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HYPERFINE FIELDS AT SOLUTES IN FERROMAGNETS: CADMIUM AND RUTHENIUM IN NICKEL*

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ABSTRACT

Perturbed angular correlation studies of temperature dependent hyperfine fields at ^{111}Cd and ^{99}Ru solutes in nickel above and below the Curie point are presented. Trends among observed hyperfine fields at solutes in Fe, Co, and Ni are discussed within the framework of a formal spin Hamiltonian. Origins of the hyperfine fields in 4f and 5p group solutes are discussed. Conduction electron and core-polarization contributions to H_{hf} in transition series solutes are analyzed, and localized moments are derived for the solutes Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt, and are compared with neutron scattering results. The observed lack of agreement may be associated with the fact that neutron scattering and hyperfine fields measure different quantities. It is suggested that a molecular field model that accounts for conduction electrons as well as core polarization might also be applicable above T_c . This model fits $H_{\text{hf}}(T)$ in ^{55}Mn Fe for all spins between 1/2 and 5/2, suggesting that j cannot be determined from $H_{\text{hf}}(T)$ alone. This analysis yields a local moment of 1.5 ± 0.5 Bohr magnetons for ^{55}Mn in iron, just in agreement with the results of Jaccarino et al., but higher than allowed by neutron data.

Angular correlation apparatus capable of 0.1% accuracy is described. A localized moment of $\cong 0.5$ Bohr magnetons is determined from H_{hf} for ^{99}Ru in Ni. For $T > T_c$, paramagnetic Knight shifts up to -80% are observed. A model due to Lovesey also fits the data below T_c for $j = 1/2$. For ^{111}Cd Ni no local moment is indicated below T_c , and comparison with a model due to Lovesey and Marshall suggests that Cd atoms have the same temperature dependent magnetization as nearest neighbor nickel atoms. Above T_c , paramagnetic Knight shifts up to -60% are in excellent agreement with predictions of the conduction-electron polarization model.

I. INTRODUCTION

Since the discovery of hyperfine fields in ferromagnetic metals,^{1,2} a great deal has been learned about this subject. Hyperfine fields are sensitive probes for studying certain details of electron wave functions in metals. Theoretical treatment of these fields is, by its nature, a many body problem: even the relatively straightforward calculation of core polarization by d electrons requires the unrestricted Hartree-Fock method.³ A really rigorous estimate of hyperfine structure in a metal would be a very complex problem indeed. A corollary is that the concepts which have been developed to explain the known hyperfine fields have forced a better understanding of electronic states in solids. All of the major mechanisms that give rise to hyperfine fields in ferromagnets are now apparently understood, and in recent years there has been increasing use of hyperfine fields as a diagnostic device for studying metals.

In 1959 Samoilov, Sklyarevskii, and Stepanov⁴ greatly extended the generality of this area of physics by their discovery that hyperfine fields also occur at nuclei of "nonmagnetic" metals as solutes in ferromagnetic lattices. Solute fields are of considerable theoretical interest because they can be used to study, separately, the particular interactions that give rise to hyperfine fields. They also have practical importance in providing magnetic fields of 10^5 to 10^6 gauss at solute nuclei.

In this paper we describe studies of the hyperfine fields at nuclei of ^{99}Ru and ^{111}Cd in nickel. Measurements were made from helium temperatures to above the Curie point, using the method of time differential perturbed angular correlation (TDPA).⁵ This method is often a useful alternative to

Fortunately $\vec{H}_{hf}^c$ and $\vec{H}_L$ are essentially parallel (or antiparallel) even in domain walls. Consequently $\vec{H}_{hf} = (\vec{H}_{hf}^c + \vec{H}_L)$, rather than $\vec{H}_{hf}^c$, is usually reported as the "hyperfine field." We shall follow this practice.

2. Hyperfine Structure and Hyperfine Fields

Although the term "hyperfine field" is widely prevalent, its use actually implies the existence of a rather special set of conditions affecting the hyperfine structure of an atom. This subject was discussed for the case of a paramagnetic sample,⁷ and the terms were defined under which a hyperfine field could be observed. It is helpful to review briefly how hyperfine fields in ferromagnets arise from hyperfine structure.

A simple free-atom spin Hamiltonian that entails hyperfine interaction is

$$\mathcal{H} = \gamma_J \vec{H}_0 \cdot \vec{J} - \gamma_I \vec{H}_0 \cdot \vec{I} + A \vec{J} \cdot \vec{I} \quad (3)$$

Here γ_J is the Lande g -factor times the Bohr magneton, and the other terms have their usual meanings. For $\vec{H}_0 = 0$, I , J , and F , but not M_I , are good quantum numbers: no "hyperfine magnetic field" exists. With increasing $\vec{H}_0$, M_I and M_J tend to become good quantum numbers, and for large H_0 the effective spin Hamiltonian may be approximated by

$$\mathcal{H} = \gamma_J H_0 J_z - \gamma_I H_0 I_z + A J_z I_z \quad (4)$$

For $J\gamma_J \gg I\gamma_I$, the system is resolved into $2J+1$ manifolds of $2I+1$ states. Within each manifold M_I is (nearly) a good quantum number, and the nuclear

states have relative energies $-\gamma_I H_{\text{eff}} M_I$. Thus an operational definition of H_{hf} is

$$H_{\text{hf}} = H_{\text{eff}} - H_0 = - \frac{AM_J}{\gamma_I} \quad (5)$$

Of course, this definition is only exact to the extent to which H_{hf} is meaningful, i.e., to order $(AI/\gamma_I H_0)^2$. For this (free atom) case, three features stand out:

- i) $\vec{H}_0$, $\vec{H}_{\text{eff}}$, and $\vec{H}_{\text{hf}}$ are necessarily collinear.
- ii) Each M_J manifold has a unique H_{hf} .
- iii) The system is isotropic.

3. Weak Crystal Field Case

If spin-orbit coupling is large compared with the crystal field, as in the rare earths, the definition of H_{hf} is less obvious, but still straightforward. In some cases the free-ion approximation is still valid, but this is not generally true. Following Elliott and Stevens⁸ we may write a spin Hamiltonian for each crystal-field multiplet

$$H = -\sum_i \gamma_i H_i S'_i - \gamma_I \vec{I} \cdot \vec{H}_0 + \sum_i A_i S'_i I_i \quad , \quad (6)$$

where S' is the effective spin of the electronic multiplet. Because this Hamiltonian is anisotropic, we must be careful in defining hyperfine fields. In the high field limit $\gamma_i H_0 \gg \gamma_I H_0$, $A_i S'_i I_i$, each crystal-field level is resolved into $2S'+1$ manifolds of $2I+1$ states. Within each manifold the nucleus is subject to an effective field,

$$\vec{H}_{\text{eff}} = \vec{H}_0' - \frac{1}{\gamma_I} A_I M_S \quad (7)$$

The effective hyperfine structure constant, A_f , and effective external field, H_0' , can be obtained from the paramagnetic resonance literature. For the very common case of axial symmetry ($A_z \neq A_x = A_y$; $\gamma_z \neq \gamma_x = \gamma_y$), for example, we have^{9,10}

$$A_f = \gamma^{-1} [A_z^2 \gamma_z^2 \cos^2 \theta + A_x^2 \gamma_x^2 \sin^2 \theta]^{1/2} \quad (8a)$$

$$H_0' = (H_0 / A_f \gamma) [A_z \gamma_z \cos^2 \theta + A_x \gamma_x \sin^2 \theta] \quad (8b)$$

Here $\gamma = (\gamma_z^2 \cos^2 \theta + \gamma_x^2 \sin^2 \theta)^{1/2}$, θ is the angle between H_0 and the z axis, and it is understood that H_0 has been corrected for demagnetization, Lorentz, and dipole fields.

The definition of H_{hf} is straightforward,

$$|\vec{H}_{\text{hf}}| = |\vec{H}_{\text{eff}} - \vec{H}_0'| = - \frac{1}{\gamma_I} A_I M_S \quad (9)$$

While this is superficially similar to Eq. (5), it should be noted that none of the three observations quoted under Eq. (5) hold for this case. To quote a hyperfine field in the weak-crystal-field case without carefully stating the conditions is therefore meaningless.

In a ferromagnet, the spin-spin exchange "field" takes the place of an external field. For the weak-crystal-field situation, this will tend to diagonalize the spin Hamiltonian in the $J, M, (S', M_{S'})$ representation if the exchange energy is large (small) compared with the crystal-field energy, and

if $\lambda \vec{L} \cdot \vec{S}$ is large compared to both. Thus exchange orients $\vec{S}$, which in turn orients $\vec{J}$ (or $\vec{S}'$) through spin-orbit coupling; and $\vec{J}$ (or $\vec{S}'$) determines H_{hf} .

4. A Formal Hamiltonian

The two cases treated above are relatively simple. Acceptable wave functions for the atom or ion core can be worked out and contributions to H_{hf} can be calculated rather rigorously. For the general case of a solute in a ferromagnetic metal the situation is less tractable. We must proceed more empirically, as in Section IIB. It is useful to do so within the framework of a formal spin Hamiltonian for the solute:

$$\begin{aligned} \mathcal{H} = & V_{cf} + 2\beta \vec{H}_{ex} \cdot \vec{S} + \lambda \vec{L} \cdot \vec{S} - \gamma_I \vec{H}_c \cdot \vec{I} + 2\beta \gamma_I \langle r^{-3} \rangle (\vec{L} \cdot \vec{I} + [\frac{1}{2}L(L+1) - K] \vec{S} \cdot \vec{I}) \\ & - \frac{3}{2} \xi [(\vec{L} \cdot \vec{S})(\vec{L} \cdot \vec{I}) + (\vec{L} \cdot \vec{I})(\vec{L} \cdot \vec{S})] \end{aligned} \quad (10)$$

This Hamiltonian is general and can be applied to all the situations encountered in Section IIB. In using it, we think of the system in terms of the coordinates of the lattice (the crystal-field potential V_{cf} and the exchange field H_{ex}) and those of the solute ion core ($\vec{L}, \vec{S}$, and $\vec{I}$). Here β is the Bohr magneton, and $\langle r^{-3} \rangle$ is evaluated for the open electronic shell (if any) of the solute. The first three terms must be evaluated first, as they are large and determine the zeroth-order wave functions for evaluating matrix elements of the six terms linear in I . The fourth term describes conduction electron polarization: H_c is essentially proportional to the lattice magnetization. The five terms in curly brackets represent the familiar magnetic hfs interaction¹¹ in operator-equivalent notation.¹² The $\vec{L} \cdot \vec{I}$ term represents orbital magnetism, the $K \vec{S} \cdot \vec{I}$

term core polarization, and the three terms in $\mathbf{L}$ spin-dipolar-nuclear-dipolar interaction.

The complexity of the H_{hf} concept for rare earths in ferromagnets arises because the $\lambda \vec{L} \cdot \vec{S}$ term is not small compared to the first two terms in Eq. (10). For most other solutes the opposite is true. The orbital angular momentum is quenched, and the other terms in $\mathbf{L}$ contribute negligibly to H_{hf} .

B. Trends Among Observed Fields

To study the relative importance of the mechanisms that produce hyperfine fields at solutes in ferromagnets it is useful to survey the fields reported in the iron, cobalt, and nickel lattices. Many of these fields were given in two recent tabulations,¹³ but the large number of new results, have led us to bring the list up to date in Table I. A complete set of references is given elsewhere.¹⁴ The earlier observation⁶ that solute fields vary smoothly with atomic number has been very nicely confirmed for all three host lattices. This variation is displayed for the iron lattice in Fig. 1. We discuss, in turn, the few specific H_{hf} mechanisms that are suggested by the iron-host data, noting that most of our conclusions hold, also, for cobalt and nickel hosts, though fewer data are available for these lattices.

1. Conduction-Electron Polarization (CEP)

The large negative fields found in the d^{10} solutes Cu, Ag, and Au, and perhaps those on the $d^{10}s^2$ solutes, arise largely from the outer s electrons via CEP, and the $-\gamma_I \vec{H}_c \cdot \vec{I}$ term in Eq. (10) dominates. Freeman and Watson have used the unrestricted Hartree-Fock method to deduce negative spin density

(relative to the 3d spin polarization) in the 4s orbital of iron,¹⁵ in the outer portion of the iron atom. For a "nonmagnetic" solute atom in an iron lattice this negative (conduction-electron) polarization at the cell boundary would be expected to persist across the solute cell. Daniel and Friedel have proposed a simple model¹⁶ to relate this polarization to screening by conduction electrons. Treating this as a free-electron scattering problem, in which the solute is represented by a square well, these authors allowed the bottom of the conduction band to be offset by twice the s-d exchange energy for electrons in "spin-up" and "spin-down" half-bands. The well depth was derived from the excess solute "valence," Z, using the Friedel Sum Rule. The difference between s-wave phase shifts at the solute in the two half-bands produces a net negative spin polarization and (by contact interaction) a hyperfine field at the solute nucleus. Daniel and Friedel found that the CEP is negative and increases in magnitude by about a factor of two as Z increases from 0 to 1.

The conduction-band s-wave states resemble solute atomic functions near the solute nucleus. The hyperfine fields that they produce may therefore be derived from the field, H_{ns} , that can arise from a free atom atomic ns state. For silver, for example, this is given by

$$H_{5s} = -a_{5s} [Ag(I)] / 2\gamma_I \quad . \quad (11)$$

The results of the CEP picture may then be summarized in the equation

$$H_{CEP} = p H_{ns} \quad . \quad (12)$$

In an earlier discussion of solute fields, Shirley and Westenbarger⁶ wrote the right hand side of this equation as npH_{ns} . Here the coefficient n was the occupation number of the s -wave in the conduction band at the solute and p was a host-dependent polarization. There were not enough data available to deduce anything about n , and it was assumed to be ~ 1 . The Daniel-Friedel model provides a detailed description of these two factors, p being proportional to the s - d exchange energy, ϵ , and n proportional to $[\partial\rho(0)]/[\partial(k_0^2/2)]$, the derivative of s -wave density at the solute with respect to well depth below the bottom of the conduction band. The factor p in Eq. (12) is empirical and thus absorbs all host- and solute-dependent factors. In using this simple notation we are anticipating the result found below, that there is no clear trend of p with Z .

Values of p derived from observed fields in d^{10} s and $d^{10,2}$ solutes are given in Table II. The CEP picture requires that these data pass three tests:

1. All H_{hf} must be negative.
2. For each host p must vary by less than a factor of about two, the range allowed for these solutes by the Daniel-Friedel theory.
3. The parameter p must be proportional to host magnetization.

From Table II it is clear that all three conditions are satisfied. It is, however, disconcerting that the increase of p with Z predicted by the Daniel Friedel model is not observed. Perhaps this is due to additional core-polarization contributions to H_{hf} , which are not considered in the model.

The CEP model would be expected to apply to transition-metal solutes, but would, at best, describe only contributions of the s -band to H_{hf} . In fact, we shall find below that while CEP alone can fit the observed values of H_{hf} for transition-series solutes to the left of Mn, Ru, and Os in the periodic table, core polarization is large in the upper part of the d groups. We defer discussion of these latter solutes to Section II.B.2, and take up now the transition series solutes to which the CEP picture applies. In Table III, thirty-six hyperfine fields are estimated, using Eq. (12), for twelve elements as solutes in iron, cobalt, and nickel hosts, using $p = 0.059$ for iron and $p = 0.015$ for nickel, determined from Table II, and $p = 0.061 (1.71/2.22) = 0.047$ for cobalt (because not enough data are available for cobalt in Table II). The values H_{ns} in Table III were estimated by drawing smooth curves through the values given in Ref. 6. This simple estimate gives surprisingly accurate predictions for the seventeen cases observed to date. The sign (where measured) is correct, the average deviation is only 2 kG and the rms magnitude of the deviation is 5^4 kG in a quantity of average magnitude 260 kG. We may summarize this agreement by the empirical relation

$$H_{hf} = 0.027 \mu H_{ns} \quad (13)$$

for solute fields, where μ is the host moment in Bohr magnetons, and H_{ns} for the solute is just $-a_{ns}/2\gamma_I$ for a given isotope.

Equation (13) is clearly a useful empirical relation, and the CEP model is quite plausible. It is also perhaps reasonable that p should be essentially

constant for the solutes in Tables II and III. Still it is very likely that some fraction of the observed values of H_{hf} in both tables comes from core polarization of inner electrons, discussed below.

2. Core polarization and localized moments

The regular variation of H_{hf} with solute atomic number in the 3d, 4d, and 5d transition series is striking. In Fe, Co, and Ni hosts, the fields are negative across the three series, but they increase suddenly in magnitude at the solutes Mn, Ru, and Os, and remain large for several elements before returning to the CEP "baselines" at the noble metals. The inadequacy of the CEP estimates for these large fields is illustrated in Fig. 2. Apparently core polarization by localized moments in the solute d shell contributes strongly to H_{hf} for these solute elements. To describe this behavior we truncate Eq. (10), assuming that V_{cf} is strong enough to quench the orbital angular momentum of solute d shells. This leaves, in lattices with cubic symmetry,

$$H = 2\beta\vec{H}_{ex} \cdot \vec{S} + \gamma_I \vec{H}_c \cdot \vec{I} - 2\beta\gamma_I \langle r^{-3} \rangle \kappa \vec{S} \cdot \vec{I} \quad (14)$$

The exchange term is by far the largest; we may imagine that it is evaluated first to give $\langle S_z \rangle$ (a molecular field picture for this process is described in Section III). Then we have

$$H_{hf} = p H_s + 2 \langle S_z \rangle H_d \quad , \quad (15)$$

where we have used the definition $H_d = \beta \kappa \langle r^{-3} \rangle$; and H_d is the (core polarization) hyperfine field arising from one unpaired d electron. For the 4d group,

Freeman and Watson have calculated $H_{4d} = -370 \text{ kG}$.¹⁷ For the 5d group, the situation is not clear. Evidence for core polarization in platinum metal was found by Butterworth¹⁸ from measurements of the Knight shift. From analysis of Knight shifts in platinum, Clogston et al.,¹⁹ found $H_{5d} = -1.18 \times 10^6 \text{ Oe}$. However, Armstrong and Marrus²⁰ found no evidence for core polarization in atomic rhenium in the $5d^5 6s^2$ configuration. By comparing observed values of H_{hf} with Eq. (15), we may derive $\langle S_z \rangle$ and μ , the magnitude of the d-electron spin moment on each solute. These values of μ are set out in Table IV. The estimates of pH_s in Table IV are based on the observed H_{hf} for light transition element and noble metal solutes. Two other sets of values for μ are given for comparison. They were determined from the same neutron scattering data by Collins and Low and by Campbell.²¹

In comparing the three sets of localized moments in Table IV, we note: (1) the trends of μ with solute atomic number are in qualitative agreement among the three sets of values, and they establish localized solute moments in the upper ends of the transition series. (2) The neutron data seem to offer scope for considerable variation in derived values of μ depending on interpretation, and (3) the detailed agreement of the three sets of values of μ is poor, suggesting systematic errors. These three points are illustrated in Fig. 3, which shows solute moments in iron.

The most disturbing cases of quantitative disagreement between neutron and H_{hf} values of μ are FeMn and the trend in FeRu, FeRh, and FePd. In trying to understand these discrepancies it must be remembered that the two methods involved measure two rather different quantities, viz. the spin density at the

solute nucleus versus a magnetic disturbance near the solute atom.²² In comparing the values given in Table IV and shown in Fig. 3 it should be noted that the smooth variation of μ as deduced from H_{hf} indicates the high precision (and probably the reliability of trends with atomic number) of these moments, but tells little about their accuracy. This depends on the validity of Eq. (15). For this reason we have not assigned errors for these moments in Table IV. Considerations of possible systematic errors suggest that the moments are probably accurate to about ± 0.2 Bohr magnetons.

In correlating solute moments determined from neutron data with hyperfine fields, Campbell obtained apparent agreement, but he assumed H_s to be constant across a transition series, whereas, as noted earlier,⁶ H_s in fact increases by a factor of two between Ta and Au because of relativistic and screening effects. With this variation included, μ becomes positive for Os, Ir, and Pt in iron, in agreement with 3d and 4d solutes. The systematic absence of these moments in the analyses of the neutron data may be due to local expansion of the lattice by these large atoms.

3. Rare Earth Solutes

The 4f shell is shielded from the crystal field: thus $\lambda \vec{L} \cdot \vec{S} \gg V_{cf}$ and J is a good quantum number. All the terms in Eq. (10) must be considered, with¹² $\xi = (2l+1-4s)/s(2l-1)(2l+3)(2L-1)$, taking $l=3$. The $\vec{L} \cdot \vec{I}$ term especially should lead to very large values for H_{hf} , and large fields have been observed (Table I). H_{hf} for rare earths in iron changes sign near the middle of the 4f shell as predicted,⁶ but with opposite signs. This happens because $\vec{L}$ gives the dominant contribution to H_{hf} for most rare earths, while $\vec{S}$ orients the solute moment by spin-exchange polarization; and $\vec{L}$ and $\vec{S}$ parallel

(antiparallel) for the 4f shell more (less) than half full. The upper limit for H_{hf} expected at rare earths in ferromagnets is just the "free-atom" field, $H_{fa} = 2\langle r^{-3} \rangle \beta N J^{8,23}$ (to within small corrections for CEP). In fact, whenever any uniaxial interaction dominates (e.g., the exchange field, transforming as Y_{10} , or the quadrupole crystal-field component transforming as Y_{20}), the doublet state $|J_z = \pm J\rangle$ (for a Kramers ion) is likely to be lowest in energy, giving $H_{hf} = H_{fa}$. This is the reason that the maximum free atom field is so often observed in Mossbauer spectra.

Integral angular correlation experiments on rare earths in iron have been analyzed²⁴ to give "hyperfine fields" at the solutes. These "fields" were consistently smaller than H_{fa} , possibly because they were really thermal averages over many crystal-field states. There are two qualitatively distinct possibilities. For $V_{cf} \ll J\gamma_J H_{ex} \sim kT$, the rare-earth atom would be a truly localized moment and the observed H_{hf} would be a thermal average over the $2J+1$ substates. At absolute zero, H_{hf} would approach H_{fa} .

If on the other hand, $J\gamma_J H_{ex} < V_{cf}$, then the observed H_{hf} is an average over several cubic crystal-field representations (mixed by H_{ex}), each of which gives $H_{hf} < H_{fa}$. For this case H_{hf} will be smaller than H_{fa} (by about 1/2 for many cases) at absolute zero.

4. The $d^{10} s^2 p^n$ Solutes

Solute elements beyond the d shell, with atomic configurations $d^{10} s^2 p^n$, tend to have $H_{hf} > 0$. This is particularly well documented in the $4d^{10} 5s^2 5p^n$ series, where H_{hf} increases rapidly with n. In the Daniel-Friedel model, a bound state appears when Z, the excess solute valence, reaches 1.2. This state has a negative polarization (relative to the host d spins)

that decreases more rapidly with increasing Z than does the positive polarization of the free s -wave. It is tempting to interpret this as the explanation for positive hyperfine fields on Sb, Te, I, and Xe in iron. Unfortunately this interpretation does not hold up under careful scrutiny. The square-well solute potential used by Daniel and Friedel cannot, of course, generate an atomic spectrum of electronic energy levels so the model must break down for large Z . In fact, the total spin density required to fit the observed H_{hf} for xenon in iron is five times that of a $5s$ electron in atomic xenon. Of course, we could modify the model to make up the bound s -state out of $5s$ atomic functions and assign $6s$, $7s$, etc., character to the free s -wave. This only makes matters worse, however, because the positively-polarized s -wave now has a much lower value of $|\psi(0)|^2$ and cannot overcome the much denser negatively polarized bound state to make a positive H_{hf} .

The observed large values of H_{hf} for Te, I, and Xe in iron can only arise from the $5s$ shell (as inner s shells), polarized positively relative to the host $3d$ spins. The solute d shell is filled, and core polarization by the p shell gives only $H_p = 3 \cdot 10^5$ gauss/electron spin.²⁵ The $6s$, $7s$, etc., atomic states in these atoms have too little electron density at the nucleus. A single $5s$ electron in neutral iodine has $H_s \approx 3 \cdot 10^7$ gauss: only 3% polarization of the $5s$ shell is necessary to yield the observed field.

Two well-known mechanisms responsible for transferred hyperfine structure, the Pauli distortion effect and covalent bonding, can create a 3% positive polarization in the $5s$ shell of iodine or xenon.²⁶ Orthogonalization of the host $3d$ and solute $5s$ states leads to an admixture of $3d$ character into the $5s$ orbital with spin parallel to the $3d$ spins, resulting in a contact solute

hyperfine field, $H_{hf} \approx \langle 3d|5s \rangle^2 H_{5s}$. Rough estimates based on Hartree-Fock free-atom wave functions for xenon and the wave functions of DeCicco and Kitz²⁷ for iron give $H_{hf} \sim 5.10^6$ for xenon in iron if the internuclear distance is 6 a.u. and for eight nearest neighbors. Clearly this mechanism is large enough to account for the experimental values in Table I. Similar calculations indicate that H_{hf} should be positive for all halogens, rare gases, and alkalis. For Cs in iron, for example, $\langle 3d|5s \rangle^2$ is about half that of Xe in iron, so H_{hf} could also be roughly 1/2 that of Xe.

III. LOCALIZED MOMENTS ON SOLUTES IN FERROMAGNETS

Localized magnetic moments are known to exist on paramagnetic ions, on rare-earth atoms in metals, and on "magnetic" metal atoms in "nonmagnetic" lattices. In all of these cases the interpretation of experimental evidence is relatively straightforward. For solutes in ferromagnets, however, the situation is more complex. The two experimental methods discussed in Section II.B.2 measure different quantities and both are subject to ambiguities of interpretation. A third method was suggested and used by Jaccarino, Walker, and Wertheim.²⁸ These workers explained the temperature dependence of H_{hf} on ^{55}Mn in iron in terms of a molecular field model involving a localized moment on the Mn atom. We discuss this model below before applying it, in Section VII, to the case of ^{99}Ru in nickel.

A. The Molecular Field Model

Jaccarino, et al., obtained very good fits for NMR data on ^{55}Mn in iron²⁹ using a model in which a localized moment on the manganese atom is oriented in the exchange field, $H_{ex} = \zeta(\sigma_T/\sigma_0)(kT_c/g\beta)$. Here H_{ex} is scaled to the reduced lattice magnetization (σ_T/σ_0) by a constant ζ that takes account of the host-solute exchange energy being different from the host-host exchange energy. The hyperfine field is then proportional to $B_j(y)$, the Brillouin function of spin j , with $y = g\beta H_{ex}/kT$. These workers found a good fit ($< 0.5\%$) for $H_{hf}(T)$, using $j = 3/2$, and rather poorer fits for other values of j .

This model took no account of contributions to H_{hf} from conduction electrons. Such contributions are clearly present in many other cases (Section

II.B.1.), and are expected to be present, to some extent, in all ferromagnetic metals. A conduction-electron term in H_{hf} is expected to follow the lattice magnetization rather closely. We shall assume that contributions to $H_{hf}(T)$ from conduction electrons and from localized moments, $H_c(T)$ and $H_L(T)$, are additive.³⁰ This is the simplest way to combine the two contributions and it is the only way that is physically sensible within the spirit of the model. For certain limiting cases, (e.g., small ζ , or in rare earths) it can be rigorously justified.

Equation (10) is useful in understanding how the Brillouin-function dependence of $H_L(T)$ might arise for a solute atom. This can happen in several ways. If $\vec{L}$ is quenched, we have Eq. (14). Evaluating $\langle S_z \rangle_T = \langle S_z \rangle_0 B_j(y)$ in the molecular field, we have

$$H_{hf}(T) = H_c(0) \frac{\sigma_T}{\sigma_0} + H_L(0) B_j(y) \quad , \quad (16)$$

which is identical to Eq. (15) if $H_c(0) = p_0 H_s$, and $H_L(0) = 2 \langle S_z \rangle_0 H_d$. Other models for the solute give similar results. For the strong crystal field case with L not quenched, j would be the multiplicity of the lowest crystal-field state. For weak crystal fields, as in the rare earths, j is the total angular momentum, J . For $V_{cf} > J \gamma_J H_{ex}$, j is given by $(2j+1) = (\text{multiplicity of lowest crystal field state})$, i.e., j is the effective spin in this state. For many real solutes none of these simple examples may be accurate, but the molecular field model may very well still describe the temperature dependence of H_{hf} accurately, even though the exact nature of j is not understood.

The model is conveniently summarized by defining the reduced lattice magnetization, $\sigma_R = \sigma_T/\sigma_0$, and by denoting by $f = H_L(0)/H_{hf}(0)$, the fraction of $H_{hf}(0)$ that has local origin. The reduced resonant frequency at the solute nucleus is then

$$\frac{\nu_T}{\nu_0} = fB_j(y) + (1-f)\sigma_R \quad (17)$$

This is a relation with which, for any j , we may try to fit ν_T using two adjustable parameters, j and f .

B. Manganese in Iron

Y. Koi's NMR data on ^{55}Mn in iron are the most accurate measurements available for a case in which the temperature dependence of the solute H_{hf} is quite different from that of the lattice magnetization. Koi attributed this behavior to the existence of a localized moment on the Mn atom. Jaccarino, et al., were able to fit the NMR data quantitatively assuming that the hyperfine field on manganese was entirely due to core polarization by a d-electron localized moment. They found a very good fit for $j = 3/2$, and a good fit for $j = 1$. For other values of j their fits were poorer. Using the model described above, we have obtained fits for $j = 1/2, 1, 3/2, 2$, and $5/2$. These fits are shown in Fig. 4, and derived parameters are given in Table V. Clearly for $1/2 \leq j \leq 5/2$ there is no significant variation in the quality of fit, and we conclude that j cannot be determined from the temperature dependence alone. It should be noted that only a very small ($< 20\%$) conduction electron

contribution to H_{hf} is needed to allow good fits of Eq. (14) to the data.

The good fits obtained by Jaccarino, et al., for $j = 1$ or $3/2$ are consistent with our finding $|1-f|$ smallest for these cases.

The FeMn case has been very useful for comparison of localized moments obtained from neutron data with those obtained from H_{hf} temperature dependence data. The initial estimates obtained from the two methods— 0 ± 0.2 and $2-3$ Bohr magnetons, respectively—were in serious conflict. (Campbell's analysis of the neutron data expanded the error limits on μ to ± 0.5 Bohr magnetons) Our value $\mu = 1.1$ Bohr magnetons (Table IV), was derived from the systematic variation of H_{hf} with atomic number. To obtain this value we assumed that conduction-electron and core-polarization contributions to H_{hf} are quite independent, neglecting s-d exchange on the solute. As exchange would tend to polarize the 4s electrons in the sense that they would contribute positively to H_{hf} , thus tending to cancel the core polarization contribution, we regard the estimate of 1.1 Bohr magnetons as a lower limit. An upper limit of $\mu = f(H_{hf}(0)/110\text{kOe})$ may be obtained from the parameters in Table V. This gives $\mu = 1.9$ Bohr magnetons. We conclude that the local moment on Mn in iron probably lies in the range $\mu = 1.5 \pm 0.5$ Bohr magnetons.

C. High Temperature Behavior

For a given j , the independent variables in Eq. (17) are the absolute temperature, T , and the lattice magnetization, σ_T . In a given host lattice, these variables are related, below T_c , by the magnetization curve, and there is no way to study the dependence of v_T/v_0 on σ or T alone. In a case such as FeMn, for which excellent fits are obtained for several values of j , but with quite different values of $f(j)$, it is desirable to determine f (and thus j) by varying σ and T separately. This is possible within the framework of the model because H_c depends on σ alone, while H_L depends, through B_j , on σ/T .

For $T > T_c$, σ and T can be varied separately. For a given applied field, H_0 , the effective field is given by

$$H_{\text{eff}} = H_0(1+K) = H_0 + H_c(0) \frac{\sigma_{T,H}}{\sigma_0} + H_L(0) B_j(y) \quad , \quad (18)$$

if Eq. (17) is still applicable. Here K is a paramagnetic Knight shift. If one then adjusts H_0 to keep $\frac{\sigma_{T,H}}{\sigma_0}$ constant, one obtains the dependence of $K(T)$ on T alone. This shift is negative, and for $T \gtrsim T_c$ can be as large as 100%. For $T \gg T_c$ it approaches zero asymptotically. The behavior of this curve should be insensitive to the value of j if one uses the values of f and ζ found below T_c . Of course, this treatment is based on the assumption that local moments exist above T_c if they exist below T_c , and that Eq. (17) is still applicable.

D. More Exact Models

The model described above is simple and may easily be applied both above and below T_c . It also takes direct conduction-electron contributions into account, albeit crudely. Justification for the molecular field approximation is provided, for cases in which j is small, by the findings of Hone, Callen, and Walker (based on a Green's function approach) that the impurity's quasiboson energy is essentially constant over a wide range of temperature when j is small.³¹

Lovesey and Marshall³² have calculated the magnetization on ferromagnetic host atoms which are nearest neighbors to a nonmagnetic impurity, using a molecular field model. If the impurity itself has no local moment, and v_T/v_0 is entirely determined by conduction-electron polarization, it is reasonable to expect the v_T/v_0 curve to lie somewhere between the σ_T/σ_0 host magnetization curve and that of the nearest neighbors, i.e., $\sigma_1(T)/\sigma_0$. We shall find that this is the case for ¹¹¹CdNi..

Lovesey used essentially the same theory to calculate the magnetization on a magnetic impurity.³³ We shall analyze the ⁹⁹RuNi data using this model, as well as the simple model outlined above.

IV. γ - γ PERTURBED ANGULAR CORRELATIONS IN FERROMAGNETS

Because several treatments of perturbed angular correlation theory (γ - γ PAC)^{5,34-36} are available, this discussion is limited to an outline of the theory for magnetic hyperfine perturbations in ferromagnets.

In γ - γ PAC, one observes two photons, γ_1 and γ_2 , which respectively populate and depopulate an excited nuclear level. The perturbed directional correlation between these two radiations is given by⁵

$$W(\vec{k}_1, \vec{k}_2, t) = \sum_{\substack{k_1, k_2 \\ N_1, N_2}} A_{k_1}(1) A_{k_2}(2) G_{k_1 k_2}^{N_1 N_2}(t) \times [(2k_1+1)(2k_2+1)]^{-\frac{1}{2}} Y_{k_1}^{N_1*}(\theta_1, \phi_1) Y_{k_2}^{N_2}(\theta_2, \phi_2) \quad (19)$$

where γ_1 and γ_2 are respectively observed in directions $\vec{k}_1(\theta_1, \phi_1)$ and $\vec{k}_2(\theta_2, \phi_2)$ from the quantization axis. The A_{k_i} factors depend solely on the angular momentum properties of the respective transitions and the $Y_{k_i}^{N_i}$ are the spherical harmonics. All the information about perturbations in the intermediate state is contained in the perturbation factor,

$$G_{k_1 k_2}^{N_1 N_2}(t) = \sum_{m_a, m_b} (-1)^{2I+m_a+m_b} [(2k_1+1)(2k_2+1)]^{\frac{1}{2}} \begin{pmatrix} I & I & k_1 \\ m_a' - m_a & N_1 & \end{pmatrix} \times \begin{pmatrix} I & I & k_2 \\ m_b' - m_b & N_2 & \end{pmatrix} \langle m_b | \Lambda(t) | m_a \rangle \langle m_b' | \Lambda(t) | m_a' \rangle \quad (20)$$

where $\Lambda(t)$ is the time evolution operator which describes the effect of the perturbing interaction on the m-substates of the intermediate state.

Several particular forms of the perturbation factor are of interest for static magnetic hyperfine interactions in metals. For a polycrystalline ferromagnetic source with a strong polarizing field transverse to the detector plane ($\theta_1 = \theta_2 = \pi/2$), we have, after making use of the orthogonality properties of the Clebsch-Gordan coefficients and some algebraic manipulation,⁵

$$W_{\perp}(\phi, t, \omega) = \sum_{k=0}^{k_{\max}} A_k(1) A_k(2) P_k[\cos(\phi - \omega t)] \quad (21a)$$

where ϕ is the angle between the detectors, P_k is the Legendre polynomial,

$$\text{and } \omega = \frac{\gamma_I}{\hbar} H_{\text{eff}}$$

For ^{111}Cd this becomes³⁸

$$W_{\perp}(\phi, t, \omega) = 1 - 0.180 P_2[\cos(\phi - \omega t)] \quad (21b)$$

and for ^{99}Ru we find³⁹

$$W_{\perp}(\phi, t, \omega) = 1 - 0.20 P_2[\cos(\phi - \omega t)] \quad (21c)$$

For both cases, terms of higher order can be neglected.

For a ferromagnetic sample in which the domains are randomly oriented, one obtains³⁷

$$W(\phi, t, \omega) = \sum_{k=0}^{k_{\max}} A_k(1) A_k(2) [2k+1]^{-1} \left[\sum_{N=-k}^{+k} \cos N\omega t \right] P_k(\cos \phi) \quad (22a)$$

For ^{111}Cd this becomes

$$W(\phi, t, \omega) = 1 - 0.180\left(\frac{1}{5}\right) [2 \cos 2 \omega t + 2 \cos \omega t + 1] P_2(\cos \phi) \quad (22b)$$

In both equations (21) and (22) the Larmor frequency, ω , is proportional to the effective field, H_{eff} . For temperatures well below the ferromagnetic Curie temperature, T_c , both polarized and randomly oriented samples can be examined, and we usually have $H_{\text{eff}} \approx H_{\text{hf}}$ since $H_{\text{hf}} \gg H_0$. However, for $T \approx T_c$ we find that $H_{\text{hf}} \approx H_0$ and, for still higher temperatures, we find that $H_{\text{hf}} \approx 0$ so that $H_{\text{eff}} \approx H_0$.

V. APPARATUS

1) Furnace

The furnace used in all the experiments above room temperature is shown in Fig. 5. It was designed to fit between the polecaps of an electro-magnet which could generate fields of up to 20kOe over the entire volume of the furnace. The furnace consisted of an alumina tube with heating tape wrapped around it, followed by a covering of aluminum foil and then asbestos tape for insulation. The thermocouple was a calibrated Pt vs. Pt-10% Rh junction, which was held in place by a piece of Pyrex glass tubing. These connections were made by using a high temperature adhesive.⁴⁰ This cement was also used to mount the sample on the thermocouple.

The thermocouple output was measured by using a Leeds and Northrup K-2 Potentiometer. The furnace temperature was controlled by adjusting the voltage applied to the heating tape with a variable transformer. It was found that by using regulated AC line voltage as a power source, the temperature variation of the furnace was less than $\pm 2^\circ\text{C}$ over the entire range of temperature reported for periods up to two days.

2) Electronics

A. Magnets

The magnet used for all experiments above T_c was an iron-core electro-magnet fed by a current regulated motor-generator. The field stability was $\pm 1\%$ for all runs.

For ^{99}Ru below T_c , various Alnico iron permanent magnets were used. These magnets were calibrated by comparing their fields to a high homogeneity

electromagnet which was in turn calibrated by NMR methods. For $^{111}\text{CdNi}$ below the Curie point, no external field was used.

B. PAC Spectrometer

For all experiments in the 20 kOe electromagnet, $1\frac{1}{2}" \times 1\frac{1}{2}"$ and $1\frac{1}{2}" \times 2"$ NaI(Tl) detectors were used, the larger crystal being used for the higher energy gamma photon. These were mounted on 56 AVP photomultiplier tubes via 10" long quartz light pipes. The FWHM for 511 keV Na^{22} annihilation radiation for this setup was 2.5 ns.

For the experiments with the permanent magnets and for those with no external field, two $1\frac{1}{2}" \times 1\frac{1}{2}"$ NaI(Tl) crystals were mounted via $1\frac{1}{2}"$ long quartz light pipes to XP1020 photomultiplier tubes. The time resolution here was 1.9 ns FWHM for Na^{22} annihilation radiation.

All experiments, except for ^{99}Ru in Ni above T_c were carried out by standard TDPAC fast-slow circuitry. For ^{99}Ru in Ni above T_c , it was necessary to use time integral PAC and normalize these results to a time differential run at 698°K.

VI. CADMIUM-111 IN NICKEL

A. Source Preparation

The parent nuclide was prepared via the reaction $^{111}\text{Cd}(p,n)^{111}\text{In}$ using a 10 MeV proton beam at the Berkeley 88" cyclotron. Natural cadmium foil, 0.005" thick was the target material and the integrated flux was typically 25 $\mu\text{amp-hrs}$.

The chemical procedure used in the separation of the ^{111}In from the target material was essentially that of E. Jacobi⁴¹ and is as follows:

- 1) Dissolve the target in a minimum amount of 1:1 HNO_3
- 2) Make the solution basic with conc. NH_4OH
- 3) Add ~200 mg $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in minimum volume H_2O
- 4) Heat in water bath to digest the precipitate. The $\text{Mg}(\text{OH})_2$ carries the $\text{In}(\text{OH})_2$ quantitatively. Centrifuge and dissolve the ppt. in hot 2M H_2SO_4 .
- 5) Repeat (2-4) and then dilute the solution with ~4 ml H_2O .
- 6) Add ammonium formate to buffer the solution at pH 2.
- 7) Prepare a clean .0005" Ni foil cathode and platinum wire anode.

Plate the In at a current density of $\sim 10 \frac{\text{ma}}{\text{cm}^2}$.

These nickel foils were melted in an argon atmosphere at 1500°C for 15 minutes and then quenched to room temperature by removing them from the furnace quickly. The resulting spheroids, generally less than 0.5 mm in diameter, were used as sources.

B. Results for $T < T_c$

The level at 247 keV in ^{111}Cd provides an excellent case for the TDPAC technique. The significant portion of the decay scheme is given in Fig. 6.⁴² More than 99% of the decays of the parent ^{111}In pass through the 247 keV level via the 173-247 keV cascade, making the true coincidence rate very large for a given source strength. The long half-life of the intermediate state allows the observation of many rotations of the nuclear spin, thus permitting very accurate determination of the rotation frequency. This level has been studied by many workers⁴² and the g-factor is accurately known ($g = -0.318 \pm 0.007$).⁴³

The great power of the TDPAC method is nicely demonstrated by the data of Fig. 7. No external polarizing field was applied for this series of measurements and a function of the form³⁷

$$F(t) = Ae^{-\lambda t} [1 + C[1 + 2 \cos(\omega t + \phi) + 2 \cos 2(\omega t + \phi)]] + B \quad (23)$$

was least-squares fitted to the statistically weighted data points, where, A, B, C, ω , and ϕ are adjustable parameters. The statistical error in the frequencies, ω , determined in this manner is on the order of 0.5% or less. Each run required about 2 days to complete.

All the data for ^{111}Cd Ni for $T < T_c$ is displayed in Fig. 8 and summarized in Table VI. The solid curve above the data points is the reduced spontaneous magnetization curve⁴⁴ for pure Ni while the dashed curve below the data points is that calculated on the model of Lovesey and Marshall³² for magnetization of the nearest neighbors of a non-magnetic impurity for

both impurity and host spins, $S' = S = 1/2$. The experimental results were expected to lie between the two curves because if the ^{111}Cd hyperfine field is created purely by short range exchange interaction then the data should follow σ_1/σ_0 while long range interactions would make $H(T)/H(0)$ approach σ/σ_0 .

C. Results for $T > T_c$

Above T_c , it was no longer possible to work without a polarizing field, and a field of 19.5 kOe was applied. The results in this region are much less accurate than those below T_c since 1) there is an added uncertainty in the magnitude of the external field, and 2) H_{eff} is much smaller, preventing the observation of more than a few cycles of nuclear precession. In Fig. 9 some typical data are shown. For these measurements, the two scintillation detectors were placed at a fixed position, 135° apart, and counts were taken for magnetic field up and down relative to the detector plane.

The data above T_c are displayed in Fig. 10. The ordinate is the paramagnetic Knight shift, $\beta = H_{\text{eff}}/H_{\text{ext}} \leq 1$. The solid curve is calculated on the assumption that the solute hyperfine field is produced purely by conduction electron polarization i.e., directly proportional to the induced lattice magnetization,

$$\beta = 1 - \frac{H_{\text{hf}}(0)}{H_{\text{ext}}} \frac{\sigma(T, H_{\text{ext}})_{\text{Ni}}}{\sigma(0, H_{\text{ext}})_{\text{Ni}}} \quad (24)$$

The excellent agreement between this very simple theory and the data supports the CEP model discussed in section II.B.1.

VII. RUTHENIUM-99 IN NICKEL

A. Source Preparation

The activity was produced by a (p,n) reaction on ^{99}Ru . Samples of approximately 10 mg of ^{99}Ru metal powder enriched to 98.8% were irradiated with 13 MeV protons at the Berkeley 88-in. cyclotron. The irradiated powder was then placed inside a weighed nickel container and melted in an argon atmosphere at 1500°C for 30 minutes and quenched to room temperature. The alloys were made up to be 1 atomic percent Ru in Ni. This material, after flattening to a thickness of ~1 mm and annealing at 300°C for 1 hour was used as the source for the experiments reported here.

B. Results for $T < T_c$

Below the Curie temperature, TDPAC measurements were carried out using the 90 keV level as the intermediate state. The pertinent levels in the decay scheme are shown in Fig. 11. The 529-90 keV cascade was used in all measurements as, in previous work by the present authors,³⁹ it was found to have a slightly larger anisotropy than the equally intense 354-90 keV cascade. In this previous work, the g-factor was accurately measured [$g = -0.189(4)$] making it possible to get accurate values for the magnetic hyperfine fields.

In Fig. 12 are shown some typical data for this set of measurements, all of which were carried out in a small external polarizing field. The attenuation of the nuclear precession frequency appears to occur at all temperatures at which we made measurements and is probably due to the existence of either a field distribution at the ^{99}Ru nucleus or to the presence of more than one type of lattice site for the Ru impurity. This interpretation is supported

by recent NMR work of Budnick on the Ru Ni system. He found a low frequency asymmetry in the resonance line shape in a .75 atomic percent alloy which is probably due to magnetic hyperfine interaction.⁴⁵

The data were least-squares fitted to a function of the form

$$R(t) = Ae^{-\lambda t} [\cos(\omega t + \phi)] + B \quad (25)$$

with A, λ , ω , ϕ , and B the adjustable parameters.

The final results are given in Table VII and plotted in Fig. 13. The Curie temperature of our 1 atomic percent Ru in Ni alloy was determined by extrapolating the measured induced magnetization vs. temperature curve at its region of greatest slope. T_c was found to be 610°K, in very good agreement with the results of Sadron.⁴⁶

The two broken curves in Fig. 13 are those calculated from Eq. (17), for $j = \frac{1}{2}$ and $j = \frac{5}{2}$. It is clear that the quality of the fit to the data is equally good in these two cases. In fact, for all $\frac{1}{2} \leq j \leq \frac{5}{2}$ the fits were uniformly good, thus indicating that one cannot uniquely determine the spin of the local moment from this type of analysis. The values of f and ζ for the best fits for all spins, j , are given in Table VIII.

It may be noted from Table VIII that the fit for $j = \frac{1}{2}$ requires the smallest contribution from polarized conduction electrons (19%). If one uses the model of Lovesey mentioned in Section III.D,³³ and calculates λ_0 , the deviation of the impurity magnetization from the host lattice magnetization one finds a best fit for solute and host spins $S' = S = \frac{1}{2}$ and with the ratio of impurity-host to host-host exchange coupling $\xi = 0.6$. This is shown in Fig. 14.

One would expect his ξ and our ζ for these conditions to be approximately equal since his model uses $H_c(0) = 0$.

It may also be noted that the model described by Eq. (16) requires the separability of $H_c(0)$ and $H_L(0)$. As was mentioned earlier, the local moment probably carries the conduction electrons through s-d exchange, making this assumption somewhat dubious. An indication of this lack of rigor is that $H_c(0)$ and $H_L(0)$ are predicted to be antiparallel, a result contrary to all previous experience.

In view of this quantitative failure of the model, the following calculation of the magnitude of the local moment is given as a qualitative estimate, using the results for $j = \frac{1}{2}$ (Table VIII). From Eq. (16) $H_L(0) = fH_{hf}(0) = (1.194)(217) \text{ kG}$, and making the same arguments as for Eq. (15) assuming $g = 2.0$, $\langle \mu_z \rangle = \frac{(1.194 \times 217)}{370} = 0.7 \text{ Bohr magneton}$.

In summary, two comments may be made about $^{99}\text{Ru Ni}$:

1) Both methods of analysis, hyperfine field vs. atomic number and $H(T)/H(0)$, agree that a local moment is present.

2) The magnitude of the local moment is not well established as these methods do not agree very well. However, for Ru in Ni it seems likely that $S \leq 1$.

C. Results for $T > T_c$

In raising the alloy temperature above T_c , it no longer was possible to use TDPAC since the precession frequency becomes too small to observe in this manner, even in an external field of 19.5 kOe. Thus it was necessary to use the less accurate time integral perturbed angular correlation technique. The integral results were then normalized to several time differential results at high temperatures. The data consisted of counts for field up and field down at a fixed detector angle of 135° .⁵ The results are displayed in Fig. 15. The horizontal line for $\beta = 1$ would be the expected behavior if the Ru moment were completely localized above T_c . The lower curve corresponds to the reduced magnetization of pure nickel. It is reasonable that the hyperfine field lie between these limits. It was not possible to apply Eq. (18) here because we did not know $\sigma(T, H)$ for our alloy.

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Footnotes and References

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Table I. Solute hyperfine fields (in kOe).^a

Solute	Host					
	Fe		Co		Ni	
	T °K	H _{hf}	T °K	H _{hf}	T °K	H _{hf}
F	0	+95.7(5) +32.8(5) +56.9(5)	0	+59.5(15)	0	-21.83(35) +11.60(35) +15.20(35) R +90.2(14) +17.8(4)
Al	1.4	-55(1)	1.4	32(1)		
Sc		58				
V	77	-87.3	-1.4	48(1)	1.4	7.5(2)
Mn	0	-226.97	He	140	90	-325(1)
Fe	0	-336.9	4.8	-323	0	283(3)
Co	0	-287.7	0	-216.0	0	-120(1)
			0	227		
Ni	77	234.2	77	188.5	4.2	74.8
Cu	273	-212.7	282	157.5	290	-47.2
Ga	He	110(3)	He	62(1)		
As		339.1				
Y	4.2	+286(5)				
Zr			He	90(2)		
Nb		-253	0	-189(3)	He	-41(1)
Mo	He	-255(5)	He	150(3)		

Table I. (Cont)

Solute	Host					
	Fe		Co		Ni	
	T °K	H _{hf}	T °K	H _{hf}	T °K	H _{hf}
Ru	4.2	-500(10)	He	415(16)	He	229(9)
	4.2	-505(15)			4.2	-217(5)
Rh	He	-543(11)	He	392(8)	He	213
	O	559.6(16)			R	210
Pd	He	-594(12)	He	-400(8)	He	-194(4)
Ag	O	-282(20)			O	-87(8)
	O	336(20)				
Cd	R	-348(10)			4.2	-68.6(15)
In	O	-295(10)			He	-33(1)
	He	-283(6)				
Sn	100	-81(4)	100	-20.5(15)	100	+18.5(10)
Sb	He	+235	He	187(4)	He	+94(2)
Te	4.2	+620(20)	4.2	550(50)	4.2	+195(10)
I	R	1130(40)				
Xe	O	1040(120)				
Cs	4.2	<24				
Nd	295	+1680(290)	295	+1100(190)	295	+107(18)
	R	+3100(600)				
Sm	R	+1400(160)	300	+1119(64)	300	+352(13)
	R	+1500(500)				

Table I. (Cont)

Solute	Host					
	Fe		Co		Ni	
	T °K	H _{hf}	T °K	H _{hf}	T °K	H _{hf}
Eu	R	+750(250)				
Gd	R	-200(50)				
	R	-180(90)				
Dy	R	-2000(300)				
Er	R	-1640(190)				
Yb	R	-720(240)				
Lu	R	-483(60)				
Hf	R	-300(60)				
Ta	He	-656(13)			He	-98(2)
W	He	-643(13)	He	-388(8)	R	-78(7)
					4.2	90(25)
Re	He	-760(15)	He	442(9)	He	-100(2)
Os	He	1130(23)	He	870(17)	He	300(6)
Ir	He	-1400(28)	He	965(19)	He	440(9)
Pt	He	-1280(26)	He	830(17)	He	-340(7)
Au ^b	He	-1175(24)	He	-733(15)	He	-270(5)
Hg	R	-980(180)				
Pb	R	+262(20)				

^aDetails are given in Ref. 14.

^bThe values for Au¹⁹⁷ are corrected for an 3.6% hyperfine anomaly as reported recently by P. A. Vanden Boet, V. J. Ehlers, W. A. Nierenberg, and H. A. Shugart, Phys. Rev. Letters 18, A9 (1967).

Table II. Derived values of conduction electron polarization for d^{10} s and $d^{10} s^2$ solutes.

Solute	H_s (MOe)	Fe host		Co host		Ni host	
		H_{hf} (kOe)	p	H_{hf} (kOe)	p	H_{hf} (kOe)	p
Cu	- 2.6	-213	.082	158	.061	- 47	.016
Ag	- 5.0	-282	.056			- 87	.017
Cd	- 6.75	-348	.052			- 65	.010
Au	-18.0	-1175	.065	-733	.041	-270	.015
Hg	-21.5	-980	.046				
Average p			0.060		0.051		0.015
Host moment (B.M.)			2.22		1.71		0.62
Ratio			0.027		0.030		0.024

Table III. Solute hyperfine fields (in kOe) for transition metals without localized moments.

Solute	$-H_{ns}$ (MOe)	Fe host		Co host		Ni host	
		H_c (calc)	H_{hf} (exp)	H_c (calc)	H_{hf} (exp)	H_c (calc)	H_{hf} (exp)
Ti	1.2	-73		-55		-18	
V	1.4	-85	-87	-65	48	-21	8
Cr	1.6	-98		-75		-24	
Zr	2.6	-160		-120	90	-40	
Nb	2.95	-180	-258	-140	-189	-45	-41
Mo	3.3	-200	-256	-155	150	-50	
Tc	3.65	-210		-170		-55	
Lu	7.2	-440	-338	-340		-110	
Hf	7.7	-470	-300	-360		-115	
Ta	8.3	-505	-656	-390		-120	-98
W	9.3	-565	-643	-435	388	-140	-90
Re	10.8	-660	-760	-510	488	-160	-100

Table IV. Derived localized moments on solutes (in Bohr magnetons).

Solute	Fe host					Ni host		
	$-H_{cep}$ (kOe)	$-H_{cp}$ (kOe)	μ (this work)	μ (Ref 21)	$\mu^a)$ (Ref 22)	$-H_{cep}$ (kOe)	$-H_{cp}$ (kOe)	μ (this work)
Mn	100	125	1.1	0 ± 0.2	0 ± 0.5	20	305	2.8
Fe	120	220	2.0			20	263	2.4
Co	140	190	1.7	2.1 ± 0.5	2.1 ± 0.3	30	90	0.8
Ni	170	80	0.7	0.9 ± 0.15	1.2 ± 0.3	30	50	0.5
Ru	260	245	0.7	0.9 ± 0.5	0.7 ± 0.4	64	153	0.4
Rh	270	290	0.8	0.5 ± 0.3	0.5 ± 0.3	71	142	0.4
Pd	280	314	0.9	0.1 ± 0.2	0.3 ± 0.3	79	115	0.3
Os	830	300	0.3	0 ± 0.5	0.1 ± 0.3	160	140	0.1
Ir	930	470	0.4	0 ± 0.5	0.2 ± 0.3	190	250	0.2
Pt	1040	240	0.2	0 ± 0.3	0.1 ± 0.3	230	107	0.1

^{a)} Errors estimated from error flags in Ref. 22.

Table V. Local-moment parameters for Fe Mn^{55}

j	f	ξ	Std. deviation	Reference
1/2	.837	.338	0.56%	this work
(1/2)	5/6	.72		G. G. Low ²¹
1	(1)		> 1%	28
1	.897	.549	.38%	this work
3/2	(1)	.51	< 0.5%	28
3/2	(1)	.25		31
3/2	0.966	.711	0.29%	this work
2	1.041	.850	0.32%	this work
5/2	1.124	.976	0.41%	this work

Table VI. Cd^{111} in Ni below T_c ($\approx 628^\circ\text{K}$).

Temperature $^\circ\text{K}$	T/T_c	$\omega(\frac{\text{radians}}{\text{sec}}) \times 10^6$	$\frac{\omega(T)}{\omega(4.2)}$
4.2	0.0067	104.4(2)	[1.000](2)
194.5	0.310	101.3(2)	0.970(3)
293.0	0.467	97.60(20)	0.935(3)
408.0	0.651	88.00(20)	0.843(3)
454.0	0.724	82.55(21)	0.791(3)
501.0	0.799	74.35(10)	0.712(7)
512.0	0.816	71.94(23)	0.689(3)
534.0	0.851	68.24(23)	0.654(2)
569.0	0.907	53.57(31)	0.513(3)
582.0	0.928	49.77(20)	0.477(2)
607.0	0.968	41.63(23)	0.399(2)
621.0	0.973	34.00(21)	0.326(2)

Table VII. ^{99}Ru in Ni below T_c ($=610^\circ\text{K}$ for 1 atomic % alloy).

Temperature $^\circ\text{K}$	T/T_c	$H_{\text{hf}}(T)$ kOe	$\frac{H_{\text{hf}}(T)}{H_{\text{hf}}(4.2)}$
4.2	0.00656	217.20(113)	[1.000](7)
77.0	0.126	212.50(147)	0.978(8)
194.5	0.319	206.58(45)	0.951(6)
298.0	0.489	175.60(148)	0.808(8)
396.0	0.649	141.70(338)	0.652(16)
444.0	0.728	126.39(319)	0.582(15)
506.0	0.829	98.89(271)	0.455(13)
568.0	0.931	60.00(166)	0.276(8)

Table VIII. Ru^{99} in Ni

$$\frac{H(T)}{H(4.2)} = (1-f) \frac{\sigma}{\sigma_0} + f B_J \left(\zeta \frac{\sigma}{\sigma_0} \cdot \frac{T}{T_c} \right) \quad T_c = 610^\circ\text{K}$$

Values of parameters for best fits

J	f	ζ
1/2	1.194	0.621
1	1.490	1.049
3/2	1.965	1.416
2	2.209	1.662
5/2	1.958	1.757

Figure Captions

- Fig. 1. Solute hyperfine fields in an iron lattice. $\odot$ sign measured;
 $\circ$ sign not measured.
- Fig. 2. Variation of H_{hf} with atomic number for 4d and 5d solutes in iron showing abrupt increase. Curves are CEP estimates using Eq. (12).
- Fig. 3. Derived localized moments for solutes in iron. $\circ$ this work; $\odot$ Ref. 21, Collins and Low; $\blacksquare$ Ref. 21, Campbell.
- Fig. 4. The NMR data of Y. Koi et al. (Ref. 29) for $^{55}\text{MnFe}$ fitted with Eq. (17).
- Fig. 5. Furnace and angular correlation apparatus.
- Fig. 6. Partial decay scheme, $^{111}_{49}\text{In} \rightarrow ^{111}_{48}\text{Cd}$.
- Fig. 7. Time-differential angular correlation for $^{111}\text{CdNi}$ below the Curie point. The time spectra were recorded at a detector angle of 180° and no external polarizing field was used. The modulation pattern is characteristic of a randomly oriented magnetic interaction. The solid curve represents the weighted least-squares fit to the data of Eq. (23).
- Fig. 8. Reduced hyperfine field vs. reduced temperature for $^{111}\text{CdNi}$ below the Curie point. ($T_C = 627.2^\circ \text{K}$, the value for pure Ni.) — $\frac{\sigma}{\sigma_0}$ for pure Ni, Weiss and Forrer (Ref. 44); - - - - - $\frac{\sigma_1}{\sigma_0}$, Lovesey and Marshall (Ref. 32), showing demagnetization of first neighbors by nonmagnetic impurity.
- Fig. 9. Time differential perturbed angular correlation spectra for $^{111}\text{CdNi}$ with $T > T_C$. The function,

$$R = \left[W_{\perp}\left(\frac{3\pi}{4}, t, +H_{\text{ext}}\right) - W_{\perp}\left(\frac{3\pi}{4}, t, -H_{\text{ext}}\right) \right] / \left[W_{\perp}\left(\frac{3\pi}{4}, t, +H_{\text{ext}}\right) + W_{\perp}\left(\frac{3\pi}{4}, t, -H_{\text{ext}}\right) \right]$$

is least-squares fitted to Eq. (25) with $\lambda = 0$.

- Fig. 10. Temperature dependence of the paramagnetic Knight shift, $\beta = H_{\text{eff}}/H_{\text{ext}}$, for $^{111}\text{CdNi}$, measured with a polarizing field of 19.5 kOe. The curve was calculated using Eq. (24) with $H_{\text{hf}}(0) = 68.52 \text{ kG}$.
- Fig. 11. Partial decay scheme for $^{99}_{45}\text{Rh} \rightarrow ^{99}_{44}\text{Ru}$.
- Fig. 12. Time differential perturbed angular correlation spectra for $^{99}\text{RuNi}$ with a polarizing field of 5.00 kOe. The indicated hyperfine fields have been calculated using $g = 0.189 \pm 0.004$, (Ref. 39). The amplitude damping is probably caused by either a magnetic field distribution or the existence of at least two different magnetic hyperfine fields.
- Fig. 13. Reduced hyperfine field vs. reduced temperature for $^{99}\text{RuNi}$ below the Curie temperature ($T_C = 610^\circ \text{ K}$ for the 1 at. % alloys used) and $H_{\text{hf}}(0) = H_{\text{hf}}(4.2) = 217.2 \text{ kG}$. The broken curves are theoretical fits based on Eq. (17). The values of the parameters are given in Table VIII.
- Fig. 14. Reduced hyperfine field vs. reduced temperature for $^{99}\text{RuNi}$ with $T < T_C$. The ordinate, λ_0 , measures the deviation of the impurity magnetization from the host magnetization, as defined in the model of Lovesey (Ref. 33). The curve is calculated on this model.
- Fig. 15. Temperature dependence of the paramagnetic Knight shift, $\beta = H_{\text{eff}}/H_{\text{ext}}$, for $^{99}\text{RuNi}$ in an external field of 19.5 kOe. $\square$ measured by time-differential perturbed angular correlation; $\odot$ measured by time-integral perturbed angular correlation.

XBL 6711 - 5661

Fig. 1

XBL6711- 5662

Fig. 2

XBL67II-5663A

Fig. 3

XBL 6711-5664

Fig. 4

Fig. 5

XBL6711-5666

Fig. 6

MUB-9282

Fig. 7

XBL6711- 5667

Fig. 8

MUB-9071

Fig. 9

MUB-12003

Fig. 10

XBL67II-5668

Fig. 11

MUB-10195

Fig. 12

MUB 12734

Fig. 13

Fig. 14

XBL 6711-5670

Fig. 15

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