These deviations are limited to $T/T_c<0.5$ only by working at low amplitudes. For higher ultrasonic amplitudes, they spread throughout the superconducting range. The amplitude-dependent attenuation which gives rise to the deviations appears to be a property of the superconducting state only. This amplitude dependence, while certainly not as large in the other superconductors thus far studied by ultrasonic attenuation may still be present in them and give rise to some of the other observed deviations from the theoretical temperature dependence.

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Temperature and Field Dependence of Hyperfine Fields and Magnetization in a Dilute Random Substitutional Ferromagnetic Alloy: $Fe_{2.65}Pd_{97.35}$†

P. P. CRAIG, R. C. PERISHO,* AND R. SEGNAN‡
Brookhaven National Laboratory, Upton, New York

AND

W. A. STEYERT
Los Alamos Scientific Laboratory, Los Alamos, New Mexico and Brookhaven National Laboratory, Upton, New York

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The assumption of proportionality between hyperfine magnetic field and bulk magnetization, which has been shown to obtain in elemental ferromagnetic Fe, is shown to apply as well in the random substitutional cubic dilute ferromagnetic alloy $Fe_{2.65}Pd_{97.35}$. The same sample of this alloy was studied by means of both the Mössbauer effect and bulk magnetization. The Mössbauer data represent the first detailed study of the hyperfine field in a ferromagnet in the presence of large external fields. Proportionality between the bulk magnetization and the hyperfine field is found over an extended range of temperature and applied external magnetic field. Extrapolations of the bulk-magnetization data to yield the Curie point disclose significant discrepancies with the Mössbauer results when standard extrapolation techniques are used. Good agreement is obtained if one assumes that the magnetization varies near the Curie temperature θ as $(\theta-T)^\beta$ with β between $\frac{1}{4}$ and $\frac{1}{3}$. This type of behavior suggests that the sample may be describable in the region of the Curie temperature by recent Padé-approximant calculations based upon Ising and Heisenberg models. The temperature variation of the hyperfine field is compared to molecular-field calculations in both zero and nonzero external fields. Although qualitative agreement is found, there are significant quantitative discrepancies, indicating the inapplicability of the molecular-field model. A description is included of the Brookhaven cryogenic Mössbauer apparatus involving a variable-temperature cell mounted inside a high-field superconducting magnet.

I. INTRODUCTION

THE temperature dependence of the hyperfine magnetic field in ferromagnetic materials has been studied by means of the Mössbauer technique in pure Fe and at Fe in $Fe_{08}Pd_{92}$ by Nagle *et al.*[1] and by Preston *et al.*[2] in pure Fe. These measurements were performed in zero external magnetic field. Comparison between the Mössbauer measurements and bulk-magnetization measurements showed that the two quantities vary with temperature in the same way. That is, the hyperfine field is proportional to the bulk magnetization. This result indicates that for fixed sample composition the magnetic hyperfine interaction is temperature-independent and that in addition the spatial distribution of the magnetic moment is temperature-independent.

We have extended the study of Nagle *et al.*[1] by applying external magnetic fields to a relatively dilute ferromagnetic Fe-Pd alloy, $Fe_{2.65}Pd_{97.35}$, and have used the same sample for both Mössbauer and bulk-magnetization studies We find excellent agreement between the temperature dependence of these two quantities over a wide range of temperature and externa magnetic field. The region close to the Curie temperature (about 90°K) and in low external fields is of especial interest. In this region the sample magnetization and the hyperfine field appear to vary with tem-

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* Summer Research Assistant from Haverford College, Haverford, Pennsylvania.

‡ Present address: University of Pennsylvania, Philadelphia, Pennsylvania.

[1] D. E. Nagle, H. Frauenfelder, R. D. Taylor, D. R. F. Cochran, and B. T. Matthias, Phys. Rev. Letters 5, 364 (1960).

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perature in a manner consistent with recent Padé approximant calculations on the Ising and Heisenberg models of ferromagnetism.[3-9] That is, $X \propto (\theta - T)^{\beta}$ where X denotes either the hyperfine field or the bulk magnetization, θ is the Curie point, and β is a constant which our experimental results indicate probably lies between $\frac{1}{4}$ and $\frac{1}{3}$. Padé-approximant calculations favor values for β of $\frac{1}{3}$ and $\frac{5}{16}$. Although our experimental results cannot as yet distinguish between these two values, the Mössbauer technique should in principle be capable of the required precision. In this paper we present only a preliminary discussion of the hyperfine field in the Curie-point region. Our major emphasis is upon the intercomparison of bulk-magnetization and hyperfine-field data over a wide range of temperature and external field.

Section II is devoted to the characteristics of the Fe-Pd alloy system both as determined from bulk-magnetization techniques and from the Mössbauer effect. Section III presents a reasonably complete discussion of our experimental apparatus, including the cryostat system used in conjunction with a superconducting magnet, a variable temperature cell, and a means for introducing the motion required to Doppler shift the source with respect to a resonant absorber. Section IV considers hyperfine magnetic fields, and the molecular-field model used in discussing part of the experimental results. Section V presents results of the present Mössbauer and magnetization measurements, together with an intercomparison of the two. This intercomparison is straightforward at high magnetic fields and agreement is excellent. At lower fields and particularly in the zero-external-field limit the deduction of the shape of the magnetization versus temperature curve becomes difficult. The zero-field Mössbauer measurements serve to define precisely a Curie temperature more than 10% below that found using two different conventional extrapolations (linear and quadratic) of the magnetization data to zero field. Extrapolations assuming cubic or quartic variation of the magnetization with temperature yield fit much closer to the Mössbauer results. For accurate determination of the temperatures of magnetic transitions in random substitutional alloys, and of the details of the magnetization near the critical points, the use of hyperfine magnetic fields appears to be one of the most precise techniques available.

II. THE Fe-Pd SYSTEM

Pd forms a body-centered cubic lattice with an electronic configuration which is $3d^{10}$, $3d^{9}4d^{1}$ or some intermediate between these two states. The pure metal probably does not order magnetically down to liquid-helium temperatures.[10] However, the susceptibility is not temperature-independent but shows a gradual rise below room temperature, with a slight peak near 85°K followed in the purest samples by a small drop at low temperatures, and in slightly impure samples by flattening out or even a slight continued rise.[11] The addition of slight amounts of Fe (which enters the lattice as a random substitutional impurity) induces a magnetic transition, thereby offering evidence for the existence of extremely long-range interaction mechanisms. The Curie temperature increases smoothly with increasing Fe concentration up to large Fe concentration.[12,13]

The bulk magnetization of the Fe_xPd_{1-x} system has been studied by Crangle[12] in the relatively dilute region between 1.25 and 15.75% Fe. (All compositions are expressed in at.%.) He finds the Curie temperature to vary approximately linearly from 66°K at 1 25% to 377°K at 15.75% Fe. The magnetic moment associated with each Fe atom, as determined at the lowest temperatures, where the magnetization versus temperature curves saturate, is a smoothly decreasing function of temperature, varying from 7.4 μ_B (Bohr magnetons) per Fe impurity at 1.25% Fe to 5.1 μ_B per Fe at 15.75% Fe. These results agree with measurements in the paramagnetic regime, in which Curie temperatures and magnetic moments are determined from the intercept and slope of graphs of the inverse magnetic susceptibility versus temperature.[13]

In deducing magnetic moments associated with each Fe impurity it is necessary to assign an atomic g factor. This factor has usually been taken as two although little evidence exists to support such a value. EPR studies by Shaltiel *et al.*[11] on rare earths in Pd alloys show slight shifts with composition. A g factor of 2 ± 0.4 for Fe in Pd has been obtained from paramagnetic Mössbauer measurements on a highly dilute sample made by dissolving radioactive Co^{57} into high-purity Pd metal.[14] The Co^{57} decays through the 14-keV level in Fe^{57} which may be studied using the Mössbauer technique. These measurements yielded in addition to the g factor a magnetic moment of 12 μ_B for infinite Fe dilution, in agreement with paramagnetic measurements of 1% Fe in Pd.[13] The spin associated with each Fe impurity is about six.

[3] W. Marshall, *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962* (Butterworths Scientific Publications Ltd., London, 1963), p. 215.
[4] G. A. Baker, Phys. Rev. **124**, 768 (1961); **129**, 99 (1963); **136**, A1376 (1964).
[5] J. W. Essam and M. E. Fisher, J. Chem. Phys. **38**, 802 (1963).
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[7] Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964 (to be published).
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[13] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).
[14] P. P. Craig, D. E. Nagle, W. A. Steyert, and R. D. Taylor, Phys. Rev. Letters **9**, 12 (1962).

The large magnetic moments associated with each Fe impurity are largely localized not upon the Fe atoms but rather upon surrounding Pd.[15] Neutron-diffraction measurements[16] have shown a moment of 3 μ_B to exist on the Fe in both $Fe_{03}Pd_{97}$ and $Fe_{07}Pd_{93}$, which have total moments per Fe atom of 8 μ_B and 6.5 μ_B, respectively. In the ordered alloy $FePd_3$ neutron-diffraction studies yield a moment of 2.83 μ_B at Fe sites.[17]

Crangle's measurements yield the temperature dependence of the bulk magnetization in a series of Fe-Pd alloys.[12] For 15.8% Fe he finds a shape for the magnetization curve which approximates that found in metallic Fe, but is slightly flatter. As the Fe concentration is reduced his magnetization curves tend to flatten out (to become less convex upwards) and to deviate more and more from any molecular-field calculations, even for infinite spin. In a preliminary publication[18] we compared Crangle's magnetization curves with our Mössbauer data and suggested that the large apparent discrepancies between the two types of measurement might be related to lack of proportionality between the hyperfine magnetic field and the bulk magnetization as the sample temperature is varied. Our subsequent work has shown that the bulk magnetization appeared flatter because the extrapolation methods used by Crangle to determine the Curie temperature yield a value about 15% high. A detailed discussion of the extrapolation methods we have used in analyzing our magnetization data is presented in Sec. IV, from which we conclude that in our alloy the hyperfine field appears to be proportional to the bulk magnetization at all temperatures in both zero and nonzero external fields. We note that while such proportionality holds in our alloy containing only a small quantity of Fe, non-proportionality has recently been observed at impurity sites in dilute Fe-base[19] and Ni-base alloys.[20]

III. EXPERIMENTAL TECHNIQUE

Sample Preparation

The experiments reported herein were all performed on a foil of composition $Fe_{2.65}Pd_{97.35}$ which was prepared by arc-melting Fe metal isotopically enriched to 75% in Fe^{57} together with Johnson-Matthey five-nines purity Pd metal. Following repeated arc melting the sample was alternately rolled and annealed down to a final thickness of 0.001 in. Two identical circular disks of $\frac{1}{2}$-in. diam, were cut from the rolled foil and were used singly for the Mössbauer measurements and together (for increased sensitivity) in the magnetization study. The composition was verified by chemical analysis to a precision of 0.01 at.%.

The source used in the Mössbauer studies was Co^{57} deposited onto Cu foil and annealed. This source when studied with a 0.00016-in. natural Fe foil absorber yielded a resonance width of 0.24 mm/sec, 20% greater than ideal. With the Pd absorber the linewidth was about 40% greater than ideal. Part of this excess width is due to building vibration.

Magnetometer

Magnetization measurements were performed on a commercial Foner-type vibrating sample magnetometer built by Princeton Applied Research and attached to a Varian 12-in. electromagnet equipped with "Fieldial." The two foils were mounted together in a sample holder of four-nines purity copper which was in turn mounted in an evacuable container in a helium cryostat. A thermocouple (Au–2.1% Co against either Ag–0.37% Ag or five-nines purity Cu)[21] was attached to the sample with G.E. 7031 cement. A heater coil was noninductively wound about a part of the Cu sample holder located about 2 in. away from the magnetometer pickup coils. The sensitivity of the magnetometer was far greater than required for the present measurements and this instrumentation will not be discussed further. Temperature control in both the magnetization and Mössbauer phases of the experiments was identical and will now be described.

Temperature Control

The temperature control system is a feedback unit capable of long term control to about 0.1 μV. With Au–2.1% Co thermocouples this implies temperature constancy within 0.25 mdeg near 90°K. The error signal is primarily electronic noise, and the sample stability is probably an order of magnitude better. Reference baths of liquid helium or nitrogen were used in various phases of the experiments. Oxygen contamination of the nitrogen used in the reference bath was the major source of systematic temperature error in the experiments. This error was almost constant in the course of any single experimental series, but led to possible errors in intercomparing various series such as, for example, the magnetization data with the Mössbauer data. A series of cross checks using a liquid-helium reference bath disclosed that the maximum systematic error arising from this source probably did not exceed two degrees.

In order to attain rapid temperature equilibration helium exchange gas at adjustable pressure surrounded

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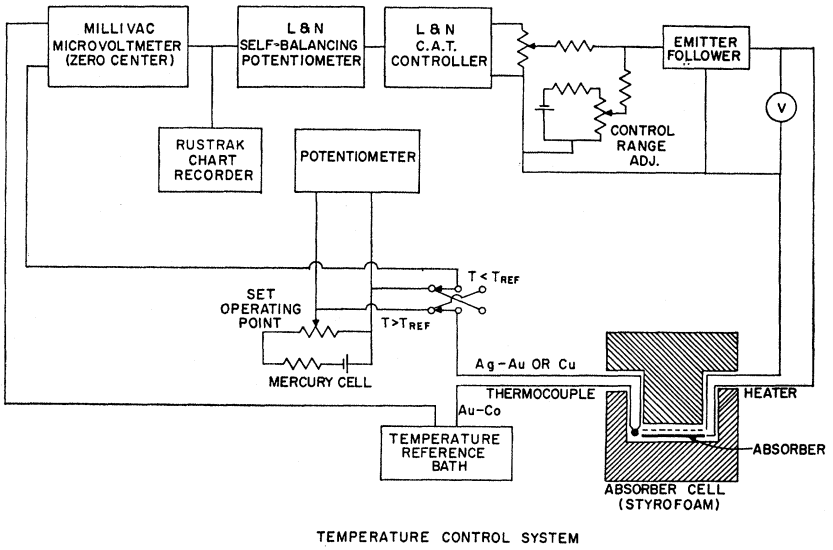

FIG. 1. Temperature-control system used in Mössbauer and magnetization measurements. The system uses commercial components for the major functions and provides proportional, derivative and integral control action. The ultimate precision obtained approximates 0.1 μV. An absorber cell used in Mössbauer studies is shown.

the sample. The arrangement of the controller electronics is presented in Fig. 1. The unit is a null device, operating about a set point determined by a mercury battery and a divider, which is initially adjusted against a potentiometer. A reversing switch permits operation either above or below the reference bath temperature. The Leeds and Northrup C.A.T. controller is a commercial furnace control device designed to operate from the Leeds and Northrup self-balancing potentiometer. This unit offers derivative and integral control action in addition to the usual proportional band control. An emitter follower power amplifier supplies up to 2 W to the heater. A chart recorder continuously displays deviations from the set operating point and permits verification of temperature stability during long runs. The cell schematized in Fig. 1 is that used in the Mössbauer phase of the experiments. The vacuum assembly surrounding the cell is not shown. The use of the self-balancing potentiometer following the microvoltmeter was for convenience and is not necessary. A new version drives a controller directly from the microvoltmeter output. Also, a stirred ice or liquid-helium reference bath is used together with a General Resistance Company Dial-A-Volt high-stability adjustable bucking-voltage source. These modifications obviate drifts associated with oxygen contamination of the nitrogen bath, and with thermal drifts of the mercury cell, and permit long-term, reproducible temperature control to about a millidegree.

Cryostat and Mössbauer Assembly

The Mössbauer experiments were performed in a variable temperature cell mounted inside a superconducting solenoid with 1-in. bore capable of producing up to 34 kOe. Convenience in mounting the solenoid and the need to use axial access in the present experiments lead to a vertical system orientation. In order to optimize the counting geometry a long source drive rod was required to produce the Doppler-shift velocity. The triangular velocity waveform (constant acceleration) was produced with a feedback system described below, and a double coil transudcer designed by Kistner[22] and employing the magnet assemblies from two Jensen loudspeakers. A novel feature of the Kistner suspension system is the use of specially shaped phosphor bronze springs which are capable of supporting a rather large load, and which do not fatigue as does the more usual cloth suspension.

Motion of the transducer was fed into an evacuable region through a double-bellows assembly, which prevented changes in forces on the drive system as the cell pressure was changed. The absorber was mounted in a styrofoam assembly and inside the superconducting magnet. Radiation passed through the bottom of the magnet and through three beryllium windows into a continuous-flow proportional counter (also designed by Kistner) with a fourth beryllium window, which was insensitive to the large stray magnetic fields from the solenoid. The total length of the Doppler-shift drive rod was about 40 in., and the gamma-radiation path length was about 3 in. (including $1\frac{1}{2}$ in. inside the magnet).

The entire drive and cryostat system including the glass Dewar with demountable tail section is shown in Fig. 2. The Doppler-shift velocity produced by the Kistner transducer is coupled through a double-bellows coupler into an evacuable tube of 1-in. i.d. thin-wall stainless steel into which variable pressure exchange gas may be introduced. Triclover vacuum couplings are used where required for demounting of the assembly. The Doppler motion is transmitted to the bottom of the cryostat by a shaft which at its lower end is micarta, in order that the magnetic field not perturb the velocity

[22] O. C. Kistner (unpublished).

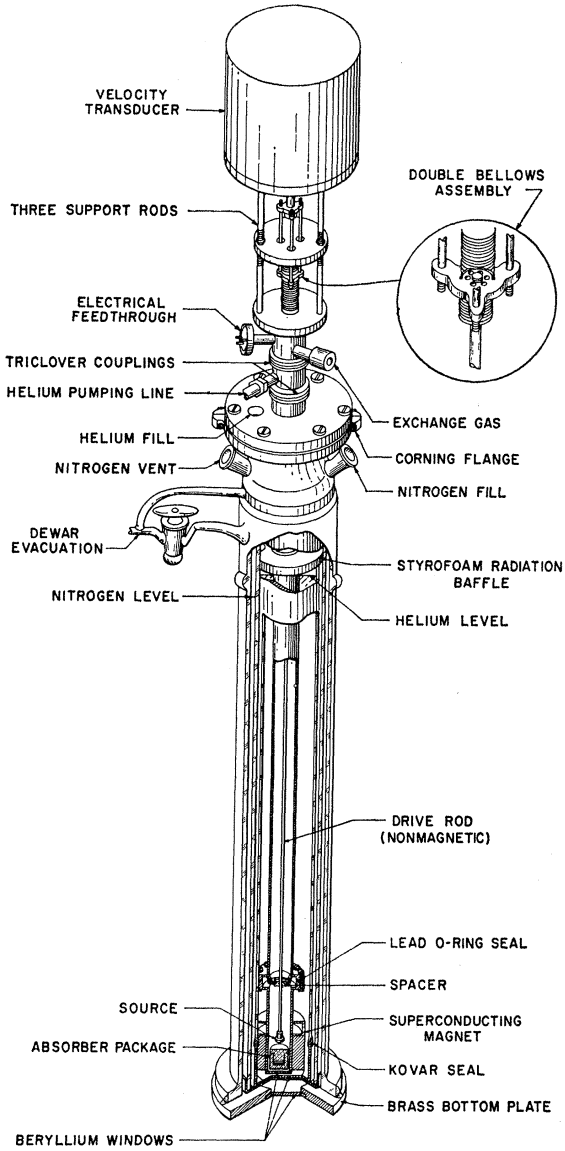

FIG. 2. Helium cryostat showing installation of superconducting magnet and the low-temperature Doppler-shift drive assembly. Details are shown of the mechanism for coupling motion into an evaculable can through a double-bellows system which is insensitive to variations in internal and external pressures.

waveform. A spring centering device is located near the magnet. A demountable seal with lead "O"-ring provides access to the source and absorber. The absorber is mounted in a styrofoam package as shown in Fig. 1. The bottom of the helium region of the Dewar is Kovar metal, into which a 0.040-in. beryllium window is mounted. This window is obtained commerically already mounted to a monel ring.[23] Nitrogen shielding is provided by a section of aluminized Mylar stretched across the bottom of the nitrogen jacket. The bottom of the cryostat is a brass plate waxed in position, which is also equipped with a beryllium window. Other details of the design are evident from the figure.

Resistors in the helium bath serve to turn off the electronics if the helium level falls too low. When the magnet is in use, a field detecting device turns off the counters if the field should fail.

Doppler-Shift Electronics

The Doppler drive transducer is driven in a constant acceleration mode at a frequency usually between 6 and 12 cps by a servo system designed at Brookhaven by R. L. Chase (Fig. 3). A Hewlett-Packard model 202A function generator provides a triangular waveform which is added to the amplified and phase-reversed output of the pickup coil of the transducer. The sum signal is fed through a power amplifier to the transducer. Two Philbrick transistorized operational amplifiers are used for voltage gain and a transistorized power amplifier is used in the output stage. Controls are provided to optimize the over-all gain of the feedback loop, the velocity amplitude, and the gain and bias of a signal used to modulate the base line of a Radiation Instrument Development Laboratories multichannel pulse-height analyzer. The system can also be used in multiscalar mode[24] using a RIDL modular crystal-controlled pulse generator. Switching is provided to permit disconnection of the function generator and insertion of a dc voltage (monitored by a potentiometer) for calibration and for stability tests.

The output of the proportional counter is amplified and fed to a Cosmic coincidence box which selects the 14-keV gamma ray and routes this resonance signal together with a reference signal (produced by another source, detector and amplifier) to two separate quadrants of the analyzer. A Spectrostat high-voltage power supply and regulator (connected in series with another high-voltage supply to supply the 3500 V required for operation of the proportional counter, which is typically operated at about 35 psi) is set on the 14-keV Fe peak and provides a feedback loop around the entire detector, pulse amplifier, and power supply, thereby stabilizing the gain of the entire gamma radiation detection system.

Final resonance spectra are obtained by division of the resonant spectrum stored in the multichannel analyzer by the nonresonant spectrum. Because of the long drive rod used in the present system the velocity waveform is not ideally triangular and such a normalization procedure is mandatory when weak resonances are under study. The primary velocity calibration is a metallic Fe^{57} absorber.

IV. INTERPRETATION OF MEASUREMENTS

The Mössbauer Technique

The Mössbauer effect and its application to the measurement of hyperfine magnetic fields in ferro-

[23] Machlett Laboratories, Springdale, Connecticut.

[24] H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin, Inc., New York, 1961).

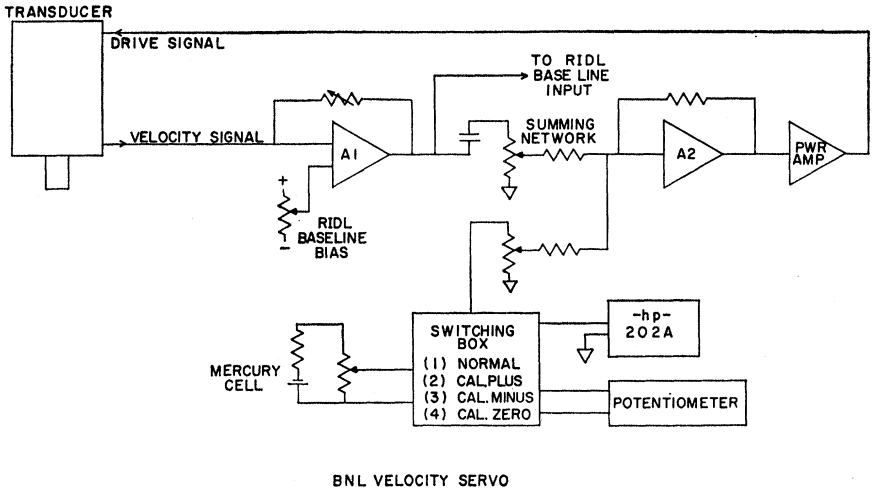

FIG. 3. Velocity servo system to produce constant-acceleration Doppler shift. A function generator (Hewlett-Packard 202A) produces a triangular waveform which is fed into a closed loop including a velocity transducer, operational amplifiers A1 and A2, and a power amplifier. A switching network permits calibration using a potentiometer standard.

magnets have been discussed in detail in numerous publications.[24] The relationship between conduction-electron polarization and hyperfine fields has been discussed by Marshall and Johnson[25] and Freeman and Watson.[26] The paper on Fe by Preston, Hanna, and Herberle[2] goes into considerable detail on decay schemes, polarization effects, and data analysis, which are directly applicable to our experiments and will not be repeated here. We merely summarize some of the essential parameters of the Fe^{57} resonance used in our experiments and certain features of the Mössbauer technique which are of importance in the interpretation of our results. The Fe^{57} resonance occurs in the 14-keV, 10^{-7} sec first excited level of Fe. The resonant level is populated by the decay of 270-day Co^{57}, dissolved in our experiments in a foil of Cu metal. In the presence of a magnetic field, the excited and ground states are split by magnetic hyperfine interactions into four and two levels, respectively. Magnetic-dipole transitions between the excited and ground states give rise to four emitted gamma rays in the direction of external magnetic field, and to six hyperfine lines in other directions. These emitted lines may be resonantly absorbed by a similarly split absorber, giving rise to a complex overall hyperfine resonance spectrum.

In our experiments the Cu source is nonmagnetic and shows no hyperfine splitting at the temperature of 4 °K used, in the absence of an external field. In the presence of a field from the superconducting magnet (in which the source as well as the absorber is located) the Cu source shows some unresolved hyperfine splitting which appears as line broadening. Because Fe in Cu at low temperatures shows some "shielding," which is thought to arise from spin-density wave effects,[27] the broadening does not correspond to the full magnetic field applied. For the source temperature of 4.2 °K in our experiments the field at the Fe^{57} nucleus in Cu is only 56% of the applied field.[28] The experimental data are corrected for this broadening.

The hyperfine splitting in our $Fe_{2.65}Pd_{97.35}$ sample is -314 kOe at low temperatures and in zero field. This corresponds to a spacing between the outermost peaks of 10.0 mm/sec, which may be compared to the experimentally obtained overlap linewidth of the peaks of 0.28 mm/sec, showing that the lines are well resolved. The variation of the hyperfine field with composition at low temperatures has been studied and discussed by Craig *et al.*,[29] who interpret their measurements in terms of long-range conduction-electron polarization produced by scattering from Fe impurities. Evidence for long-range polarization has also been obtained by Low.[15] Near the Curie point the absorber spectrum collapses into a single broad line from the width of which the effective hyperfine magnetic field at the Fe nuclei may be deduced. In zero external field the resonance pattern consists of six hyperfine lines, but in the presence of an external field large enough to align the domains the four-line pattern characteristic of polarization along the field lines is obtained.

Because of the finite lifetime of the 14-keV Fe excited state (10^{-7} sec) averaging effects may in certain circumstances occur which can cause discrepancies between static-magnetization measurements and the Mössbauer results. Thus in paramagnets the full hyperfine splitting has been observed even in zero external field.[30,31] The occurrence of such effects requires that relevant relaxation times be longer than the

[25] W. Marshall and C. E. Johnson, J. Phys. Radium **23**, 733 (1962).
[26] A. J. Freeman and R. Watson, *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, to be published), Vol. II.
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[31] G. K. Wertheim and J. P. Remeika, Phys. Letters **10**, 14 (1964).

nuclear lifetime. Such a situation can occur in nonconductors but is exceedingly unlikely in a metal. Hence we do not discuss this possibility further. Within a few millidegrees of the Curie temperature, critical fluctuation phenomena could play a role, and in this very restricted regime special effects might be observed. Neutron-scattering measurements have already suggested the observability of fluctuation phenomena in ferromagnets[32] and the possibility of their observance with the Mössbauer technique is deserving of consideration.

Molecular Field Model

In interpreting the shape of magnetization data and of hyperfine-field data it is desirable to have a model for the phenomenon of spontaneous magnetization. We have chosen to discuss our results in terms of the molecular field model. In applying the results of this model to the hyperfine fields we make the assumption (borne out by the experimental results) that the hyperfine field is proportional to the bulk sample magnetization. That is, we assume $H_i/H_{\rm sat}=M/M_{\rm sat}$ where H_i is the hyperfine field at temperature T and $H_{\rm sat}$ is the hyperfine field at zero temperature.[14,33] Similarly M and $M_{\rm sat}$ refer to sample magnetization at temperature T and at zero temperature. For a spin J associated with the Fe-plus-polarized-Pd complex, and a Curie temperature θ, the molecular-field model yields

$$H_i/H_{\rm sat}=M/M_{\rm sat}=B_J\left(\frac{Jg\mu_B H}{kT}+\frac{3J}{J+1}\frac{\theta}{T}\frac{M}{M_{\rm sat}}\right) \quad (1)$$

in an external field H. The Brillouin function of argument x for spin J is $B_J(x)$. Because no tabulated results of the solutions to Eq. (1) appear to exist we have computed a table in normalized form[34] for a wide range of spins and fields which we have used in analyzing our experimental data.

Demagnetization Corrections and Host Susceptibility

The B field inside a magnetic sample results from the superposition of the external field, the Lorentz field and the demagnetization field. In addition domain effects may complicate matters further. Because we are concerned primarily with intercomparing hyperfine-field data and magnetization data, and most of these fields affect both types of measurement in the same manner, only a few corrections are necessary. In zero external field the Mössbauer technique measures a quantity proportional to the domain magnetization. Thus this technique is excellent for determining the shape of the zero-field magnetization versus temperature curve. The random orientation of domains introduces a great deal of complication in any attempt to determine zero-field magnetization data, and these considerations occupy the major portion of Sec. V. The Lorentz field is presumably the same in both types of measurement, so no correction is made for this factor.

The demagnetization factor, at fields high enough so that domain effects are unimportant, would play the same role in both Mössbauer and magnetization measurements if the sample were oriented in the same way with respect to the external field in both measurements. In our Mössbauer experiments the field is normal to the plane of the sample. The demagnetization correction for this orientation is $-4\pi M$. In the bulk-magnetization experiments the sample had to be folded, in order to fit it into the apparatus, so that part of it was parallel to the field. The estimated demagnetization correction in these measurements was $-8M$. We have chosen to use the Mössbauer data as a standard and have, when required for intercomparison purposes, corrected the magnetization results to an effective demagnetization factor of $-4\pi M$. Because the total moment even at $T=0°$K is small for our sample this correction is usually rather small. In two of the extrapolation schemes (Sec. VI) the correction is significant. In those cases it is discussed explicitly.

The susceptibility of the host element Pd varies with temperature, and the pure element has a susceptibility peak near 85°K. This host susceptibility led to some difficulty in the interpretation of the high-temperature susceptibility of 1% Fe in Pd.[11,13] In the present experiments we are intercomparing two sets of measurements on the same sample and the effect of the host is unimportant. This effect may, however, be responsible in part for the apparent failure (discussed in the next section) of the molecular-field calculation.

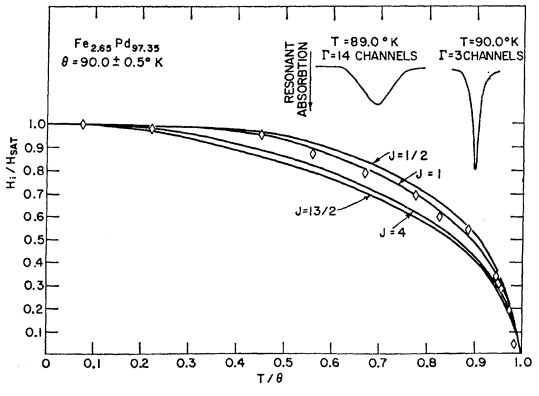

FIG. 4. Temperature dependence of the hyperfine magnetic field at Fe nuclei in $Fe_{2.65}Pd_{97.35}$ measured in zero external field using the Mössbauer effect. The experimental results are compared to molecular-field calculations for several spins. The excellent fit afforded by a spin $J=1$ is probably not significant. The inset shows Mössbauer spectra obtained at 90 and at 89°K, demonstrating the sharp onset of hyperfine splitting at the Curie point.

[32] L. Passell, K. Blinowski, T. Brun, and P. Nielsen, J. Appl. Phys. **35**, 933 (1964).
[33] A. J. Freeman, Phys. Rev. **130**, 888 (1963).
[34] To be issued as a Brookhaven National Laboratory Report.

V. RESULTS

The Mössbauer technique permits the observation of the temperature dependence of the hyperfine magnetic field in zero external field. Since there are no complications associated with domain effects there is no need to extrapolate from finite-field measurements to zero field in determining the Curie temperature. In Fig. 4 we present zero-field Mössbauer measurements on the $Fe_{2.65}Pd_{97.35}$ sample together with molecular field calculations for several values of spin. (There is no *a priori* reason to expect this model to be relevant.) The experimental data define the Curie temperature to be 90 ± 0.5°K. As the Curie temperature is approached from above, the single unbroadened Mössbauer line suddenly begins to broaden, and the onset of this broadening can be determined easily within about one degree. Spectra at 89 and 90°K shown in the inset of Fig. 4 illustrate this. Hyperfine fields are deduced from the line broadening. The sample shows a well-defined, sharp transition with no evidence of smearing such as can arise in poorly annealed samples.

The molecular field calculation for a spin $J=1$ is seen to offer an excellent fit to the experimental data. Although paramagnetic studies indicate a spin $J=4$ for our composition, in contrast to the spin $J=1$ observed, there is no reason to expect a molecular-field calculation to be applicable to our alloy, and probably no significance attaches to this discrepancy. In nonconducting ferromagnets it has been shown that an extremely small amount of bilinear admixture in the spin Hamiltonian is sufficient to produce variations from the molecular field result large enough to account for the discrepancies from the $J=4$ curve which we find.[35]

The application of an external magnetic field to the sample induces magnetization. Near the Curie temperature the induced alignment can be quite large even for a small external field. Curves of the observed hyperfine field versus external field at several fixed temperatures above and below the Curie point are shown in Fig. 5. Below the Curie point θ a spontaneous field exists even in the absence of an external field, while above θ the splitting vanishes in zero external field.

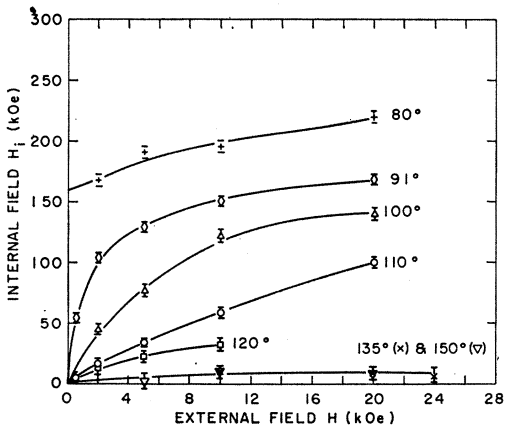

FIG. 5. Variation of the (negative) Fe hyperfine magnetic field in $Fe_{2.65}Pd_{97.35}$ at several fixed temperatures as the external field is varied. Near the Curie temperature, a small external field induces large moments on the Fe.

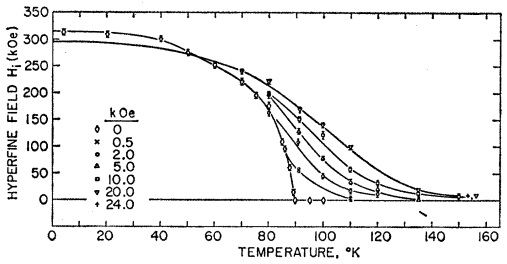

FIG. 6. Hyperfine-field data similar to that of Fig. 5 but plotted for fixed external fields with temperature as a parameter. At low temperatures external fields decrease the observed splitting because the hyperfine field is negative.

In Fig. 6 are presented a set of curves plotted now for various fixed fields with temperature as a variable. Even a small external field is seen to smear out the Curie point, and in a field of 20 kOe the transition temperature is entirely obscured. Because the sign of the hyperfine field is negative, the external field adds with reversed sign and decreases the observed splitting. The 20-kOe curve, therefore, approaches $T=0$ at a hyperfine field of $-314+20=-294$ kOe. The negative hyperfine field for Fe in Pd has been established from the dilute alloy measurements[14] as well as the present studies. At high temperatures where the negative-induced field becomes comparable to the positive external field the total field at the nucleus approaches zero and then reverses sign (becoming positive). Although we have not extended our measurements to sufficiently high temperatures so as to observe this crossover, the effect has been observed for Fe in Mo by Kitchens *et al.*[36] Figure 7 presents a comparison of the $H=0$ and $H=20$ kOe experimental results with molecular-field calculations for several spins. In making this comparison, the 20-kOe data have been corrected for the external field by adding 20 kOe to each experimentally determined splitting. Thus all curves approach a splitting of -314 kOe at $T=0$°K. At the highest temperatures studied a spin $J=4$ is seen to yield a good fit to the data. At the lowest temperatures $J=1$ offers a better fit. At intermediate temperatures the molecular-field calculation fails for all spins. Thus it becomes clear that the magnetization of this alloy system must be described by a more complex model than a simple exchange field. As we shall now show, this complexity of behavior manifests itself in the bulk-magnetization

[35] D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters **11**, 10 (1963).

[36] T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. **138**, A467 (1965).

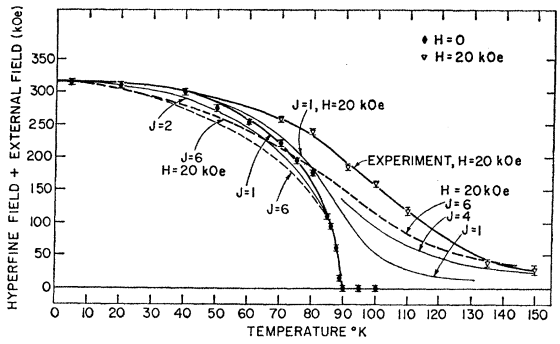

FIG. 7. Experimentally obtained (negative) hyperfine fields at Fe nuclei in $Fe_{2.65}Pd_{97.35}$ in external fields of zero and 20 kOe compared to molecular-field calculations for several values of spin. At high temperatures agreement is found with a spin $J=4$ associated with the Fe, in agreement with the results of paramagnetic-susceptibility data.

data in almost the same manner as in the Mössbauer results.

Magnetization

Magnetization data were obtained at various fields over a range from 70 Oe up to 18.5 kOe at each of a number of temperatures from 20 to 150°K. At the lowest temperatures the resulting isothermal magnetization curves showed a slope which was shown to arise from paramagnetism of the sample holder. The low-temperature data was corrected for this effect. At higher temperatures the contribution of the sample holder was unimportant and no correction was made. A convenient method of displaying the resulting magnetization data is as a family of constant field curves of magnetization versus temperature. A portion of this family is presented in Fig. 8 for the temperature range near to the sample Curie temperature. At lower temperatures (below about 70°K) the curves tend to coalesce and become field-independent (after correction for the sample holder paramagnetism). In this region the temperature dependence of the normalized magnetization curves (normalized to the magnetization M_{sat} at $T=0$) is in agreement with that of the hyperfine field. In the higher temperature regime shown in Fig. 8 the behavior is complex, and it is clear that even the lowest field measurements do not permit the direct estimation of a Curie temperature. This type of problem is of course not a new one, and a number of schemes have been proposed to permit extrapolation of magnetization data to zero field.[37] We shall refer to three of these schemes and discuss in detail two of them. In addition, we introduce two other extrapolations which appear more appropriate to our alloys.

At low temperatures a direct extrapolation of the fixed-temperature-magnetization versus field data to zero field yields the zero-field magnetization. However, at higher temperatures the magnetization versus field lines develop substantial curvature and this technique becomes inapplicable.

An early technique applicable at high temperatures is that of Weiss and Forrer. This method for determining the Curie temperature is illustrated in Fig. 9. Starting from a family of curves (Fig. 8) of $M(H,T)/M_{sat}$ versus T for fixed H one selects fixed values of M/M_{sat} (dashed lines in Fig. 8) and prepares plots of H versus T for each such M value. These plots are then extrapolated back to zero H, thereby yielding a set of $M(H=0,T)/M_{sat}$ data for zero field. These values when plotted against T yield a value for the Curie temperature. In Fig. 9 such a plot is presented. A field H^* corrected for demagnetization is used $[H^*=H-8M_{sat}(M/M_{sat})=H-1.1M/M_{sat}(\text{kOe})]$. The plot of $M(H=0,T)/M_{sat}$ versus T (right-hand axis in Fig. 9) yields a constant magnetization Curie point (denoted by $\theta_{c.m.}$) of 106.6°K, significantly greater than the 90°K value obtained from the Mössbauer technique. The Weiss-Forrer technique uses a linear extrapolation of the magnetization, and since this extrapolation is over a large distance it is perhaps not surprising that the resulting critical temperature is rather high. In addition, the extrapolations at constant M are subject to some question due to the large amount

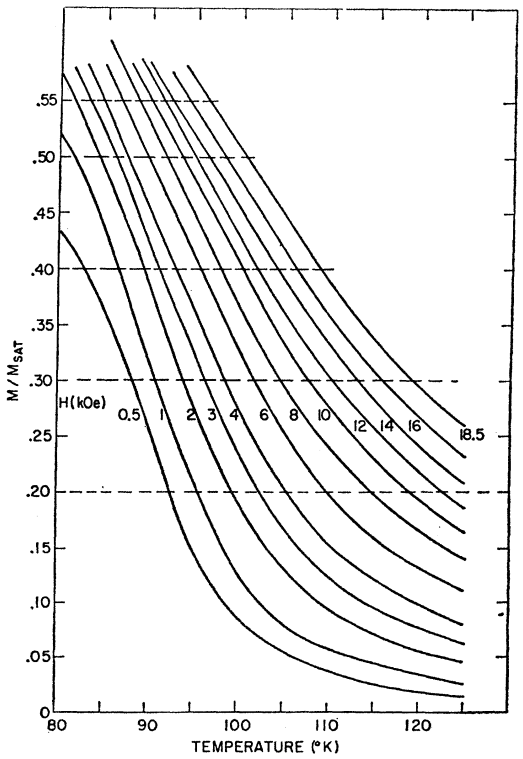

FIG. 8. A portion of the family of bulk-magnetization curves for the same Fe-Pd sample used for Mössbauer studies. The region shown is near the Curie point, and may be used to deduce the Curie point by applying various extrapolation schemes. The dashed lines are lines of constant sample magnetization and are used in the Weiss-Forrer extrapolation method.

[37] K. P. Belov, *Magnetic Transitions* (Consultants Bureau Enterprises, New York, 1961).

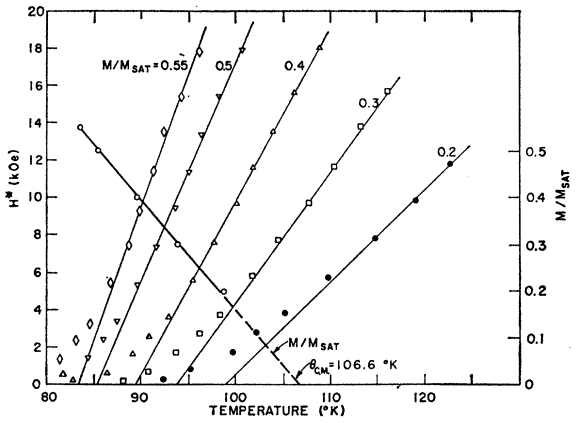

FIG. 9. A Weiss-Forrer plot for the data of Fig. 8. This is a linear, double extrapolation method which yields a Curie temperature $\theta_{c.m.}$ 17.5% greater than the value found from hyperfine-field data. The field H^* used in the extrapolation includes a small correction for demagnetization effects.

of curvature occurring near the Curie temperature. We note that this Curie temperature is in agreement with that interpolated from Crangle[12] who obtained his Curie temperatures by extrapolations of M^2 versus T to $M=0$.

A more recent extrapolation scheme is based upon the molecular-field model and makes use of a second-order expansion of the Brillouin function.[38] In this method one plots M^2 versus H^*/M at fixed temperatures and extrapolates to zero H. The resulting values $M^2(H=0)$ are then plotted against temperature and that temperature at which $M^2=0$ is taken as the Curie point. A qualitative feature of the method is that for temperatures above θ, deviations from linearity in the M^2 versus H/M plot are generally upward, while for $T<\theta$, deviations are downward. Such a plot for our sample is shown in Fig. 10 for the temperature range close to θ. The $M^2(H=0)$ versus T plot is shown in the inset, and yields a critical temperature $\theta_{M2}=100°$K. The subscript $M2$ used in Fig. 10 denotes the use of the square of the magnetization. Because this technique uses a quadratic extrapolation the resulting magnetization curve in zero field approaches the Curie point quadratically, and is in better agreement with the Mössbauer results. However, even with this technique the critical temperature found is appreciably greater than that obtained with the Mössbauer technique.

The linear and quadratic magnetization extrapolations are compared with the Mössbauer results in Fig. 11. The linear approach to θ is clearly inadequate, and the quadratic approach, while better, still does not approach zero magnetization sufficiently rapidly. The discrepancies between the three Curie temperatures thus far presented are well outside of measurement errors and suggest that some other solution is required.

[38] K. P. Belov and A. N. Goriaga, Fiz. Metal. i Metalloved. 2, 3 (1956); A. Arrott, Phys. Rev. **108**, 1394 (1957); J. S. Kouvel, C. D. Graham, and J. J. Becker, J. Appl. Phys. **29**, 518 (1958).

In an effort to obtain an independent check on the Curie temperature a study was made of the temperature dependence of the resistivity of our sample. The resistivity was found to vary linearly with temperature between 80 and 110 °K with a temperature coefficient of resistivity of 7×10^{-3}/°K. Any change in slope of the resistance in this range was not greater than 1%.

Padé-Approximant Analysis

Recently there have appeared a number of calculations of the behavior of the Ising and Heisenberg models near to critical points based upon the use of Padé approximants.[3–9] In these calculations one uses, as a starting point, power-series expansions of the partition function valid in some particular temperature range, but which converge slowly or fail to converge at all in the neighborhood of the critical point. Padé approximants are formed which extend by analytic continuation the region of convergence to the critical point. Padé approximants are ratios of power series, the (N,M) Padé approximant being the quotient of a polynominal of degree N divided by one of degree M. The resulting fraction has $N+M$ coefficients, which may be determined in terms of the first $N+M$ terms in the partition-function power-series expansion. By using a

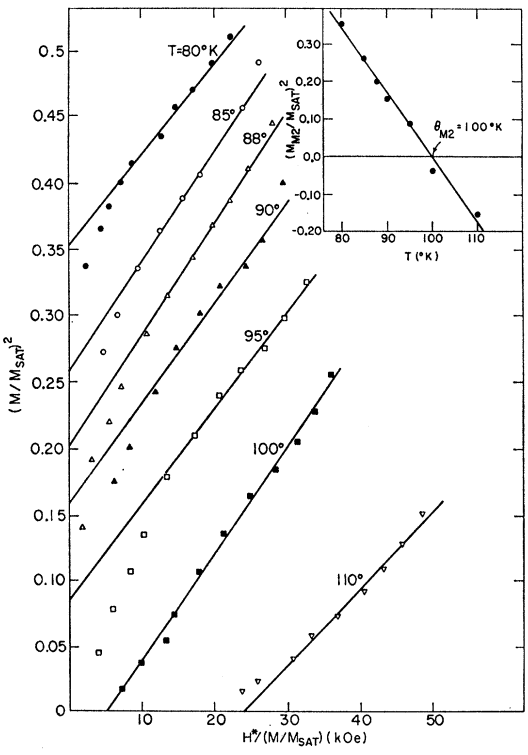

FIG. 10. A quadratic double-extrapolation scheme involving the square of the magnetization used to deduce a Curie temperature θ_{M2} from the magnetization data of Fig. 8. The value of 100°K found, while below that obtained from the linear extrapolation of Fig. 9, is still well above the value 90°K obtained from hyperfine-field data.

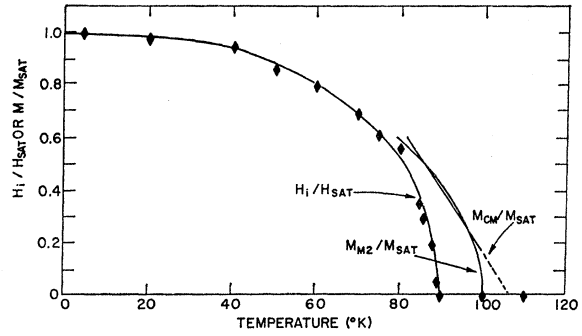

FIG. 11. The dependence of the hyperfine field is $Fe_{2.65}Pd_{97.35}$ in zero external field compared to extrapolations of finite-field bulk-magnetization data to zero field. Below 80°K the magnetization and hyperfine results are in excellent agreement. At higher temperatures the agreement is poor when the hyperfine-field data are compared to linear and quadratic extrapolations of the finite-field bulk-magnetization measurements.

sufficiently high-order approximant the partition function may be approximated to any desired degree of precision. Examples and investigations into regions of applicability of the method have been given by Baker and co-workers.[8,9] Expressions for the susceptibility above and below the critical point have been derived on several models in a number of papers.[4–6] A recent investigation of the zero-field magnetization of the Ising model is that of Essam and Fisher,[5] who find that the magnetization may be represented by $M\sim(\theta-T)^{\beta}$, where β is a constant which depends upon the model and upon the lattice assumed. In two dimensions the exact result is $\beta=\frac{1}{8}$. Essam and Fisher conclude that in three dimensions and for various lattices, $0.303<\beta<0.318$, and conjecture that $\beta=\frac{5}{16}=0.31250$. Baker,[4] using lower order approximants, has suggested $\beta=\frac{3}{10}$. A value resulting from several studies,[3] and one with excellent experimental confirmation,[39] is $\beta=\frac{1}{3}$.

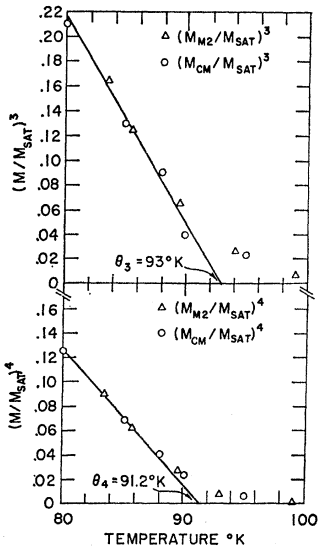

FIG. 12. Cubic and quartic extrapolations of the bulk magnetization of a sample of $Fe_{2.65}Pd_{97.35}$ are found to yield Curie temperatures in close agreement with the value of 90°K found from hyperfine-field data. This result suggests the applicability of Padé approximate calculations to this ferromagnetic dilute alloy, and suggests the inapplicability of molecular-field calculations to the system.

[39] P. Heller and G. B. Benedek, Phys. Rev. Letters 8, 428 (1962).

In order to test whether such models may have relevance to our Fe-Pd sample we have tried cubic and quartic extrapolations, which are shown in Fig. 12. The data used are the $M(H=0,T)/M_{sat}$ obtained from the extrapolations of Figs. 9 and 10. The Curie temperatures obtained by the cubic and quartic extrapolations, denoted by θ_3 and θ_4, are 93 and 91.2°K, respectively. These temperatures are sufficiently close to the 90°K Mössbauer value as to be within range of systematic (estimated as less than 2°K) and extrapolative error. The agreement of the cubic and quartic extrapolations with the Mössbauer Curie temperature makes it appear quite likely that our $Fe_{2.65}Pd_{97.35}$ alloy is not a molecular-field type of ferromagnet but may well be a Heisenberg or Ising ferromagnet. Experimental precision is at present insufficient to permit an accurate study of the approach of the magnetization to the Curie temperature.

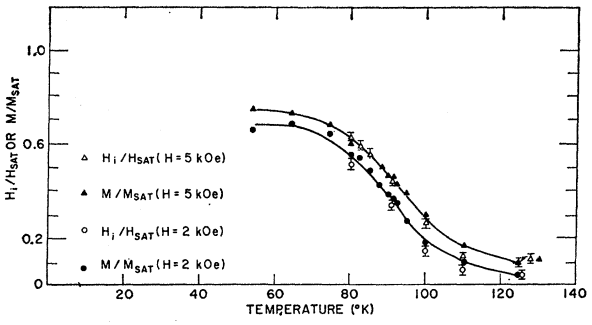

FIG. 13. Comparison of the temperature dependence of the hyperfine magnetic field in $Fe_{2.65}Pd_{97.35}$ to bulk-magnetization data obtained on the same sample in applied external fields of 2 and 5 kOe. Both hyperfine and bulk-magnetization data are normalized to their respective values at low temperatures. These external fields are not sufficient to fully destroy domain effects. The domain effects remaining are, however, slight, and the agreement between the two types of measurement is good.

The Mössbauer data in zero field may be analyzed directly in terms of the Padé-approximant calculations. Such an analysis shows that a value $\beta=\frac{1}{2}$ as predicted by the molecular-field model is too large, but the experimental precision is as yet not sufficient to permit an accurate determination. The method requires excellent temperature stability, together with careful estimation of hyperfine fields from small line-broadening effects. The Mössbauer technique does, however, appear to have unique advantages and to permit in principle an exceedingly precise determination of the behavior of the magnetization near to the Curie point. Experiments designed to yield the requisite precision are in progress.

Intercomparison of Results in an External Field

The results of the hyperfine field and the magnetization determinations may be compared in finite as well

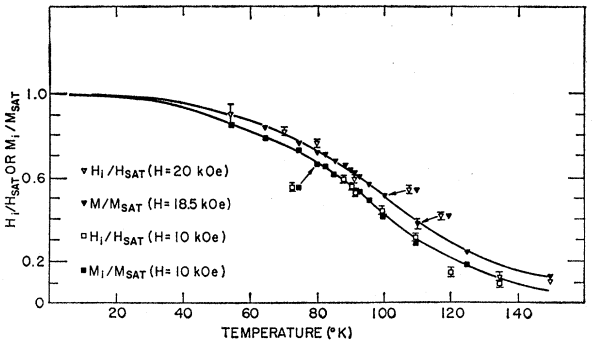

FIG. 14. A comparison between bulk-magnetization and hyperfine-field measurements similar to that of Fig. 13 but in external fields sufficiently large as to overcome domain effects. Agreement between the two types of measurement is excellent, showing proportionality between hyperfine fields and bulk magnetization as the sample temperature is varied.

as zero external fields. In the presence of external fields, comparable to or larger than the demagnetization fields, agreement between the two techniques is found to be excellent. Figure 13 displays magnetization and Mössbauer results obtained in field of 2 and 5 kOe. The agreement is excellent at higher temperatures and the deviations at lower temperatures are indicative of demagnetizing corrections larger than the applied field. Figure 14 shows similar results near 10 and 20 kOe. Here the agreement is excellent over the entire range of temperatures. It is important to note that this agreement implies that the critical temperatures obtaining in the two types of measurement are indeed the same, and that the zero-field discrepancies result from deficiencies in the extrapolation techniques used. The high-field results show that the discrepancies can not result (for example) from temperature errors, for a 10-deg shift in the temperature scale would destroy the agreement exhibited in Figs. 13 and 14.

VI. CONCLUSIONS

A detailed series of measurements of the magnetization and of the hyperfine magnetic field at Fe sites has been made as a function of both temperature and of an external magnetic field in a dilute random substitutional ferromagnetic alloy, $Fe_{2.65}Pd_{97.35}$. At high fields, such that domain effects are unimportant, the hyperfine field and the magnetization are found to be accurately proportional. There is thus no evidence that the moment localized upon the Fe sites changes or redistributes as a function of temperature or field. Although hyperfine field and magnetization vary together their behavior can be only qualitatively described by a molecular field model.

The behavior of the hyperfine field and magnetization is discussed in some detail in the region near to the Curie temperature of the sample. Some evidence is adduced indicating a rapid change in magnetization as the Curie temperature is approached, in agreement with the predictions of recent theoretical calculations. A precise intercomparison awaits, however, the performance of additional and precise Mössbauer effect measurements. Such measurements require exceedingly good sample preparation and temperature control. Attempts to adequately satisfy these requirements are being made. The discrepancies obtained between the Curie temperature deduced from Mössbauer data and those obtained from conventional linear and quadratic extrapolations of bulk-magnetization data suggest the reinterpretation of results on the variation of the Curie temperature with sample composition in the FePd system and also in related alloy systems. Such an effect has already been observed in very dilute Co in Pd.[40] The effect of such reinterpretation will be to lower the presently established Curie temperatures and increase the linearity of the variation of Curie temperature with composition.

ACKNOWLEDGMENTS

These investigations are the outgrowth of questions raised some four years ago by Dr. Darragh Nagle.

We wish to thank Dr. E. F. Hammel and Dr. G. H. Vineyard for making possible the visit of W. A. S. to Brookhaven. Dr. D. E. Cox made available to us and instructed us in the use of the vibrating sample magnetometer.

[40] R. D. Dunlap, J. G. Dash, R. M. Riggs, D. G. Howard, and J. D. Siegwarth, Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964 (to be published).