Fe	N3			3Fe	N7	3Fe	N5
1Fe	N5					3Fe	N6
						6Fe	N 8
						3Fe	N9
		$Fe^n = 2nd$	nearest nei	ighbor to C	о		
4Fe	N1	1Co		4Fe	N2	4Fe	N1
4Fe	N4	4Fe	N3	4Fe	N5	8Fe	N4
		1Fe	N6	4Fe	N 8	8Fe	N7
						4Fe	N10
		$Fe^{n} = 3rd$	nearest nei	ighbor to C	o		
2Fe	N1	2Fe	N2	1Co		4Fe	N1
4Fe	N4	2 Fe	N5	4Fe	N3	6Fe	N4
2Fe	N7	2Fe	N8	2Fe	N6	4 Fe	N7
				4Fe	N9	6Fe	N10
				1Fe	N11	4Fe	N12
		$Fe^n = 4th$	nearest nei	ghbor to C	o		
1Fe	N2	1Fe	N1	2Fe	N1	1Co	
2Fe	N 3	2Fe	N4	3Fe	N4	2Fe	N2
1Fe	N5	2Fe	N7	2Fe	N7	3Fe	N3
1Fe	N6	$1 \mathrm{Fe}$	N10	3Fe	N1 0	2Fe	N5
2Fe	N8			2Fe	N12	4Fe	N8
1Fe	N9					4Fe	N9
						2Fe	N11
						3Fe	N13
						2 Fe	N14
						1Fe	N16

$H_{\text{Fe}} = H_{\text{cp}} + H_s + H_{\Sigma}$.

The first two terms are due to the moment on the Fe atom itself and will be called $H_{\rm M}$. The last term is due to the moments on the surrounding Fe atoms. For pure Fe, $H_{\rm E}$ was measured to be -145 kG ($\pm \sim 10\%$) and $H_{\rm Fe}$ is -346 kG (the measured value -339 kG is corrected by $-\frac{4}{3}\pi M_s$ to obtain the true hyperfine-field value). Thus

$$H_{\rm M} = H_{\rm cp} + H_{\rm s} = -201 \ \rm kG$$

or 90.5 kG/ μ_B . The hyperfine-field shift at an Feⁿ atom due to a nearby Co atom is thus composed of the change due to the moment change on the Feⁿ atom itself plus the changes in the CEP contribution of neighboring atoms due to their moment changes (including the Co atom). Thus for an Fe¹ atom which is the nearest-neighbor to a Co atom, we get a hyperfine-field shift in kG of

$$\Delta H_{F_{\theta}}^{N1} = -90.5(\Delta\mu_{1}) - 12.1(\mu_{C_{\theta}} - \mu_{F_{\theta}})$$

-12.1(3 $\Delta\mu_{2}$ + 3 $\Delta\mu_{3}$ + $\Delta\mu_{5}$)
-2.7(3 $\Delta\mu_{1}$ + 3 $\Delta\mu_{4}$)
+2.4(3 $\Delta\mu_{1}$ + 6 $\Delta\mu_{4}$)
+0.6(3 $\Delta\mu_{2}$ + 6 $\Delta\mu_{3}$ + 3 $\Delta\mu_{5}$ + 3 $\Delta\mu_{6}$). (4)

For a $1/r^3$ moment perturbation this reduces to

$$\Delta H_{\rm Fe}^{N1} = -121.6 \Delta \mu_1 - 12.1(\mu_{\rm Co} - \mu_{\rm Fe}) . \qquad (4a)$$

For a $1/r^2$ moment perturbation this would be

$$\Delta H_{\rm Fe}^{N1} = -130.1 \Delta \mu_1 - 12.1(\mu_{\rm Co} - \mu_{\rm Fe}) . \tag{4b}$$

We can similarly evaluate the shifts for a second through fourth Fe neighbor to a Co atom and get for a $1/r^3$ moment perturbation

$$\Delta H_{\rm Fe}^{N_2} = -106.2\Delta\mu_1 - 2.7(\mu_{\rm Co} - \mu_{\rm Fe}), \qquad (5)$$

$$\Delta H_{\rm Fe}^{N3} = -50.6 \Delta \mu_1 + 2.4(\mu_{\rm Co} - \mu_{\rm Fe}), \qquad (6)$$

and

$$\Delta H_{\rm Fe}^{N4} = -25.1 \Delta \mu_1 + 0.6(\mu_{\rm Co} - \mu_{\rm Fe}) . \tag{7}$$

We have assumed that the Co atom does not perturb the basic form of the CEP in the Fe matrix and thus has the same form of CEP surrounding it as any Fe atom. Equations (4)-(7) should be good for very dilute alloys but will begin to break down when there is more than one Co atom within the four shells surrounding each Fe atom. A listing of the shifts for a $1/r^2$ and $1/r^4$ moment perturbation is given in Appendix B.

4. Calculation of spectra

The procedure is now to assume a value for μ_{C_0} , obtain $\Delta \mu_1$ from Eq. (3), and the hyperfine-field shifts from Eqs. (4)-(7) and then for a given alloy calculate the spectra on a computer to compare with the measured spectra. We have kept all spectral

components which have areas greater than 0. Q02 that of the total area. In Fig. 2 we show how the hyperfine shifts $\Delta H_{\rm Fe}^n$ vary as a function of $\mu_{\rm Co}$ for a $1/r^3$ and $1/r^2$ moment perturbations. In Fig. 3 we show the spectra calculated for matrix perturbations which go at $1/r^2$, $1/r^3$, and $1/r^4$ for the values of μ_{Co} which give the spectrum closest to the experimental spectrum. This value was $\mu_{C_0} = 1.9 \mu_B$ for all three moment-perturbation distributions. The solid lines are the calculated curves and the experimental points are those of Budnick et al.¹⁴ This spectrum is similar to many of the other measured spectra but it is the most carefully taken spectrum. We assumed each lineshape to be given by a Gaussian with a width = 1.0 kG. A Lorentzian lineshape did not give as good fits. We see in Fig. 3 that the $1/r^3$ perturbation with $\mu_{C_0} = (1.9)$ $\pm 0.1)\mu_B$ gives the best fit. In this case ΔH_{Fe}^{N1} and ΔH_{Fe}^{N3} are about the same giving rise to the prominent peak in the spectrum. Also $\Delta H_{F_0}^{N2}$ and $\Delta H_{F_0}^{N3}$ $+ \Delta H_{Fe}^{N4}$ happen to be about the same, giving rise to the smaller peak at about 47.5 MHz. The bump on the high-frequency side of the main line is due to ΔH_{Fe}^{N4} . Thus all the features seen in the FeCo spectrum are reproduced by a $1/r^3$ moment perturbation. We found as shown in Fig. 3 that a $1/r^2$ perturbation gave about the same shift for ΔH_{Fe}^{N1} and ΔH_{Fe}^{N4} leading to a prominent peak at about 2.5 kG and $1/r^4$ does not give enough structure since the components are too evenly distributed. As can be seen from Figs. 2 and 3, $\Delta H_{F_e}^{N3}$ is very insensitive to the power of the moment



FIG. 2. Variation of the hyperfine-field shifts as a function of the Co moment at Fe atoms which are the first-through fourth-nearest neighbors to the Co solute atom. The solid and dashed lines are for moment perturbations which vary as $1/r^3$ and $1/r^2$, respectively. The number labels on the lines indicate in which shell the Fe atom is with respect to the Co atom.

sitivity of the shifts to the value of H_{Σ} . We found that for reasonable changes in $H_{\Sigma}(\pm 10\%)$ the shifts did not vary much. This is shown in Fig. 4 by the



FIG. 3. Calculated and experimental spectra for FeCo for different moment perturbations of the Fe matrix surrounding the Co atom. The solid lines are the calculated curves and the data points are those of Budnick, Burch, Skalski, and Raj (Ref. 14). As discussed in the text, the best fit is obtained for a $1/r^3$ moment perturbation with $\mu_{Co}=1.9\pm0.1\mu_B$. The positions of the hff shifts for each shell are indicated by the numbers.



FIG. 4. Variation of the hyperfine-field shifts as a function of Co moment for $H_{\rm E} = -145 \,\rm kG$ (solid lines) and for $H_{\rm E} = -170 \,\rm kG$ (dashed lines).

dashed curves where $H_{\Sigma} = -170$ kG. The H_{Fe}^{Nn} were slightly adjusted so their values summed to -170 kG. Thus the final FeCo spectrum does not change appreciably for $\pm 10\%$ changes in H_{Σ} . This is about the limit of error we expect for H_{Σ} .

We list in Table III the best values obtained for the hyperfine-field shifts in the first four shells surrounding a Co atom. We have also listed the value of the sum of the shifts $\sum_{n} M_n \Delta H_{Fe}^{N_n} / H_{Fe}$ which should be close to 0.51 as discussed earlier. We see that our result, 0.51 ± 0.05 , fits this criteria excellently. We also list two other solutions that have been given by other authors.^{15,21} An arbitrary condition that was imposed on these two other solutions was that the shifts decreased in value as the distance from the Co atom increased. There is no justification for such a condition; in fact it is guite unreasonable since the basic CEP curve in the pure Fe matrix does not have this behavior but actually oscillates in sign. The value obtained for μ_{c_0} is in agreement with that derived from neutron-scattering experiments, $\mu_{C_0} = (2.1)$ ± 0.4) $\mu_B^{2,22}$; see Table IV. The moment perturbation at the N1 Fe neighbors is $0.070\mu_B$ and the distribution is shown plotted in Fig. 5.

The FeCo spectra are by far the most investigated spectra of a solute atom which develops a moment in Fe. Therefore for the other solute atoms we will begin by assuming that the moment perturbation surrounding a solute atom that develops a moment varies at $1/r^3$. This assumption is probably very good for a Ni solute atom but may be questionable for solute atoms from the higher transition series where we might expect that the perturbation be of longer range.

TABLE III. Moments and hyperfine-field shifts $\Delta H_{F_{\bullet}}^{Nn}$ (relative to the field in pure Fe) at an Fe atom in the *n*th shell surrounding a solute atom (in kG).

 Solute	$\mu_{\rm Sol_{*}}(\mu_{\rm B})$	$\Delta \mu_1(\mu_{\rm B})$	$\Delta H_{\rm Fe}^{N1}$	$\Delta H_{\rm Fe}^{N2}$	ΔH ^{N3} Fe	$\Delta H_{\rm Fe}^{N4}$	$\Sigma M_n \Delta H_{\rm Fe}^{Nn}/H_{\rm Fe}$	-
Co	1.9±0.1 S Wert	0.070 ± 0.005 stauss ^a	-4.6 ± 0.5 -12.35 -11.9 ± 1.0	-6.5 ± 0.3 -5.3 -10.2+2.0	-4.3 ± 0.5 -4.4 ^b -4.4 ^b	-1.9 ± 0.2 ~ -0.6^{b} ~ -0.6^{b}	0.51 ± 0.05 0.58 0.67	
Ni Rh	1.4 ± 0.1 1.1 ± 0.2	$\begin{array}{c} 0.\ 093 \pm 0.\ 005 \\ 0.\ 11 \pm 0.\ 01 \end{array}$	-1.4 ± 0.6 -0.3 ± 1.0	-7.7 ± 0.3 -9.1 ± 0.6	-6.7 ± 0.5 -8.4 ± 1.0	-2.8 ± 0.2 -3.5 ± 0.4	0.60 ± 0.05 0.7 ± 0.1	
 Pd	0.7±0.2	0.07 ± 0.01	$+10.3 \pm 1.6$	-2.95 ± 0.4	-7.0 ± 1.0	-2.6 ± 0.4	0.2±0.1	

^aReference 15.

^b From Ref. 10.

^cReference 21.

B. FeNi spectra

We follow a procedure similar to that used for the FeCo spectra but now assume the moment perturbation goes as $1/r^3$. The variation of the saturation moment with Ni content x has been measured²³ to be

 $\overline{\mu}(x) = [1 + (0.45 \pm 0.05)x]\mu_{\rm Fe}$.

Following the procedure of Eqs. (1)-(3), we get

$$\mu_{N_1} = 3.22 - 19.6\Delta\mu_1, \tag{8}$$

where μ_{N_1} and $\Delta \mu_1$ are in units of μ_B . We then obtain the shifts at the first four Fe shells by using Eqs. (4)-(7). The shifts as a function of the value of μ_{N_1} are shown in Fig. 6. The spectra which agreed best with the experimental spectra of Ref. 14 had $\mu_{N_1} = (1.4 \pm 0.1) \mu_B$ and $\Delta \mu_1 = 0.09 \mu_B$. Both spectra are shown in Fig. 7 where we used a Gaussian lineshape and a width of 1.3 kG. Since the moment on the Ni atom is less than that on the Co, we expect some of the lines to be more broadened for Ni alloys due to dipolar effects and shielding or saturation effects.³ The moment on the Ni atom agrees with the neutron-scattering analysis of Ref. 22. They are listed in Table IV. We list the hyperfine-field shifts for the first four shells in Table III. We also list

$$\sum_{n=1}^{4} M_n \Delta H_{\rm Fe}^{Nn} / H_{\rm Fe} = 0.60 \pm 0.05.$$

This value is not as well known from other data as

TABLE IV. Derived moments of solute atoms in Fe from Fe hyperfine-field spectra and from neutron-scattering data (in μ_B).

	This work	Ref. 2	Ref. 22
μ _{Co} μ _{Ni} μ _{Rh}	$1.9 \pm 0.1 \\ 1.4 \pm 0.1 \\ 1.1 \pm 0.2$	$2.1 \pm 0.5 0.9 \pm 0.15 0.5 \pm 0.3 1.0 \pm 0.1a$	$2.1 \pm 0.3 \\ 1.2 \pm 0.3 \\ 0.5 \pm 0.3$

Obtained for ordered alloys, see Ref. 24.

for Co. We show Mössbauer data taken by the author on alloys from 0- to 6-at.% Ni in Fe in Fig. 15 of Appendix A. The initial slope of the curve drawn through the data is 0.5 ± 0.1 which is in agreement with the value of $\sum_{n=1}M_n \Delta H_{Fe}^{nn}/H_{Fe}$. From Fig. 7 we see that the fit to the experimental curves gives all the dominant features seen in the experimental curve. Considering all the restrictions (all satellites the same width, cut off at four neighbors, etc.) on the analysis the fit is considered good. We also tried a $1/r^2$ moment perturbation but it did not give as good a fit as a $1/r^3$ distribution.

C. FeRh spectra

We proceed in the same manner to obtain spectra for Rh in Fe and compare it with the measured spectrum of Ref. 14. However, it should be emphasized that many of the assumptions made in the analysis are not as valid for the higher transition series. These elements probably distort the band



FIG. 5. Radial variation of the moment perturbation surrounding a Co solute atom in an Fe matrix.

2318



9



FIG. 6. Variation of the hyperfine shifts as a function of Ni moment for Fe atoms in the first four shells surr rounding a Ni solute atom. The moment perturbation of the Fe matrix is assumed to vary as $1/r^3$.

structure of the nearby Fe lattice more than the 3d-transition-series elements. Also we know that these elements, as hosts, tend to give more non-local effects than the first series of transition elements. On the other hand, the neutron-scattering data² for these as solute atoms in Fe looks similar



FIG. 7. Calculated (solid line) and measured spectra (data points) for $\text{Fe}_{0,99}\text{Ni}_{0,01}$. A $1/r^3$ moment perturbation was used for the Fe matrix. The data points are those of Budnick *et al.*¹⁴

to that for Co and Ni. It indicates that the moment of the solute atom is lower than that of Fe and that the moments on the surrounding Fe atoms are increased. As in the case of Ni we assume that the moment perturbation goes as $1/r^3$. From Fallot²³ we have the saturation magnetization of Rh in Fe goes as

$$\overline{\mu}(x) = (1+0.5x)\mu_{\mathrm{Fe}} .$$

This, however, is not as accurately determined as for Co and Ni. From Eqs. (1)-(3), we get

$$\mu_{\rm Rh} = 3.33 - 19.6\Delta\mu_1 \,. \tag{9}$$

The $\Delta H_{F_{e}}^{Nn}$ are obtained from Eqs. (4)-(7) and are shown in Fig. 8. We show the calculated (solid line) and measured¹⁴ spectra of $Fe_{0.985}$ Rh_{0.015} in Fig. 9. We see that in the measured spectrum the main line is very asymmetrical. From the behavior of the low-frequency side it appears that the Fe line with no Rh near has about the same width as the main peaks in FeCo while the satellites seem considerably broadened. This is not surprising since we already noted that the higher-transition-series elements often seem to produce rather long-range distortions and also as the solute moment varies more from that of Fe we expect larger dipolar and nonsaturation effects.³ (However, we do not find that a $1/r^2$ moment perturbation is better than a $1/r^3$, but the contrary.) We have taken this into account in the calculated spectrum by assigning the main unshifted peak about the same linewidth as for the FeCo alloy ($\Gamma = 1.0 \text{ kG}$) while the satellites were given a width of 2.3 kG. The areas of each component were adjusted to be the correct calculated area for a 1.5% alloy. All components with areas greater than 0.006 of the total



FIG. 8. Variation of the hyperfine-field shifts as a function of Rh moment for Fe atoms in the first four shells surrounding a Rh solute atom. The moment perturbation of the Fe matrix is assumed to vary as $1/r^3$.



FIG. 9. The calculated (solid line) and measured spectra (data points) of the $Fe_{0,985}Rh_{0,015}$. For reasons explained in the text the main line was taken to have a width of 1.0 kG while the satellites width was 2.3 kG. The data points are those of Budnick *et al.*¹⁴

area were kept in the calculated spectrum. From Fig. 9 we see that the high-energy side of the main peak is considerably broadened. This is probably mainly due to shifts of the N5 and further out shells which we have left out, these become more evident the larger the shifts. The best fit was made with $\mu_{\rm Rh} = (1.1 \pm 0.2)\mu_B$ and $\Delta\mu_1 = (0.11 \pm 0.01)\mu_B$. The $\Delta H_{\rm Fe}^{Nn}$ values are listed in Table III. We also list

$$\sum_{n=1}^{4} M_{n} \Delta H_{\rm Fe}^{Nn} / H_{\rm Fe} = 0.7 \pm 0.1 ,$$

but in this case we have no Mössbauer measurements for comparison. The value of $\mu_{Rh}=1.1$ $\pm 0.2\mu_B$ is a little larger than that obtained from the neutron analysis of dilute alloys. This gave $(0.5+0.3)\mu_B$; however alloys of a higher concentration²⁴ gave $\mu_{Rh} = (1.0\pm0.1)\mu_B$. This is probably a more reliable value.

Another complication that may exist for the higher-transition-series solute atoms is that as previously mentioned their moments may be more spatially spread out than the Fe moments. In that case the CEP oscillations will be weaker in amplitude and the shifts will be less (more positive) than those calculated for N1 and N2 and greater (more negative) for N3 and N4. [See Ref. 3(b) for a discussion of this effect.] Such an effect was investigated by reducing the CEP amplitude (keeping the same shape) caused by the Rh atoms. No improvement in fitting the spectrum was obtained by this type of consideration. Thus, although we do not believe the assumptions that go into the analysis are as good for the higher transition series, it

appears as if the analysis is still quite valid for the 4d transition series.

D. FePd spectra

The FePd alloys are interesting because the saturation-magnetization curve has a negative slope as opposed to the positive slope for all the other alloys considered so far. (See *note added in* |proof.) It varies as²³

$$\overline{\mu}(x) = (1 - 0.1x)\mu_{\rm Fe}$$
,

but it is not measured very accurately, only to about $\pm 0.05x$. Using Eqs. (1)-(3) which assumes a $1/r^3$ moment perturbation gives

$$\mu_{\rm Pd} = 2.00 - 19.6\Delta\mu_1. \tag{10}$$

Following the same procedure as before, this gives the $\Delta H_{F_{e}}^{N_{n}}$ shown in Fig. 10 and listed in Table III. We see that small or negative slopes of the saturation moment result in positive values (the low-frequency side) for ΔH_{Fe}^{N1} . This is the situation similar to most of non-transition metals in Fe. The calculated (solid line) and measured spectra are shown in Fig. 11. We find the best fit for μ_{Pd} $= (0.7 \pm 0.2)\mu_B$ and $\Delta \mu_1 = (0.07 \pm 0.01)\mu_B$ with the width of the unshifted peak = 1.0 kG and the shifted peaks = 2.4 kG. We have not shown the N1 satellite at +10.6 kG or 45.2 MHz; on Fig. 11 it would be only one-half a division high and frequency side of the main peak; part of this may be due to omitting the spectrum. We see the fit is not too good in the region on the high-energy side of the main peak; part of this may be due to omitting the higher neighbor shifts. However, the fit to the general shape is quite good. We find



FIG. 10. Variation of the hyperfine-field shifts as a function of Pd moment for Fe atoms in the first four shells surrounding a Pd solute atom. The moment perturbation of the Fe matrix is assumed to vary as $1/r^3$.

48



FIG. 11. The calculated (solid line) and measured (data points) spectra of $Fe_{0,99}Pd_{0,01}$ for a moment perturbation of the Fe matrix varying as $1/r^3$. The data points are those of Budnick *et al.* (Ref. 14).

FREQUENCY IN MHz

47

$$\sum_{n=1}^{4} M_n \Delta H_{\rm Fe}^{Nn} / H_{\rm Fe} = 0.2 \pm 0.1 ,$$

46

but again we have no experimental value for a comparison. The moment value of $(0.7 \pm 0.2)\mu_B$ is in agreement with the upper limit of the value $(0.3 \pm 0.3)\mu_B$ derived from the neutron-scattering data²² from the dilute alloys. A value of $\mu_{\rm Pd} = (0.4 \pm 0.1) \times \mu_B$ was obtained in more concentrated alloys.⁶ These values are listed in Table IV.

E. FePt spectra

The average saturation-magnetization behavior²³ of FePt has been very accurately measured and is given by

$$\overline{\mu}(x) = (1 + 0.85x)\mu_{\rm Fe}$$

For a $1/r^3$ moment perturbation of the Fe matrix this leads to

$$\mu_{\rm Pt} = 4.11 - 19.6\Delta \mu_1. \tag{11}$$

We tried to fit the measured spectra of a Fe_{0.99} Pt_{0.01} alloy of Ref. 14 but could get no satisfactory fits. The best fits were obtained with moments that seem much too high, $\mu_{Pt} \sim 1.2\mu_B$. The same trends in poor quality of fit are seen in the *Fe*Pt spectrum as are beginning to be seen in the *Fe*Rh and *Fe*Pd spectra, i.e., a broadening on the high-energy side of the main unshifted line. However, in the *Fe*Pt spectrum it is so pronounced that a satisfactory fit is unobtainable. Changing the distribution of moments in any reasonable way from

a $1/r^3$ dependence does not improve the fit. Apparently a Pt solute atom perturbs the band structure of the nearby Fe atoms so badly that the assumptions of additivity and superposition of the CEP contributions are not valid in this case.

Thus we conclude that the above procedure is very good for the 3d transition series where the band structure and moment are similar to that of Fe. It is not valid for the 5d transition series but appears to be quite applicable to the 4d transition series.

IV. DISCUSSION OF ORIGIN OF MOMENT VARIATIONS

In Table IV we list the moments obtained in this work and those obtained from analysis of the neutron-scattering experiments. The agreement is quite good if the moments obtained from the higher concentration alloys are considered to be more reliable than those from the neutron scattering data of Ref. 2.

The explanations²⁵ of the moment variations obtained by neutron-scattering experiments follow the treatment by Friedel where it is assumed that the moment variations are a result of the charge perturbation, $\Delta Z = Z_{solute} - Z_{host}$, which is present due to the solute atom. The impurity potential is assumed to be spin dependent and therefore gives rise to the solute-atom moments. However, this model is often far from successful. For example, Ref. 26 shows that the magnetic disturbances of nontransition solute atoms in Ni all have similar spatial form with a considerable extension of the host magnetic perturbations. Thus Comly et al.²⁶ conclude that this "precludes any direct link between electrostatic screening charge and magnetic disturbance." The charge-perturbation point of view is further refuted by hyperfine-field data which shows that in dilute Fe alloys essentially the same hyperfine field (or spin) perturbation, $(\sim 7-8\% H_{\rm Fe})$, exists at a Fe atom which is the nearest neighbor to any nontransition solute atom irrespective of the solute atom's column in the periodic table (Z_{solute}) . Furthermore, the field at the solute atom can be quantitatively fit very satisfactorily by a model³ that does not involve the charge perturbation ΔZ . Thus for nontransition solute elements both neutron-scattering and hyperfine-field measurements indicate that all charge perturbations lead to similar spin perturbations. Upon introducing a solute atom into a ferromagnetic metal both a charge perturbation and a spin perturbation (via exchange²⁷ and interband mixing²⁸) are introduced and although there should be some cross interaction apparently it is suppressed by electron-correlation effects²⁹ so that each perturbation acts quite independently of the other. We recognize, of course, that charge perturbations do exist and are dominant in some effects which depend mainly on charge screening, but spin perturbations and the behavior of moments do not appear to be in this category.

The behavior of moment perturbations arise from the strong tendency for each solute atom to retain an electron structure in its vicinity similar to that in its elemental solid state. This is moderated, however, by the necessity of the solute atom to contribute to the conduction band and share its outer valence electrons with the nearby host atoms. In general, because charge effects envolve at least one electron per atom, charge screening is quite short ranged (mainly within the nearestneighbor distance). On the other hand, since a moment's influence depends mainly on the number of itinerant d electrons, ^{3b} if there are a small number of itinerant d's, the interactions can be quite long range, extending over several near neighbors. Two host alloy systems, Fe and Ni, have been studied rather extensively and we will discuss their magnetic behavior.

A. Nontransition solute elements

These atoms develop no moment and show very different behavior in their average saturation magnetization and the extension of the host-moment perturbations in Fe and Ni. This different behavior can be understood by considering the density of states of these hosts at the Fermi level. In Fig. 12 we show schematically the density of states for the majority and minority spins of Fe as obtained from recent band-structure calculations.³⁰ We assume for the present discussion that the rigid-band approximation is adequate and indicate also on Fig. 12 the position of the Fermi levels for Fe, Co, and Ni. We see that for Fe the Fermi level falls at a position such that the density-ofstates curves for the spin-up and spin-down d electrons are rather flat and about equal in number. On the contrary for Ni the spin-up d bands are full, so that only the spin-down d electrons have appreciable density of states at the Fermi level. Thus upon alloying Fe with nontransition metal solutes both spin-up and spin-down states are equally filled by any excess electrons that may be shared by the solute atom with the host Fe atoms. Thus no moment changes occur on the Fe atoms surrounding the solute atom and experimentally we observe that the average saturation magnetization²³ follows simple dilution and from neutron scattering that the moments surrounding the solute atom are not appreciably perturbed.³¹ Since the solute atoms have no moment this leads to a hff shift at the nearest-neighbor Fe atoms which is independent of the charge perturbation due to the solute atom. This hff shift thus mainly arises from the



FIG. 12. Sketch of density-of-states curves of majority and minority spin as obtained from Fe band-structure calculations (Ref. 31). The Fermi levels for Fe, Co, and Ni are depicted by the vertical lines. The density of states for the itinerant d electrons in Fe is indicated by the darkened area.

absence of a CEP contribution of the Fe atom that was replaced by the solute atom.

Ni alloys behave very differently from the Fe alloys. The average saturation-magnetization measurements show that the average moment decreases at a rate dependent on the difference in the number of outer valence electrons of the solute atom and the Ni host.³² This occurs because all these excess electrons tend to fill the spin-down bands of the surrounding host Ni atoms. The extent of the moment perturbation will depend on the extent of the d-electron CEP and since this is rather long ranged for Ni (due to its small number of itinerant d-electrons), the moment perturbations are rather extensive, as has been shown by neutron-scattering experiments.²⁶ Moreover, since the number of itinerant d electrons is mainly determined by the Ni host we expect all the nontransition-metal solute atoms to show a universal behavior in the host moment perturbation; this is also observed to be the case experimentally.²⁶ The hff shifts in Ni alloys with nontransition solutes cannot be simply interpreted as in the case of Fe alloys. Since the moment is perturbed on Ni atoms near a solute atom its hff shifts are due both to CEP terms and a core-polarization term.

B. Transition-metal solute atoms

In alloys of Fe and Ni with other transition elements the behavior of the alloys is a compromise between that of the pure solute and pure host.

The average moment behavior is understandable from a simple consideration of the density-ofstates curves. In Fig. 13 we show the average total number of spin-up, n_d^{\dagger} , and spin-down, n_d^{\dagger} , d electrons which would be obtained in going from



FIG. 13. Number of spin-up and spin-down electrons and their difference according to a rigid-band approximation for the 3d transition series.

Fe to Ni in Fig. 12. The number of spin-up electrons decreases only slightly between Ni and Fe and then starts to decrease rapidly beyond Fe due to the large peak in the density of states below the Fe Fermi level of the spin-up electrons. The number of spin-down electrons decreases rapidly in the region of the large peak between Ni and Fe and then starts to level off as the Fe Fermi level is approached. The difference between n_d^{\dagger} and n_d^{\dagger} gives the alloy moment μ . This is shown by the dashed curve in Fig. 13. It, of course, closely resembles the Slater-Pauling curve which corresponds to the average moment behavior. As discussed in Ref. 3(b), as we cross the 3d transition series from left to right we expect the *d* electrons to be initially all itinerant. Then as the d levels are more tightly bound due to the increased nuclear charge we get to a region where some of the delectrons become localized (between Cr and Mn) but where there are still a large enough number of itinerant d electrons that the first node of the CEP curve of the itinerant d's is inside the nearestneighbor distance and thus the atoms are antiferromagnetically coupled (Mn). For Fe and beyond there are few enough itinerant d's that the first node of the itinerant d's CEP curve is beyond the nearest neighbor and thus the atoms are ferromagnetically coupled. Fe is near the borderline and in this sense a weak ferromagnetic with a tendency to easily go antiferromagnetic. Co and Ni should have progressively less itinerant d's and therefore should be more stable ferromagnets. Thus we expect that Mn alloys with Ni might begin following the dashed curve of Fig. 13, but soon deviate from it with a reduced average moment when the Mn atoms tendencies begin to dominate. Similarly the MnCo alloys should follow over an

even shorter range before deviating from the Slater-Pauling curve. This is the observed behavior. Systematically we expect Cr and V to show a more pronounced behavior in this direction such that they would tend to be antiferromagnetically coupled even as dilute alloys. In agreement with this picture Cr is observed to have little or no moment in Ni and V has a negative moment.² A similar behavior is expected in Fe, only the tendency of antiferromagnetic coupled solute atoms to the left of Fe should be greater since Fe has more itinerant *d* electrons than Ni. In agreement both Cr and V are antiferromagnetically coupled² in Fe.

In general the extent of the moment perturbation in the host upon alloying will depend on the number of itinerant d's in the vicinity of the solute atom. Thus Ni or Co in Fe will tend to increase the hostperturbation range because of the decrease in number of itinerant d's, whereas Fe or Mn in Ni will tend to cause a smaller range to the host perturbation than the nontransition-solute atoms. These are just the type of host-moment perturbations that are observed to occur from neutron-scattering experiments.^{2,26}

Thus the behavior of solute moments and hostmoment perturbations are very naturally explained by a model in which mainly localized moments are coupled by a small number of itinerant *d*-like electrons³ and the dominating source of the interactions are exchange interactions and interband mixing. The above picture is oversimplified in that we are discussing general trends. In a particular case the details of course depend upon the details of the band structure which may involve more complications than are represented by a rigid-band model.

V. EVALUATION OF H_{cp} AND H_s IN Fe FROM EXPERIMENTAL DATA

Thus far the value of the core-polarization hyperfine field in Fe has been obtained from only band-calculation estimates. It is therefore of interest to obtain a purely experimental value if possible. Having a model for the origin of the hyperfine field we can use it and measured hyperfinefield data to evaluate the various hyperfine-field contributions. The model is that

$$H_{z} = H_{cp} + H_{s} + H_{\Sigma} + H_{v} , \qquad (12)$$

where H_z is the hff at a solute z in Fe and H_v is the volume-overlap contribution.³ Choosing Fe systems where $H_v = 0$, since H_{Σ} is measured, we can combine any two pairs of hyperfine field data and solve for $H_{cp}+H_s$. Two of the best sets of pairs for such an analysis are the field at Co in Fe and pure Fe and the field at Ni in Fe and pure Fe. Since the fields at Co and Ni in Fe are measured for very dilute alloys the number of s electrons can be

assumed to be the same in the alloys as in pure Fe. Also since in these cases the CO and Ni atoms have moments closer to that of Fe than in the pure metals Co and Ni, systematic errors will tend to cancel out.

The field at Co in Fe is given by

$$H_{Co}^{in \ Fe} = H_{cp}^{Co} + H_{s}^{Co} + H_{s}^{Fe} .$$
(13)

In very dilute alloys a Co atom will be entirely surrounded by Fe atoms, so using the scaling equations^{3b} of

$$H_{cp}^{z} = (\mu_{z}/\mu_{Fe})H_{cp}^{Fe} ,$$

$$H_{s}^{z} = (H_{ns}^{z}/H_{4s}^{Fe})(\mu_{z}/\mu_{Fe})H_{s}^{Fe} , \qquad (14)$$

and

$$H_{\Sigma}^{z} = (H_{ns}^{z}/H_{4s}^{Fe})H_{\Sigma}^{Fe}$$

we get

$$H_{Co}^{\ln Fe} = \frac{\mu_{Co}^{Fe}}{\mu_{Fe}} \left(H_{cp}^{Fe} + \frac{H_{4s}^{Co}}{H_{4s}^{Fe}} H_{s}^{Fe} \right) + \frac{H_{4s}^{Co}}{H_{4s}^{Fe}} \sum_{n=1}^{M} M_n \Delta H_n^{Fe} (\mu_{Fe} + \Delta \mu_n) , \qquad (15)$$

where H_{ns}^{s} is the hyperfine-coupling constant of element Z. All the other quantities have been previously defined. The values of any quantities not given earlier are listed in Table V. We have used a $1/r^{3}$ distribution for the $\Delta \mu_{n}$'s. All quantities but H_{cp}^{Fe} and H_{s}^{Fe} are known, so substituting in their values Eq. (15) becomes

$$-150 = H_{cp}^{Fe} + 1.1 H_{s}^{Fe}$$
.

Combining this with $H_{\rm Fe} = H_{\rm cp}^{\rm Fe} + H_{\rm s}^{\rm Fe} + H_{\rm \Sigma}^{\rm Fe}$, we get $H_{\rm s}^{\rm Fe} = +510$ kG and $H_{\rm cp}^{\rm Fe} = -710$ kG. From the equivalent evaluation for Ni in Fe we get $H_{\rm s}^{\rm Fe} = +560$ kG and $H_{\rm cp}^{\rm Fe} = -760$ kG. These values are listed in Table VI as $H_{\rm cp,h}^{\rm Fe}$. Another pair of hyperfine data which can be used is that for pure Co and Fe. Here we assume that the number of s-like conduction electrons is the same for the two metals and that the H_{Σ} term in Co is given by the scaling

TABLE V. Quantities used in the evaluation of H_{cp}^{Fe} and H_{d}^{Fe} .

z	H ^{in Fe²} (kG)	H ^g _{ns} (MG)	$\mu_{g}(\mu_{B})$
Fe	- 346	2.0	2.22
Co	- 295	2.2	1.9
Ni	-241	2.4	1.4
Rh	- 557	4.4	1.1
Pure Co	- 222	2.2	1.715

The measured values have been corrected by the Lorentzian term $-\frac{4}{3}\pi M_s$.

equation^{3b} of

$$H_{\Sigma}^{Co} = (H_{4s}^{Co}/H_{4s}^{Fe})(\mu_{Co}/\mu_{Fe})H_{\Sigma}^{Fe} = -123 \text{ kG}$$
.

We then have for Co,

$$H_{\rm Co} = (\mu_{\rm Co}/\mu_{\rm Fe})H_{\rm cp}^{\rm Fe} + (H_{4s}^{\rm Co}/H_{4s}^{\rm Fe})$$
$$\times (\mu_{\rm Co}/\mu_{\rm Fe})(H_{s}^{\rm Fe} + H_{\Sigma}^{\rm Fe}) . \tag{16}$$

Using the values in Table V we obtain $H_s = +730$ kG and $H_{cp}^{Fe} = -930$ kG. We have neglected any orbital contribution in deriving the above values. We can obtain an estimate of this effect by approximating the orbital contribution by

$$H_{\rm orb} = \frac{1}{2} \mu_z \Delta g (1/r^3)_{\rm eff} , \qquad (17)$$

where Δg is the deviation of the gyromagnetic ratio from 2 and $(1/r^3)_{\text{eff}}$ was taken as $4.53a_0^{-3}$, the Fe⁺⁺ value,³³ and $\Delta g = 0.15$ and 0.07 for Co and Fe respectively. This gives

$$H_{\text{orb}}^{C_0} \simeq +35 \text{ kG}, \quad H_{\text{orb}}^{F_0} \simeq +20 \text{ kG}.$$

Correcting for these contributions in $H_{\rm Fe}$ and $H_{\rm Co}$ we find $H_{{\rm cp},h} = -700$ kG and $H_{s,h} = +480$ kG. These values are listed in Table VI. However, none of the systematics of the hyperfine fields seems to indicate that much orbital correction is present. It is difficult to judge exactly how accurate the hyperfine-coupling-constant values are and since $H_{\rm cp}$ and H_s depend sensitively on these values it is difficult to know how much reliability should be given. However, the $H_{\rm cp,h}^{\rm Fe}$ values all seem a bit larger then band-calculation values.

The values of H_{cp}^{Fe} and H_{ce}^{Fe} obtained from various band calculations are listed in Table VII. We see that with the exception of the Muto et al.³⁵ the calculations give about -350 to -400 kG for H_{cp}^{Fe} . (A value of $H_{cp}^{Fe} = -400 \text{ kG}$ results in $H_{s,b}^{Fe} + 200 \text{ kG}$.) The results of Muto et al. have been strongly criticized in Ref. 38 for an arbitrary choice of the hybridization contribution and 3d wave functions and for using an inaccurate form of perturbation theory. The band calculations do not take into account any correlations between electrons but in many cases this seems to be a small effect, e.g., Li and Ni; however, for P it was found to be large.³⁸ Thus there appears to be some discrepancy between the band-calculation values and the values derived from experimental data only. It is difficult to assess which is more reliable, but since the values determined from only hyperfinefield data are so dependent on the hyperfine-field constants, we will defer this decision and use the band-calculation values in the rest of this paper. If these turn out to be in error the derived values can be easily altered at a future date.

TABLE VI. Quantities evaluated from hyperfine-field data.

Data	$H^{\mathrm{Fe}}_{\mathrm{cp},\hbar}(\mathrm{kG})$	H ^F € _{s,h} (kG)
H _{Fe} , H ^{in Fe} _{Co}	- 710	+ 510
$H_{\rm Fe}, H_{\rm Ni}^{\rm in Fe}$	- 760	+ 560
H _{Fe} , H _{Co} (no orb.)	- 930	+730
H _{Fe} , H _{Co} (orb. corr.)	- 700	+480
$H_{cp}^{Fe} \approx -700 \text{ kG}$	$H_s^{\mathbf{Fe}} \simeq \mathbf{H}$	- 500 kG

VI. EVALUATION OF H_{cp}^{4d} FROM HYPERFINE-FIELD DATA

It is also of interest to obtain an estimate of the hyperfine field induced in an atom of the 4*d* transition series in Fe due to the core polarization from its own moment. Using the spin-polarized Hartree Fock method, ³⁴ H_{cp}^{4d} has been calculated³⁹ to be $\sim -370 \text{ kG}/\mu_B$ for 4*d* ions as compared with $-110 \text{ kG}/\mu_B$ for the 3*d* series from Fe ions. By using the moment value determined here for Rh in Fe and the measured hyperfine-field values of these solute atoms in Fe, we can obtain

$$H_{M}^{\mathrm{Rh}} = H_{\mathrm{cp}}^{\mathrm{Rh}} + H_{\mathrm{s}}^{\mathrm{Rh}} , \qquad (18)$$

we emphasize that all these values are for Rh in Fe. We then have

$$H_{\rm Rh}^{\rm in \ Fe} = H_{M}^{\rm Rh} + (H_{5s}^{\rm Rh}/H_{4s}^{\rm Fe}) \sum_{n=1}^{4} M_{n} \Delta H_{n}^{\rm Fe} (\mu_{\rm Fe} + \Delta \mu_{n}) .$$
(19)

All quantities except $H_M^{\rm Rh}$ are known and those that have not previously been listed are given in Table V. Substituting these known values into Eq. (19) we get $H_M^{\rm Rh} = -210$ kG. Dividing by $\mu_{\rm Rh}$ we get $H_M^{\rm Rh} \simeq -190$ kG/ μ_B . These values are listed in Table VIII.

These values are listed in Table VIII.

This H_M^{4d} value includes the quantity H_s^{4d} in Fe, which is the hyperfine field resulting from the polarization which a 4d atom with a moment of μ_B would impart to the 4s conduction electrons of Fe. In order to evaluate H_{cp}^{4d} in Fe we make the assumption that the usual type scaling law holds for H_s^{4d} in Fe, thus

$$H_{s}^{4d \text{ in } Fe} = (H_{5s}^{4d}/H_{4s}^{Fe})H_{s}^{Fe}/\mu_{Fe} \text{ kG}/\mu_{B} .$$
 (20)

There is not much justification for this assumption since the self-polarization of the *s*-like conduction electrons may be different for an Fe atom than for a Rh atom due to different radial positions of the 3d and 4d unpaired electrons. But assuming this difference is small, we use Eq. (20) and evaluate H_s^{4d} in Fe for $H_s^{Fe} = +200$ kG. Then subtracting these values of H_s^{4d} in Fe from the H_{μ}^{4d} value obtained earlier we find the value for H_{cp}^{4d} listed in Table VIII. The value of H_{cp}^{4d} (~ - 390 kG/ μ_B) obtained in this manner is reasonably in agreement with the calculated H_{cp}^{4d} value for 4d ions (- 370 kG/ μ_B).³⁹ We expect it to be slightly larger in going from an ionic to a metallic environments as occurred for the case of Fe.

VII. EVALUATION OF MOMENTS OF OTHER 4d AND 5d TRANSITION SOLUTE ATOMS IN Fe

In earlier papers 3a,40 the moment of 4d and 5dtransition solute atoms in Fe were evaluated from the hyperfine fields measured at the solute atoms. In both these papers H_{M}^{4d} was mistakenly taken as - 370 kG/ μ_B , that is, the H_s^{4d} in Fe term was not properly included. The H_s^{4d} in Fe term, which is positive, should have been added to H_{cp}^{4d} which would have led to larger derived moments. This results in moments for Rh and Pd which are in closer agreement with those obtained here from the Fe spectra. The same error was made for the 5dtransition series, i.e., the value⁴¹ used as H_M^{5d} = -1180 kG/ μ_B is H_{cp}^{5d} not H_M^{5d} . We correct that treatment now by using an expression for H_s^{5d} equivalent to Eq. (20). For this revaluation we will neglect the field contribution due to the moment perturbations in the Fe matrix, i.e., we set the $\Delta \mu_n$'s = 0 in Eq. (15). Since the $\Delta \mu_n$ are positive this procedure will give slightly too large values for the moments. This effect is small and estimated to be less than $0.1\mu_B$ in all cases. We thus use

$$H_Z = H_{cp}^{nd} + H_s^Z + H_{\Sigma}^Z ,$$

where each term can be calculated from Eqs. (14). We list in Table IX the measured hff at the solute

TABLE VII. Core contribution obtained in band calculations for Fe.

		H _{ce} ^{Fe}	
	$H_{cp}^{Fo}(kG)$	Exchange	Hyb.
Atomiclike + <i>s-d</i> exchange Watson and Freeman ^a			
$3d^{6}4s^{2}$	- 320	+	195
3 <i>d</i> ⁸	- 350		
Atomiclike + <i>s-d</i> exchange + hybridization			
Muto, Kobayasi, and Hayahawa ^b	- 1145	+650	+150
Wakoh and Yamashita ^e	- 355	-	52
Duff and Das ^d	- 400	+ 3	33
^a Reference 34.	cRefere	nce 36.	
^b Reference 35.	dReferen	nce 37.	

TABLE VIII. Values of H_{cp}^{Rh} and H_{cp}^{Pd} derived from hyperfine-field data.

	$H_M^{4d}(\mathrm{kG}/\mu_B)$	$H_s^{4d ext{ in Fe}}(ext{kG}/\mu_B)$	$H_{cp}^{4d \text{ in Fe}}(\mathrm{kG}/\mu_B)$
Rh	- 190	+200	- 390

atom H_Z , the derived value of H_{Σ}^Z and the derived values H_s^Z . Then using $H_{cp}^{4d} \simeq -390 \, \text{kG}/\mu_B$ and $H_{cp}^{5d} \simeq -1180 \, \text{kG}/\mu_B$ we can derive the solute atom moment μ_Z . These values are given in the fifth column of Table IX. In the last column we list the values obtained from the neutron-scattering data. An error of about $\pm 0.2 \mu_B$ should be assigned to all the moment values obtained in this way for the 4d solute atoms.

Using the $H_{s,h}^{\text{Fe}}$ value determined for only hff data would have results in larger values of H_{cp}^{4d} but not much different moments since it is H_{μ}^{4d} that comes into the moment determinations.

VIII. SUMMARY AND CONCLUSIONS

A method has been developed to analyze the Fe spectra of dilute alloys of Fe which indicates that the transition-metal solute atoms Co, Ni, Rh, and Pd cause a perturbation in the surrounding Fe moments which varies as $1/r^3$. The moment values on the solute atoms are also obtained. A consideration of neutron-scattering and hyperfinefield data indicates that the moment perturbation arises mainly from d-d exchange interactions and interband mixing rather than from charge-screening effects by itinerant d electrons. A variation of this method has been extended to transition solute atoms to the left of Fe in the Periodic Table. In these further analyses it becomes clear that the host-moment perturbations are caused by the spindensity oscillations of the itinerant d electrons.



FIG. 14. Average hyperfine fields and isomer shifts as a function of atomic percent Co for FeCo alloys.

The Ruderman-Kittel-Kasuya-Yosida²⁷ (RKKY)-like spin-density oscillations³ have a behavior that varies very much like $\sim 1/r^3$ near the first node and this is the reason we observe a $1/r^3$ host-moment perturbation. The description of these further results will be given in a forthcoming publication.

The hyperfine-field shifts of Fe atoms in the first four shells around a solute atom are obtained in a much more fundamental way than previous determinations. As might be expected, we find quite different values than previously obtained for some of the shifts since here we start with the observed CEP shifts in pure Fe and do not arbitrarily

z	$-H_{g}^{\mathrm{in} \mathrm{Fe}}(\mathrm{kG})$	<i>– H</i> € (kG)	H ^z s	$\begin{array}{l} \mu_{g} \\ (H_{cp}^{4d} \simeq - 430 \ \mathrm{kG}/\mu_{B}) \end{array}$	Neut. ²
Nb	265	210	130	0.2	
Mo	270	240	150	0.1	-0.1 ± 0.6
Ru	510	290	180	1.0	0.9 ± 0.5
Rh	560	320	200	1.1	0.5 ± 0.3
Pd	540	350	220	1.0 ^e	$\begin{array}{c} 0.1 \pm 0.2 \\ 0.4 \pm 0.1^{26} \end{array}$
				$(H_{cp}^{5d} \simeq -1180 \text{ kG}/\mu_B)^{b}$	
Re	770	780	490	0.0	-0.3 ± 0.6
Os	1140	890	560	0.4	0 ± 0.5
Ir	1400	995	630	0.7	0 ± 0.5
Pt	1290	1160	730	0.5	0 ± 0.3

TABLE IX. Derived values of the moments on 4d and 5d transition elements in Fe.

^aReference 2. ^bReference 41.

"See Note added in proof.



FIG. 15. Average hyperfine fields and isomer shifts as a function of atomic percent Ni for *Fe*Ni alloys.

assume that the shifts decrease with distance from the solute atom.

Having determined the moments of the solute atoms in these dilute alloys and knowing the origin and scaling rules for each term in the hyperfine field, we can then self-consistently use the hyperfine-field data to evaluate the core polarization and CEP self-polarization terms in Fe. We find indications that the core-polarization term obtained in this manner may be larger than that obtained from band calculations. However, this depends strongly upon the reliability of the hff constants.

We can also evaluate the core-polarization contribution per μ_B for a 4*d*-transition-series atom. We find a value in reasonable agreement with the calculated value for this series.

Note added in proof. Upon more careful investigation of past measurements on Pd in Fe we find that Pd has a room-temperature solubility in bcc Fe of only about 1 at.%. The most dilute alloy which Fallot²³ measured was 2.15 at.%. Thus most likely Fallot's samples contained regions of fcc Fe embedded in bcc Fe. The volume of the fcc regions would be proportional to the Pd content and

¹NiFe, FeCr, and CoCr: C. G. Shull and M. K. Wilkinson, Phys. Rev. <u>97</u>, 304 (1955); CoFe, NiFe, and NiCo: M. F. Collins, R. V. Jones, and R. D. Lowde, J. Phys. Soc. Jap. Suppl. <u>17</u>, 19 (1962); R. D. Lowde and D. A. Wheeler, *ibid.*, p. 342; M. F. Collins and D. A. Wheeler, Proc. Phys. Soc. Lond. <u>82</u>, 633 (1963); M. F. Collins and J. B. Forsyth, Philos. Mag. <u>8</u>, 401 (1963); J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. <u>138</u>, A755 (1965).

- ²M. F. Collins and G. G. Low, Proc. Phys. Soc. Lond. <u>86</u>, 535 (1965).
- ³(a) M. B. Stearns, Phys. Rev. B <u>4</u>, 4069 (1971); B <u>4</u>,

since fcc Fe is not ferromagnetic this would tend to make the average moment of the Pd alloys fall with increasing Pd content. Since the slopes of the average magnetization curves for all other solute atoms to the right of Fe in the Periodic Table are positive, it is most likely that Pd also has a positive slope for small enough Pd concentrations. Thus the analysis given here for Pd is most likely wrong and its behavior in Fe is expected to be very similar to that of Rh.

APPENDIX A

We give some unpublished data on some systems relevant to this paper which were previously measured by the author. These data are shown in Figs. 14 and 15. All the data were taken with Mössbauer apparatus and computer analyzed with programs previously described in Ref. 19. The isomer shifts were measured relative to that in Armco Fe.

APPENDIX B

The equivalents to Eq. (3) for a $1/r^2$ and $1/r^4$ dependent moment perturbations are

 $\mu_{C_0} = 3.26 - 22.7\Delta\mu_1, \quad 1/r^2$ $\mu_{C_0} = 3.26 - 15.6\Delta\mu_1, \quad 1/r^4.$

The hyperfine-field shifts for a $1/r^2$ moment perturbation are

$$\begin{split} \Delta H_1 &= -130.0 \Delta \mu_1 - 12.1(\mu_{\rm Co} - \mu_{\rm Fe}) ,\\ \Delta H_2 &= -120.7 \Delta \mu_1 - 2.7(\mu_{\rm Co} - \mu_{\rm Fe}) ,\\ \Delta H_3 &= -68.9 \Delta \mu_1 + 2.4(\mu_{\rm Co} - \mu_{\rm Fe}) ,\\ \Delta H_4 &= -43.7 \Delta \mu_1 + 0.6(\mu_{\rm Co} - \mu_{\rm Fe}) . \end{split}$$

The hyperfine-field shifts for a $1/r^4$ momentperturbation are

$$\begin{split} \Delta H_1 &= -115.5 \Delta \mu_1 - 12.1(\mu_{\rm Co} - \mu_{\rm Fe}) ,\\ \Delta H_2 &= -95.7 \Delta \mu_1 - 2.7(\mu_{\rm Co} - \mu_{\rm Fe}) ,\\ \Delta H_3 &= -39.7 \Delta \mu_1 + 2.4(\mu_{\rm Co} - \mu_{\rm Fe}) ,\\ \Delta H_4 &= -14.9 \Delta \mu_1 + 0.6(\mu_{\rm Co} - \mu_{\rm Fe}) . \end{split}$$

4081 (1971); Phys. Lett. <u>34A</u>, 146 (1971); Phys. Rev. B <u>6</u>, 3326 (1972); (b) M. B. Stearns, Phys. Rev. B <u>8</u>, 4383 (1973).

- ⁴C. E. Johnson, M. S. Ridout and T. E. Cranshaw, Proc. Phys. Soc. Lond. <u>81</u>, 1079 (1963).
- ⁵G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. Lett. <u>12</u>, 24 (1964).
- ⁶M. B. Stearns (unpublished). We present in Appendix A some of the data relevant to this paper. The isomer shifts are also presented there.
- ⁷Y. Koi, A. Tziyimura, T. Hihara, and T. Kushida, J. Phys. Soc. Jap. <u>16</u>, 1040 (1961); J. I. Budnick, R. C.

LaForce, and G. F. Day, Bull. Am. Phys. Soc. <u>6</u>, 441 (1961).

- ⁸R. C. LaForce, S. F. Ravitz, and G. F. Day, J. Phys. Soc. Jap. Suppl. <u>17</u>, 99 (1962).
- ⁹G. V. Wilson, Proc. R. Soc. Lond. 84, 689 (1964).
- ¹⁰E. F. Mendis and L. W. Anderson, Phys. Rev. Lett. <u>19</u>, 1434 (1967); and Phys. Status Solidi <u>41</u>, 375 (1970).
- ¹¹M. Rubinstein, G. H. Stauss, and M. B. Stearns, J. Appl. Phys. <u>37</u>, 1334 (1966).
- ¹²M. B. Stearns, Phys. Rev. <u>162</u>, 496 (1967).
- ¹³M. Rubinstein, Phys. Rev. <u>172</u>, 277 (1968).
- ¹⁴J. I. Budnick, T. J. Burch, S. Skalski, and K. Raj, Phys. Rev. Lett. <u>24</u>, 511 (1970).
- ¹⁵G. H. Stauss, Phys. Rev. B 4, 3106 (1971).
- ¹⁶G. K. Wertheim, Phys. Rev. B 1, 1263 (1970).
- ¹⁷M. Rubinstein, G. H. Stauss, and J. Dweck, Phys. Rev. Lett. 17, 1001 (1966).
- ¹⁸M. B. Stearns, Phys. Rev. <u>162</u>, 496 (1967); <u>187</u>, 648 (1969); M. B. Stearns and J. F. Ullrich, Phys. Rev. B 4, 178 (1972).
- ¹⁹M. B. Stearns, Phys. Rev. <u>147</u>, 439 (1966).
- ²⁰P. Weiss and R. Forrer, Ann. Phys. (N. Y.) <u>5</u>, 153
- (1926); D. I. Bardos, J. Appl. Phys. <u>40</u>, 1371 (1969). ²¹G. K. Wertheim, D. N. E. Buchanan, and J. H. Wernick, J. Appl. Phys. <u>42</u>, 1602 (1971).
- ²²I. A. Campbell, Proc. Phys. Soc. Lond. <u>89</u>, 71 (1966).
- ²³M. Fallot, Ann. Phys. (N. Y.) <u>10</u>, 291 (1938).
- ²⁴G. Shirane, R. Nathans, and C. W. Chen, Phys. Rev. 134, A1547 (1964).
- ²⁵J. Friedel, Nuovo Cimento Suppl. 2, 287 (1958); J.
 Kanamori, J. Appl. Phys. <u>36</u>, 929 (1965); H. Hayakawa,
 Prog. Theor. Phys. <u>37</u>, 213 (1967); I. A. Campbell and
 A. Gomes, Proc. Phys. Soc. Lond. 91, 319 (1967).
- ²⁶J. B. Comly, T. M. Holden, and G. G. Low, J. Phys.

C 1, 458 (1968).

- ²⁷M. A. Ruderman and C. Kittel, Phys. Rev. <u>96</u>, 99 (1954); T. Kasuya, Prog. Theor. Phys. 16, 45 (1956);
- K. Yosida, Phys. Rev. <u>106</u>, 893 (1957).
- ²⁸P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. <u>2</u>, 124 (1961); P. W. Anderson, Phys. Rev. <u>124</u>, 41 (1961).
- ²⁹O. Gunnarson, B. I. Lundquist, and S. Lundquist, Solid State Commun. <u>11</u>, 149 (1972).
- ³⁰K. J. Duff and T. P. Das, Phys. Rev. B <u>3</u>, 192 (1971); R. A. Tawil and J. Callaway, *ibid*. B 7, 4242 (1973).
- ³¹T. M. Holden, J. B. Comly, and G. G. Low, Proc. Phys. Soc. Lond. <u>92</u>, 726 (1967).
- ³²J. Crangle and G. C. Hallam, Proc. R. Soc. Lond. A <u>272</u>, 119 (1963).
- ³³A. J. Freeman and R. E. Watson, Phys. Rev. <u>131</u>, 2566 (1963).
- ³⁴R. E. Watson and A. J. Freeman, Phys. Rev. <u>123</u>, 2027 (1961); A. J. Freeman and R. E. Watson, *Magne*tism, edited by H. Suhl and G. Rado (Academic, New York, 1965), Vol. IIA.
- ³⁵T. Muto, S. Kubayasi, and H. Hayakawa, J. Phys. Soc. Jap. 20, 388 (1965).
- ³⁶S. Wakoh and J. Yamashita, J. Phys. Soc. Jap. <u>21</u>, 1712 (1966).
- ³⁷K. J. Duff and T. P. Das, Phys. Rev. B <u>3</u>, 2294 (1971).
- ³⁸K. J. Duff, thesis (University of California, Riverside) (unpublished).
- ³⁹A. J. Freeman, B. Bagus and R. E. Watson, Colloq. Intern. Centre Nall. Rech. Sci. (Paris) No. 164 (1966).
- ⁴⁰D. A. Shirley, S. S. Rosenbaum and E. Matthais, Phys. Rev. 170, 363 (1968).
- ⁴¹A. M. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. 134, A650 (1964).