solid rubidium and cesium. A free-electron momentum distribution in the absence of electron-positron interaction (such as momentum dependence of the annihilation rate) produces a parabolic angular correlation distribution which in turn gives rise to a linear derivative. It is, of course, possible that the momentum enhancement predicted by Kahana and Carbotte[26,27] is present and is masked by a compensating effect. Note that melting produces little or no change in the slopes and the metals retain their free-electron appearance even when molten.

In conclusion, it seems most likely that the vast majority of the higher-momentum components of rubidium and cesium should not be attributed to electrons scattered into the second zone, but are in actuality due to annihilations with core electrons. Second, (assuming that Kr and Xe are accurate core distributions for Rb and Cs) core removal by fitting of a Gaussian curve to the broad component of rubidium and cesium introduces only minor errors in the determination of the ratio of the narrow to broad component, since for these elements a Gaussian distribution approximates the core rather well. Third, the ratio of narrow to broad component is not significantly changed by melting. Fourth, in contrast to more complicated metals, at least for these simple metals, the free-electron model appears to give an adequate representation of the molten state.

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[26] S. Kahana, Phys. Rev. **129**, 1622 (1963).

[27] J. P. Carbotte and S. Kahana, Phys. Rev. **139**, A213 (1965).

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Nuclear Magnetic Resonance of ^{57}Fe in the Paramagnetic Alloys TiFe$_{1-x}$Co$_x$

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Nuclear magnetic resonances (NMR) of ^{57}Fe in isotopically enriched specimens of TiFe, TiFe$_{0.8}$Co$_{0.2}$, and FeCl$_3$, and of Ti in TiCo are reported. The results supplement existing Fe Mössbauer and Co NMR information on the pseudobinary TiFe$_{1-x}$Co$_x$. The Knight shift (and estimated uncertainty) of iron in TiFe is $+(1.29\pm0.03)\%$ at room temperature and $+(1.34\pm0.03)\%$ at 77 K, yielding a hyperfine coupling constant of $+(3\pm2)$ kG/μ_B per formula unit. Similar values are obtained for iron in TiFe$_{0.8}$Co$_{0.2}$. The Knight shift of Ti in TiCo is $+(0.07\pm0.02)\%$ at room temperature, and $-(0.06\pm0.03)\%$ at 77 K, yielding a hyperfine coupling constant of $-(12\pm3)$ kG/μ_B per formula unit for Ti in TiCo, contrasting with a near-zero coupling constant for Ti in TiFe. Both the orbital shifts and the *d*-spin hyperfine coupling constants for the Fe and Ti sites are much less dependent on cobalt concentration than these same quantities at the cobalt site. The NMR results on the three constituents of TiFe$_{1-x}$Co$_x$ suggest: (i) *s*-*d* admixture in the wave-function character at the Fermi surface for the (Fe,Co) sublattice, (ii) greater *s* admixture and perhaps a greater *d*-spin moment at an iron site than at a cobalt site in the iron-rich compounds, and (iii) a nuclear moment for cobalt corresponding to a nuclear gryomagnetic ratio $\gamma=2\pi\times1.003$ kHz/G. The Knight shift of dilute Fe in Ti as measured by the Mössbauer effect is $(0\pm1)\%$. The chemical shift of Fe in enriched aqueous FeCl$_3$ is found by NMR to be $+(0.40\pm0.04)\%$.

I. INTRODUCTION

We have observed the nuclear magnetic resonance (NMR) of ^{57}Fe in enriched samples of intermetallic TiFe, TiFe$_{0.8}$Co$_{0.2}$, and aqueous FeCl$_3$. These constitute the first NMR observations of ^{57}Fe in any nonferromagnetic material. The experiments were undertaken as part of a continuing study of TiFe$_{1-x}$Co$_x$ by NMR and Mössbauer-effect (ME) measurements.[1–3]

TiFe and TiCo, each having the CsCl structure, form a complete series of solid solutions with no evidence of crystallographic order on the (Fe,Co) sublattice.[2,4] The

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[‡] Supported by U. S. Atomic Energy Commission.

[1] L. H. Bennett, L. J. Swartzendruber, and R. E. Watson, Phys. Rev. **165**, 500 (1968).

[2] L. J. Swartzendruber and L. H. Bennett, J. Appl. Phys. **39**, 2215 (1968).

[3] L. H. Bennett and L. J. Swartzendruber, Phys. Letters **24A**, 359 (1967).

[4] S. J. Pickart, R. Nathans, and F. Menzinger, J. Appl. Phys. **39**, 2221 (1968).

magnetic properties[5] undergo major changes across the series: $TiFe_{1-x}Co_x$ is ferromagnetic below 50 K in the range $0.3<x<0.7$, except at $x=0.5$ where it is superconducting. In the regions $x<0.3$, $x>0.7$, and at $x=0.5$, the alloys exhibit temperature-dependent paramagnetism above 1 K. Neutron diffraction[4] of specimens at $x=0.45$ and 0.55 has demonstrated that the ferromagnetic moment of 0.2 μ_B per formula unit is mainly on the (Fe,Co) sublattice. According to ME measurements, the hyperfine field at the iron site is <10 kG throughout the ferromagnetic composition range.[2,3] The NMR of ^{59}Co has indicated a *d*-spin hyperfine interaction varying from -47 kG/μ_B at $x=0.05$ to $+86$ kG/μ_B at $x=0.8$.[1] To account for the positive departures of these values from the negative 3*d*-hyperfine fields usually observed for cobalt, a model involving significant *s-d* admixture at the (Fe,Co) sites was proposed.[1]

According to the present work, the Knight shift of iron in iron-rich $TiFe_{1-x}Co_x$ is only weakly temperature-dependent, which again suggests a concellation of hyperfine fields due to *s-d* admixture at the Fe site. The degree of admixture appears to be about 50% greater for iron than for cobalt in these compounds, indicating a departure from a band model which assumes common wave-function character for the iron and cobalt atoms in their sublattice.

The temperature-independent part of the Knight shift for iron in either TiFe or $TiFe_{0.8}Co_{0.2}$ is about +1.3%. This shift is attributed primarily to the orbital hyperfine interaction. Comparison of the Co and Fe Knight-shift behavior is hampered by imprecise knowledge of the ^{59}Co nuclear moment; the Co ion is never known to be diamagnetic; hence orbital and/or Pauli terms must be estimated in any experimental evaluation of the moment in bulk matter. The most recent value for the moment was obtained by Walstedt *et al.*[6] (hereafter denoted as WWJ) and relied on an estimate of relative orbital effects at different transition-metal sites. Taking our data, as well as theirs, and employing their method of obtaining orbital effects, we obtain a nuclear moment of cobalt corresponding to $\gamma/2\pi=1.003$ kKz/G.

We also report NMR results for titanium in TiFe and TiCo at 295 and 77 K, and, not relevant to the main purpose of the study, the NMR of ^{57}Fe in aqueous $FeCl_3$.

After presenting the experimental details and results, we discuss (in Sec. III) the results in terms of the usual, simple model[1] for treating the hyperfine coupling constants. In Sec. IV, we present a somewhat more detailed picture of hyperfine coupling in alloys. The conclusion concerning hybridization in $TiFe_{1-x}Co_x$ is strengthened by the more thorough treatment.

II. EXPERIMENTAL

To prepare the TiFe, a sintered compact of 0.050-moles iron powder, enriched[7] 90% in ^{57}Fe, was fitted into a hole in the center of a chunk of 0.051-moles titanium. The combination was levitation melted in purified helium. The ingot was crushed and passed through a 200-mesh/in. sieve. Annealing the powder (1 h at 900°C, then a 45°C/h cool to 600°C) to increase the degree of order approximately tripled the amplitude of the ^{57}Fe NMR. The same procedure was used to prepare $TiFe_{0.8}Co_{0.2}$. The TiCo was arc melted but otherwise was prepared similarly to TiFe. The ferric chloride was prepared by solution of isotopically enriched Fe_2O_3 in concentrated HCl with subsequent dilution to reduce the pH and partial dehydration to concentrate the ions into the active volume of the detector coil.

The resonances were measured in a field of 16 kG, using a commercial nuclear induction spectrometer. The field was amplitude modulated, typically 4 G at a frequency of 80 Hz, and swept through the resonance at a rate typically 3 G/sec. Noise was limited by a response time of 0.3 sec and reduced relative to the signal by summing at least 100 sweeps. The magnetic field was calibrated by the room-temperature NMR of ^{39}K in aqueous KI. The effective nuclear magnetic moment for ^{39}K in this salt was taken to be 0.39090 μ_N.[8]

Typical dispersion derivative signals of ^{57}Fe in annealed TiFe at 295 and 77 K are shown in Fig. 1. The resonance in TiFe was detected also at 27 K using liquid neon.

Table I gives the average width and position of the NMR signals in these materials. The width of the resonance in TiFe is an order of magnitude larger than the calculated dipolar width, and is temperature-independent. Presumably, this excessive width is caused by magnetically saturated impurity phases. The addi-

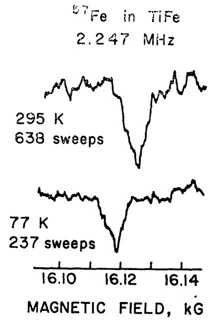

FIG. 1. Dispersion derivative NMR signals of ^{57}Fe in TiFe at two temperatures. The magnetic field was calibrated (Ref. 8) by the resonance of ^{39}K in aqueous KI.

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[5] B. F. DeSavage and J. F. Goff, J. Appl. Phys. **38**, 1337 (1967).

[6] R. E. Walstedt, J. H. Wernick, and V. Jaccarino, Phys. Rev. **162**, 301 (1967). But see R. E. Walstedt, R. C. Sherwood, and J. H. Wernick, J. Appl. Phys. **39**, 555 (1968).

[7] We are indebted to the U. S. Atomic Energy Commission for the loan of the amount of ^{57}Fe necessary to conduct this experiment.

[8] E. Brun, J. Oeser, H. H. Staub, and C. G. Telschow, Phys. Rev. **93**, 172 (1954); G. H. Fuller and V. W. Cohen, Nuclear Data Tables U. S. At. Energy Comm. **5**, 433 (1969). These references establish the effective nuclear moment of ^{39}K in KCOOH as 0.39090 μ_N. We determined the chemical shift of KI relative to KCOOH to be +0.001%.

Table I. NMR data.

Resonance	Temperature (K)	Linewidth[a,b] (G)	Position[b] $\langle \nu_{Fe}/\nu_K \rangle$	Knight shift[c] (in %)
^{57}Fe in TiFe	295	8±2	0.70146±0.00007	+1.29±0.02
^{57}Fe in TiFe	77	7±2	0.70182±0.00014	+1.34±0.03
^{57}Fe in TiFe	27	9±2	0.70171±0.00014	+1.32±0.03
^{57}Fe in $TiFe_{0.8}Co_{0.2}$	295	16±7	0.70167±0.00014	+1.32±0.02
^{57}Fe in $TiFe_{0.8}Co_{0.2}$	77	40±10	0.70184±0.00014	+1.34±0.02
^{57}Fe in $FeCl_3$ (aq)	295	6[d]	0.69532±0.00007	+0.40±0.04[e]
^{47,49}Ti in TiCo	295	11±2		+0.07±0.02
^{47,49}Ti in TiCo	77	18±7		−0.06±0.03

[a] Half-maximum of the dispersion derivative signal and peak separation of the absorption derivative signal.
[b] Estimated uncertainties.
[c] Knight shifts of ^{57}Fe are based on an effective nuclear moment of ^{39}K in the reference salt (aqueous KI) of 0.39090 μ_N and a nuclear moment of ^{57}Fe of 0.09024 μ_N. The Knight shifts of ^{47,49}Ti are relative to the mean of the resonances of ^{47}Ti and ^{49}Ti in $TiCl_4$.
[d] At $H_1=0.1$ G, increasing with H_1.
[e] Chemical shift.

tional broadening upon cobalt substitution is similar to the broadening observed for the cobalt NMR in TiCo upon iron substitution,[1,2] and presumably reflects variations of the hyperfine field with the identity of the near neighbors on the (Fe,Co) sublattice. The Knight shift of titanium in TiCo at 295 K agrees with the value reported by Drain and West.[9]

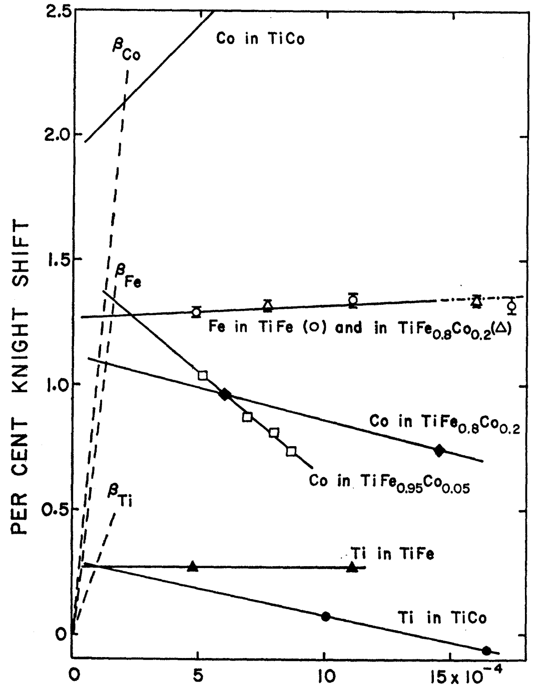

Fig. 2. Knight shifts of iron, cobalt, and titanium in $TiFe_{1-x}Co_x$ as a function of susceptibility. The susceptibilities used are those reported by DeSavage and Goff (Ref. 5). The Knight shifts for Ti are relative to Ti in $TiCl_4$. The ^{59}Co Knight shifts are based on $\gamma/2\pi=1.0030$ kHz/G. This value differs from those given by Walstedt *et al.* (Ref. 6) and by R. Freeman *et al.* (Ref. 16). The choice of the value used is discussed further in the text. The ^{57}Fe Knight shifts are based on $\gamma/2\pi=0.13758$ kHz/G as determined by Locher and Geschwind (Ref. 12).

There was no indication of saturation of the iron resonance in the intermetallic compounds. However, with ferric chloride, both the shape and rf sensitivity of the dispersion signal indicated saturation effects.[10]

To supplement the NMR data, ME measurements were made on an unenriched TiFe absorber in a 50 kG field.[11] Comparison of the separations of the ME lines at 210 and 2 K determines that the hyperfine field increases (0.2±0.6)% between 210 and 2 K. This is consistent with the NMR results within the wide uncertainty limits.

The Knight shifts of ^{57}Fe in Table I are based on the nuclear moment determined by Locher and Geschwind.[12] Figure 2 shows the Knight shift $\mathcal{K}$ of ^{57}Fe in $TiFe_{1-x}Co_x$ as a function of the molar susceptibility[5] using temperature as the implicit parameter. The data for $x=0$ and $x=0.2$ fit within experimental uncertainty the same line, the slope of which corresponds to a hyperfine coupling constant of $+(3\pm2)$ kG/μ_B per formula unit.

For comparison, Fig. 2 also shows previous data[1,13] on the Knight shifts of ^{59}Co for $x=0.05$, 0.2, and 1, and the Knight shifts of titanium for $x=0$ and 1. The slopes of the lines through the cobalt data correspond to −47, −14, and +61 kG/μ_B per formula unit for $x=0.05$, 0.02, and 1, respectively. The slopes of the titanium lines for TiFe and TiCo correspond to 0 and −12 kG/μ_B per formula unit, respectively. Evidently, as

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[9] L. E. Drain and G. W. West, Phil. Mag. **12**, 1061 (1965).

[10] Resonance in ferric chloride solutions was not often detected, partly because of the saturation problem, but also because of uncontrolled variables in the sample preparation (e.g., pH, evaporation temperature, and aging time before measurement). Complexing reactions dependent on such variables are known to occur. [J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Longmans Green and Company, Ltd., London, 1935), Vol. XIV, p. 56 ff.] The intensity of the ^{35}Cl NMR also varied with sample preparation. Interestingly, the Cl resonance was relatively weak in the solution in which the Fe resonance was detected.

[11] As an aside, the Knight shift of dilute Fe in Ti at 210 K was also measured by ME. This measurement is complicated by quadrupole effects, but after correcting for these effects we find $\mathcal{K}=(0\pm1)\%$. Despite the lack of precision, this number may be useful, since it is not likely to be measured more precisely soon.

[12] P. R. Locher and S. Geschwind, Phys. Rev. **139**, A991 (1965).

[13] The susceptibility of $TiFe_{0.95}Co_{0.05}$ was obtained by linear interpolation of the χ^{-1} versus T plots (Ref. 5) for $x=0$ and $x=0.2$.

iron is replaced by cobalt, the titanium hyperfine coupling constant becomes more negative while that of cobalt becomes less negative.

III. DISCUSSION

The Knight shifts of the two constituents of TiFe differ fivefold. Either temperature-independent Pauli paramagnetism or orbital paramagnetism can easily account for the small shift of titanium.[14] The much larger shift of iron in TiFe, as well as the temperature-independent shift of Co in TiFe$_{1-x}$Co$_x$, are predominantly orbital shifts.

The orbital susceptibilities of Fe and Co can be deduced from their Knight shifts by the technique of Clogston *et al.*[15] as discussed in more detail subsequently. We expect similar orbital susceptibilities for iron and cobalt in the same sublattice. Use of the WWJ nuclear moment[6] for ^{59}Co ($\gamma/2\pi=1.0054$ kHz/G) yields a Co-site orbital susceptibliity which is significantly smaller than that for an Fe site, contrary to the approximations employed by WWJ in theirmo ment estimate. This reopens the question of the size of the Co nuclear moment. The moments for Fe and Ti are much more accurately known. Use of a smaller Co nuclear moment (viz., $\gamma/2\pi=1.003$ kHz/G) yields orbital terms which still are smaller than those at Fe sites, but are now consistent with the WWJ treatments of orbital effects. A value of 1.003 kHz/G, consistent with WWJ's experimental data, is close to the lower bound placed on their moment value, and reduces the disagreement with an earlier moment estimate by Freeman *et al.*[16] This new value is employed in this paper. Any uncertainty in the Co nuclear moment has no effect on our consideration of *s-d* admixture effects.

Neither the iron nor titanium Knight shifts of TiFe have any significant temperature dependence to correlate with the large temperature dependence of the susceptibility. The continuity of the susceptibility[5] and of the cobalt Knight shifts[1] with composition across the series causes us to believe that most of the temperature-dependent susceptibility of TiFe is an intrinsic property of the pure ordered compound, rather than a spurious impurity or clustering effect.[17]

The temperature independence of $\mathcal{K}_{\mathrm{Ti}}$ might seem to follow from the near absence[4] of moment on the titanium. On the other hand, $\mathcal{K}_{\mathrm{Ti}}$ in TiCo *is* temperature-dependent. It is clear that *inter*atomic terms due to the presence of larger paramagnetic moments on the Fe-Co sublattice are responsible for the hyperfine field behavior on the Ti site. Positive or negative $\mathcal{K}$ versus χ slopes are known to occur in other transition-metal and rare-earth compounds due to *inter*atomic effects.

Granting a moment largely in the (Fe,Co) sublattice, one can attempt to understand the small positive hyperfine field of iron in terms of *s-d* admixture as used to interpret the cobalt NMR.[1] Other effects can be imagined, but admixture appears to be the simplest and most probable effect. According to the model for admixture discussed earlier,[1] a near-zero hyperfine coupling constant can result from a mutual cancellation of negative 3*d* and positive 4*s* hyperfine fields. A 4*s* contribution to the temperature dependence of $\mathcal{K}$ arises from *s-d* hybridization of the conduction-band states responsible for the temperature-dependent Pauli susceptibility. The simple analysis used previously[1] for the cobalt NMR (and assuming equal moments on Fe and Co) gives a fractional *s* admixture in TiFe$_{0.95}$Co$_{0.05}$ of about 8% at the iron site and about 5% at the cobalt site. Fractional admixtures of these magnitudes are quite reasonable.

Bearing in mind the numerous uncertainties and assumptions in this admixture calculation, the Fe and Co admixtures appear to be essentially the same. On the other hand, while the *d*- and *s*-spin hyperfine fields for Fe and Co are similar, the slopes of the Fe and Co data in Fig. 2, from which the admixtures are calculated, are decidedly different. This implies that the admixtures reflected in the Fe and Co NMR, though similar, are actually not the same.

Unlike the orbital effects the admixtures calculated from Fig. 2 are independent of the chosen nuclear moments, but do depend on the susceptibility data. Since the iron and cobalt slopes are opposite in sign, correction for any impurity contributions to the susceptibility only magnifies the difference between the Fe and Co slopes and, consequently the difference in inferred admixtures.

The suggestion of an admixture difference of the order of 50% implies significant deviation from common wave-function character for the (Fe,Co) sublattice. It is therefore important to ascertain the sensitivity of the deduced admixtures to various choices of hyperfine constants and moment distributions. For this purpose, we give in Sec. IV a more detailed analysis of the results shown in Fig. 2. This analysis supports the basic conclusions already obtained.

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[14] For comparison, the Knight shift of titanium in TiH$_2$ is $+(0.26\pm0.4)\%$ [R. C. Frisch and R. A. Foreman, J. Chem. Phys. **48**, 5187 (1968)] and that of pure titanium is $+(0.4\pm0.2)\%$ [A. Narath, Phys. Rev. **162**, 320 (1967)].

[15] A. Clogston, V. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

[16] R. Freeman, G. R. Murray, and R. E. Richards, Proc. Roy. Soc. (London) **A242**, 455 (1957).

[17] The possible influence of impurities or clustering on the susceptibility should not be underestimated. We note that M. V. Nevitt [J. Appl. Phys. **31**, 155 (1960)] measured susceptibilities for TiFe which are about three times larger than those of DeSavage and Goff. Moreover, the observation of practically temperature-independent Knight shifts for Ti and Fe lends credence to the *possibility* that the susceptibility of pure well-ordered TiFe is almost temperature-independent. Extension of this agrument to TiFe$_{0.8}$Co$_{0.2}$ is less plausible and the model of *s-d* admixture to account for the cobalt NMR still seems likely. Neutron diffraction of TiFe would be desirable to distinguish between intrinsic and impurity paramagnetism.

IV. MODEL

As usual, we start by writing the susceptibility as the sum of diamagnetic orbital (i.e., Van Vleck, and Pauli terms,

$$\chi=\chi_{\mathrm{dia}}+\chi_{\mathrm{VV}}+\chi_{\mathrm{p}}(T)+\chi_{\mathrm{p}}', \tag{1}$$

where $\chi_{\mathrm{p}}(T)$ and χ_{p}' refer to the temperature-dependent and temperature-independent Pauli paramagnetism. For $\mathrm{TiFe}_{1-x}\mathrm{Co}_x$, the term χ_{dia} is small relative to the others and is neglected in what follows. The temperature-independent terms χ_{VV} and χ_{p}' are empirically indistinguishable. Since we expect $\chi_{\mathrm{p}}'\ll\chi_{\mathrm{VV}}$ at least for Fe and Co, the subsequent equations omit χ_{p}'. This leaves χ_{VV} and $\chi_{\mathrm{p}}(T)$ as the two dominant susceptibility terms. Following arguments given previously,[1] we assume that only $\chi_{\mathrm{p}}(T)$ contributes to the temperature dependence of χ (and $\mathcal{K}$).

To arrive at equations for the Knight shifts, it is necessary to decompose the susceptibility into appropriately weighted contributions from the individual atoms. For $\mathrm{TiFe}_{1-x}\mathrm{Co}_x$,

$$\chi_{\mathrm{VV}}=[W_{\mathrm{Ti}}+(1-x)W_{\mathrm{Fe}}+xW_{\mathrm{Co}}]\chi_{\mathrm{VV}}, \tag{2a}$$

and

$$\chi_{\mathrm{p}}(T)=[M_{\mathrm{Ti}}+(1-x)M_{\mathrm{Fe}}+xM_{\mathrm{Co}}]\chi_{\mathrm{p}}(T), \tag{2b}$$

where W_i and M_i designate the relative contributions at the site of the ith constituent atom. The weights are normalized by equating each pair of square brackets to unity. Their exact definition awaits consideration of the Knight shift.

The Knight shifts associated with these atomic contributions to the susceptibility arise from the $4s$, $3d$, and orbital hyperfine interactions. Some preliminary discussion of the d-hyperfine interaction is necessary before writing the Knight-shift equations.

In cases where the d-hyperfine field can be easily identified (say with ferromagnetic and certain paramagnetic transition metals[18]), it is usually large and negative. Its value is roughly equal to the exchange polarization of the core s electrons as predicted by calculation or obtained experimentally for the paramagnetic ions.[19] This has led to a tendency to attribute the d-hyperfine field to "core polarization," but a d-spin density in a cubic metal will contribute hyperfine fields in at least two additional ways. First, an *intra*-atomic term arises because the d-spin density spatially polarizes the paired conduction bands below the Fermi surface, and the s-character of this polarization cloud interacts with the nucleus at the d-moment site. Unlike core polarization, this effect makes a *positive* intra-atomic contribution approaching the core polarization term in magnitude.[20] Secondly, the hyperfine field at a particular site can have *inter*atomic contributions, H_{neigh}, caused by d moments on neighboring sites.[21] The interatomic and intraatomic terms are indistinguishable in a pure metal, but their separate identification is important when attempting to understand an alloy. This is a growing body of theory and data[21] suggesting that, at least for the heavier elements of the $3d$ series, the total intra-atomic d term $H_{\mathrm{self}}{}^d$ is roughly half the core polarization term $H_{\mathrm{core}}{}^d$. Given the pure metal data, this in turn implies $H_{\mathrm{neigh}}\approx H_{\mathrm{self}}{}^d$. In the remainder of this paper, we assume

$$H_{\mathrm{self}}{}^d=\tfrac{1}{2}H_{\mathrm{core}}{}^d. \tag{3}$$

This is crude but adequate for our purposes. On this basis, we can write for $\mathcal{K}$ of the ith atom

$$\mathcal{K}_i=(\alpha_iM_i+H_{\mathrm{neigh},i})\chi_{\mathrm{p}}(T)+\beta_iW_i\chi_{\mathrm{VV}}, \tag{4}$$

where α_i is the intra-atomic coupling constant (including $3d$ and admixed $4s$ terms), and β_i is the orbital coupling constant (i.e., $\beta_i=2\,\mu_B\langle r^{-3}\rangle_i$, where $\langle r^{-3}\rangle_i$ is an appropriately averaged expectation value of r^{-3} for the d-wave functions at site i). Equation (4) operationally defines the weighting factors M_i and W_i. The spin moment at or in the vicinity of an atom is measured by M_i, in much the same way as in neutron diffraction, with proper attention to boundaries. The components of M_i are weighted here by hyperfine constants rather than by form factors. This definition of M_i retains validity in either a Heisenberg or itinerant description of the metal.

The net temperature dependences of $\mathcal{K}_{\mathrm{Fe}}$ and $\mathcal{K}_{\mathrm{Co}}$ are governed by the hybridization of the states at the Fermi level. Assuming an effective fraction f^s of admixed s character, as sampled on the (Fe,Co) sublattice, the intra-atomic coupling constant is

$$\alpha=f^sH_{\mathrm{eff}}{}^s+(1-f^s)H_{\mathrm{self}}{}^d, \tag{5}$$

where $H_{\mathrm{eff}}{}^s$ is the effective contact term for the admixed "$4s$"-conduction electron character. Combining (4) and (5), the slope of the $\mathcal{K}$ versus χ plot is

$$\frac{\partial\mathcal{K}_i}{\partial T}\bigg/\frac{\partial\chi}{\partial T}=[f^sH_{\mathrm{eff}}{}^s+(1-f^s)H_{\mathrm{self}}{}^d]_iM_i+H_{\mathrm{neigh},i}. \tag{6}$$

This equation assumes that the temperature dependence of $\mathcal{K}$ is dominated by changes in χ_{p}, i.e., that any tem-

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[18] A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. II A, Chap. 4.

[19] R. E. Watson and A. J. Freeman, in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1965), p. 53. See in particular Fig. 4.

[20] Sign and magnitude of this term have been inferred from *atomic* $4s^2$ behavior (e.g., see Ref. 18).

[21] For example, R. E. Watson and A. J. Freeman, Phys. Rev. Letters **14**, 695 (1965); S. Kobayashi, K. Asayama, and J. Itoh, J. Phys. Soc. Japan **18**, 1735 (1963); **21**, 65 (1966); M. B. Stearns and S. S. Wilson, Phys. Rev. Letters **13**, 313 (1964); and G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, *ibid.* **12**, 24 (1964).

perature dependence of the hyperfine constants, of the M_i's, or of $\mathcal{K}_{VV}$, is small.[22]

In Eqs. (4) and (6), the interatomic term H_{neigh} does not attempt to account for variation in local environment. Although local effects from the (Fe,Co) sublattice clearly appear in the NMR spectra,[2] they are disregarded in the present analysis, since each Knight shift has been determined from the "center of gravity" of the NMR spectrum. We make the simplifying approximation that

$$H_{\text{neigh,Co}} = H_{\text{neigh,Fe}} \approx H_{\text{self,Fe}}{}^{d}$$

for Fe-rich $TiFe_{1-x}Co_x$.

Solutions of Eq. (6) have been sought[19] using atomic values $H_{\text{eff,Co}}{}^{s}=1700$, $H_{\text{eff,Fe}}{}^{s}=1550$, $H_{\text{core,Co}}{}^{d}=-140$, $H_{\text{core,Fe}}{}^{d}=-135$ (all in kG/μ_B per formula unit) and the experimental slopes for $TiFe_{0.95}Co_{0.05}$ from Fig. 2. Assuming equal Fe and Co moments, i.e., $M_{\text{Fe}}=M_{\text{Co}}$, one obtains $f_{\text{Co}}{}^{s}=5\%$ and $f_{\text{Fe}}{}^{s}=8\%$. These values are relatively insensitive to the partitioning of the d-hyperfine fields between $H_{\text{self}}{}^{d}$ and H_{neigh}. The specific values for f^s do indeed depend on the choice of hyperfine field parameters, but it appears almost inevitable that $f_{\text{Co}}{}^{s}$ be significantly smaller than $f_{\text{Fe}}{}^{s}$. This follows from the negative slope for Co and positive one for Fe in Fig. 2.[23]

Alternatively, one can solve Eq. (6) by letting the $M_{\text{Fe}}/M_{\text{Co}}$ ratio deviate from one, and requiring a common f^s at both sites. The resulting moment ratio $M_{\text{Fe}}/M_{\text{Co}}$ is large and may be either positive or negative, depending on f^s. Lacking any information to the contrary, we reject negative ratios. The magnitude of $M_{\text{Fe}}/M_{\text{Co}}$ is quite sensitive to the choice of hyperfine field parameters, in particular to the magnitude of H_{neigh} relative to the observed hyperfine constants. Our choice of parameters yields $M_{\text{Fe}}/M_{\text{Co}} \approx 5$. Choice of a smaller H_{neigh} value, which might be argued as physically reasonable, would yield unlikely moment ratios even larger than 5. Correction for any spurious contribution to $\chi_p(T)$ would also tend to increase the deduced moment ratio. It would thus appear that a sensible rationalization of the results requires that variation in admixture be largely responsible for the observed Knight-shift behavior.

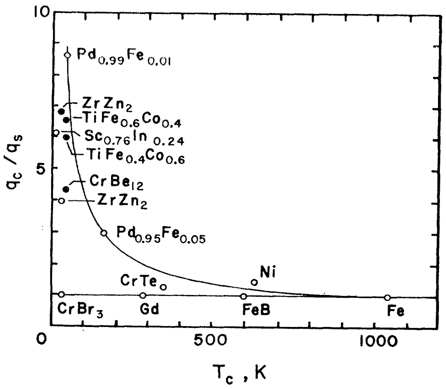

FIG. 3. Comparison of two $TiFe_{1-x}Co_x$ alloys with other ferromagnetic materials on a Rhodes-Wahlfarth (Ref. 24) type plot. q_c/q_s is the ratio of the number of magnetic carriers deduced from the paramagnetic Curie-Weiss constant to the number deduced from the saturation magnetization. T_c is the Curie temperature. The line $q_c/q_s=1$ corresponds to a localized moment model. Lines and open circles are from Rhodes and Wohlfarth (Ref. 24). $TiFe_xCo_{1-x}$ data are from Ref. 5. $CrBe_{12}$ data are from N. M. Wolcott and R. L. Falge [Phys. Rev. **171**, 591 (1968)]. $ZrZn_2$ data for the closed circle are from H. J. Blythe [Phys. Letters **21**, 144 (1966)].

Since the paramagnetic susceptibility has been measured[5] as a function of alloy concentration x, it might seem at first that a precise value for the ratio $M_{\text{Fe}}/M_{\text{Co}}$ could be derived therefrom. This is not possible, since the susceptibility data display clear evidence of band magnetism and cannot simply be interpreted in terms of a Co moment replacing an Fe moment as x varies from 0 to 1. The existence of s-d admixture and of a small moment[4] on the Ti site are symptomatic of the band magnetism of these alloys. In Fig. 3, these alloys are tested for compliance with the "intermediate model" of Rhodes and Wohlfarth.[24] It is found that $TiFe_{0.6}Co_{0.4}$ and $TiFe_{0.4}Co_{0.6}$ (each with a Curie temperature of about 50 K) are similar to the "itinerant" ferromagnetic metals $ZrZn_2$ or $CrBe_{12}$. As noted previously,[1] the temperature dependence of the NMR line broadening also indicates itinerant magnetism. Given the iterancy, it is impossible to use the susceptibility results to disentangle s-d hybridization from the M_i as defined by Eqs. (2) and (4). While the M_i's are difficult to establish experimentally, their physical meaning is well defined by these equations and is consistent with the presence either of localized moments or of band magnetism.

The f^s values (though not their ratio) are sensitive to the chosen values of $H_{\text{eff}}{}^{s}$ relative to the other hyperfine field parameters. For example, other choices which can easily be argued as "reasonable" yield an $f_{\text{Fe}}{}^{s}$ ranging between 6 and 9%. Admixture of this magnitude and as much as a 50% variation between Fe and Co sites are reasonable for transition metal d bands. Since, as discussed above, moment ratios $M_{\text{Fe}}/M_{\text{Co}} \gtrsim 5$ are unreasonably high, we conclude that variations in admixture account for most of the difference in the temperature dependences of $\mathcal{K}_{\text{Fe}}$ and $\mathcal{K}_{\text{Co}}$.

We now consider the temperature-independent

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[22] But see V. Jaccarino, M. Weger, J. H. Wernick, and A. Menth, Phys. Rev. Letters **21**, 1811 (1968), which is a case where the entire $\mathcal{K}$ versus χ slope is not attributed to the temperature dependence of χ_p alone.

[23] If the ratio $|H_{\text{eff}}{}^{s}/(H_{\text{self}}{}^{d}+H_{\text{neigh}})|$ were some 20% smaller for Co than for Fe, a common f^s value could be obtained for the two sites from Eq. (6). We have ratios which are slightly larger for Co than Fe and efforts to refine our choice of parameters by conduction-band effects, 4s induced core polarization, and the maintanance of local charge neutrality, suggest a further increase in the Co ratio relative to Fe.

[24] P. Rhodes and E. P. Wohlfarth, Proc. Roy. Soc. (London) **A273**, 247 (1963).

Knight shifts and the roles played by orbital effects. Following the graphical techniques developed by Clogston *et al.*,[15] the dashed lines from the origin of Fig. 2 have been drawn with slopes corresponding to β with $\langle r^{-3}\rangle = 4.79$, 3.88, and 1.27 a.u. for Co, Fe, and Ti, respectively. Having been drawn from the origin, these lines assume that $\mathcal{K}_{VV}$ is entirely responsible for the temperature-independent term. Their intercepts with the experimental curves yield the orbital term $W_i\chi_{VV}$ associated with the particular site in question [inspect Eqs. (2a) and (4)]. Quantitative conclusions depend on the $\langle r^{-3}\rangle$ values, hence on arguments concerning how they are affected by atomic, chemical, and environmental considerations. Whatever the choice of $\langle r^{-3}\rangle$, the value of β_{Co} should remain moderately larger than β_{Fe}, with both significantly larger than β_{Ti}. One then discovers that W_{Ti} is significantly smaller than W_{Fe}.

The ^{59}Co moment value was chosen so that the resulting W_{Fe}/W_{Co} ratio is consistent with WWJ's analysis of the relative strength of orbital effects (due to such factors as the availability of *d* states above and below the Fermi level, for orbital mixing). Assuming that the Ti temperature-independent term is entirely due to orbital effects (i.e., drawing β_{Ti} from the origin), one obtains $W_{Ti}\sim 0.4$, $W_{Fe}\sim 0.6$, and $\chi_{VV}\sim 2.5\times 10^{-4}$ emu/mole for the Fe-rich systems. Assuming that the Ti term is largely due to a temperature-independent Pauli term (its magnitude is consistent with such $\mathcal{K}_p'$ terms in other metals of the first long period), one has $W_{Ti}\rightarrow 0$, $W_{Fe}\rightarrow 1$, and $\chi_{VV}\sim 1.5\times 10^{-4}$ emu/mole. Finally, note that both orbital and spin hyperfine interactions at Fe and Ti sites are relatively independent of cobalt concentration as compared to the strong dependence[25] exhibited by the cobalt NMR.

V. CONCLUSION

The Knight shift of ^{57}Fe in iron-rich $TiFe_{1-x}Co_x$ is relatively large (+1.3%) and only weakly temperature-dependent. The dominant term in the shifts of Fe, Co, and perhaps Ti, arises from orbital effects. In attempting to understand the variation of orbital effects between Fe and Co sites, it was necessary to reassess the determination of the Co nuclear moment. Using WWJ's analysis of orbital effects, and including both their data and the present data, a value of $\gamma/2\pi = 1.003$ kHz/G is obtained for ^{59}Co.

The weak temperature dependence of $\mathcal{K}_{Fe}$ can be understood to result from *s-d* admixture as previously proposed to interpret the cobalt Knight shift. Detailed analysis of the possible hyperfine interactions shows that the fractional *s* admixture in the Fermi surface conduction electrons, as seen by the iron nucleus is about 50% greater than that seen by the cobalt nucleus in $TiFe_{0.95}Co_{0.05}$. In addition, the possibility exists that the iron atoms have a larger moment than the cobalt atoms in this compound. Uncertainties as to whether the experimental susceptibilities are affected by the possible presence of magnetic impurities suggests that we may have underestimated the difference in admixture at the two sites.

The Knight shift of titanium in TiFe is essentially independent of temperature, whereas that in TiCo decreases with decreasing temperature corresponding to a hyperfine field of -12 kG/μ_B per formula unit. This is opposite to the tendency of the cobalt hyperfine field per μ_B which becomes more positive as x increases from 0.05 to 1.

A subsidiary result of these experiments is the realization that TiFe would be a good material with which to calibrate external magnetic fields used in ME experiments. The cubic structure, known Knight shift, and its near temperature independence are all advantages not possessed by the dilute solution of ^{57}Fe in titanium previously used[26] for rough field calibration.

Quantitative conclusions shedding detailed insight into the band and magnetic properties of this system are hampered by uncertainties in the Co nuclear moment, by questions of impurity contributions (perhaps best investigated by neutron diffraction) to the TiFe susceptibility and, in the case of estimating the M_{Fe}/M_{Co} local moment ratio, by the detailed choice of hyperfine parameters. A further interesting complication is the suggestion (shown in Fig. 3) of strong itinerant character in the magnetism of this system as deduced from the Wohlfarth analysis.

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[25] See Fig. 5 of Ref. 1.

[26] G. K. Wertheim and D. N. E. Buchanan, J. Phys. Chem. Solids **28**, 225 (1967).