Nuclear Zeeman Effect in W\textsuperscript{182} in Iron

R. B. Frankel
Francis Bitter National Magnet Laboratory,* Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

AND

Y. Chow† and L. Grodzins
Laboratory for Nuclear Science and Department of Physics,‡ Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

AND

J. Wulff
Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 8 May 1969)

The Mössbauer effect in the 100-keV 2\(^+\) \rightarrow 0\(^+\) transition in W\textsuperscript{182} was observed with dilute tungsten in iron alloy absorbers with concentrations from 0.5–5.0 at.\%\(\text{W}\) at 4.2°K. From the Zeeman spectra in external longitudinal magnetic fields, the \(g\) factor of the first excited 2\(^+\) state was found to be \(0.22\pm0.02\), and the hyperfine field at tungsten nuclei in iron was found to be \(-708\pm25\) kOe. The hyperfine interaction for Fe\textsuperscript{57} in these alloys was also measured, and the results are compared with measurements on alloys of Fe with other 5d impurities and with neutron diffraction measurements.

I. INTRODUCTION

The large magnetic fields induced at the nuclei of magnetic and nonmagnetic atoms dissolved in ferromagnetic metals have been the subject of intensive experimental investigations by a variety of techniques. The result has been a growing systematics of such hyperfine fields as well as some insight into their origin. With this understanding has come an increased use for these fields for the measurement of the magnetic hyperfine interactions of short-lived excited nuclear states as well as for the polarization of long-lived nuclear states.

The experimental methods for measuring hyperfine fields in metals and alloys include nuclear magnetic resonance (NMR), heat capacity measurements, Mössbauer spectroscopy, nuclear polarization measurements at very low temperatures, and perturbed angular correlation measurements. In every case, one measures an interaction energy \(E = -\mathbf{p} \cdot \mathbf{H}\) so that a separate experiment is required to provide the value of the magnetic moment in order to determine the hyperfine field. As we show experimentally below, this second experiment can as well be the measurement of the hyperfine interaction energy as a function of an externally applied magnetic field. Such an experiment allows both the magnetic moment and the magnitude of the hyperfine field to be measured and, in addition, yields a measurement of the sign of the hyperfine field (relative to the external field and, hence, to the magnetic moment of the host metal or alloy).

One of the motivations for measuring the hyperfine magnetic field \(H_{\text{Fe}}(\text{Fe})\) on tungsten impurities in iron was to resolve the discrepancy in values obtained by NMR and Mössbauer techniques and by perturbed angular correlation following Coulomb excitation. The latter,\(^1\) called the “impact technique,” utilizes the Coulomb excitation to recoil-implant the W nuclei into the Fe host. Such measurements thus follow the disruptive entrance of the excited nucleus into the backing foil, and it is not clear that the local condition of the lattice is comparable to the static conditions as in the other experiments. In fact, recent measurements\(^2,3\) by the impact technique of the hyperfine interaction of the 100 keV, 2\(^+\) state of W\textsuperscript{182} in Fe are in sharp disagreement with measurements of the same hyperfine interaction by Mössbauer effect techniques.\(^4,5\) The present work extends and confirms the Mössbauer results by observing the hyperfine splitting of the 100-keV 2\(^+\) \rightarrow 0\(^+\) transition in W\textsuperscript{182} in W-Fe alloy absorbers polarized by longitudinal external magnetic fields up to \(128\) kOe.\(^6\)

In addition, we studied the concentration dependence of the W hyperfine interaction in order to test whether concentration effects are the source of the discrepancy between the impact-technique measurements and the Mössbauer and NMR (static) measurements.

We also studied the Fe\textsuperscript{57} hyperfine interaction \(H_{\text{Fe}}(\text{WFe})\) in the WFe alloys to see if the effects of the W impurity could be correlated with other measured properties, such as neutron diffraction, and with ob-

The sign is (+) or (−) since field, and of domain orientation is random. The solid line is theoretical, assuming a pure magnetic interaction.

II. EXPERIMENTAL

A. Method

A pure magnetic hyperfine interaction

\[ H = -g_{2+} \mu_N H_H \]  

(1)
splits an E2 2+ → 0+ nuclear transition into five equally spaced and equally intense lines which may be observed using a single line source; the spacing between lines \( \Delta \) is given by

\[ \Delta = g_{2+} \mu_N H_H, \]  

(2)

where \( g_{2+} \) is the g factor of the 2+ first excited state, \( \mu_N \) is the nuclear Bohr magneton, and \( H_H \) is the magnetic field at the nucleus. If the absorber is polarized by a longitudinal external field, only the \( \Delta m = \pm 1 \) lines are observed, and the spectrum consists of two equally intense lines with separation \( \Delta \). (For a transverse field configuration, the \( \Delta m = \pm 1 \) and \( \pm 2 \) lines are observed; the spectrum consists of four equally intense lines with separations \( \Delta, 2\Delta, \) and \( -\Delta \).) In an external field, the observed splitting \( \Delta' \) is given by

\[ \Delta' = 2g_{2+} \mu_N H_H, \]  

(3)

where

\[ H_H = H_H + (H_0 - H_{DM}), \]  

(4)

where \( H_H \) is the field at the nucleus due to hyperfine interactions in the alloy, \( H_0 \) is the externally applied field, and \( H_{DM} \) is the demagnetizing field in the absorber. The sign is (+) or (−) since \( H_H \) is positive or negative, i.e., parallel or antiparallel to the magnetization direction and hence to \( H_0 \). The Lorentz field is included in \( H_H \) because it is present in the domains even if the domain orientation is random.

The magnitude of \( g_{2+} \) is obtained from the variation of \( \Delta' \) with \( H_0 \)

\[ d\Delta'/dH_0 = \pm 2g_{2+} \mu_N, \]  

(5)

assuming that \( dH_H/dH_0 = 0 \). The latter condition is fulfilled in the case of Fe57 in iron and is probably a valid assumption for W in iron. The sign of the slope is determined by the signs of \( H_H \) and \( g_{2+} \); since \( g_{2+} \) is positive, the \( 2^+ \) state is a member of a well-defined rotational band, the measured sign of the slope immediately gives the sign of \( H_H \).

B. Spectrometer

The Mössbauer spectrometer was a constant acceleration system in which the transducer was well shielded by soft iron. Both source and absorbers were held at 4.2°K in all experiments. A superconducting solenoid was used for measurements in external magnetic fields up to 80 kOe; the measurement at 128 kOe was made in a water-cooled Bitter solenoid. In the superconducting solenoid, the fringing field fell off rapidly, and it was possible to hold the source at a position which was reasonably field free (<1 kOe), but which still had a reasonable counting geometry. In the high-field Bitter solenoids, a small water-cooled solenoid was used to cancel the (longitudinal) fringing field and allow suitable counting geometry. A GeLi detector was used in all the external magnetic field experiments; there was no noticeable deterioration in resolution even in fields as high as 7 kOe (corresponding to 128 kOe at the center of the solenoid).

C. Source and Absorbers

The 20-mCi source of 115-day Ta182 used in the experiments was prepared by thermal neutron irradiation of a 0.01-mm-thick piece of pure Ta metal in the MIT Reactor. The Mössbauer transmission spectrum obtained with this source and a 0.025-mm-thick tungsten foil absorber, which had been annealed for 8 h at 2000°C in an inert atmosphere, consisted of a single line of Lorentzian shape with a full width at half-maximum, \( F = 0.21 \pm 0.01 \text{ cm/sec} \), which may be compared with the theoretical width of 0.19 cm/sec calculated from the measured lifetime of the 100-keV level, \( \tau_{1/2} = 1.36 \text{ nsec} \).

The 0.5, 1.5, 3.0, and 5.0 at.% W in iron alloy absorbers were prepared as follows: Tungsten metal powder, prepared by hydrogen reduction of WO3 enriched in W182, was pressed with electrolytic iron metal powder and sintered in hydrogen, then melted in an argon arc furnace with a water-cooled copper hearth cathode and a tungsten anode. The samples were divided and remelted up to 15 times as 75-g buttons, which were cut and metallographically polished and etched to determine gross segregation. When no more segregation was found, the buttons were melted together and then heat treated with the arc to promote homogeneity. They were then hot-worked into discs in air, ground into shape, and given a 1300°C anneal in hydrogen for 1 h to...
make them all single phase α solution. The anneal was terminated with a quench to room temperature in water. Finally, the samples were ground and polished.

The homogeneity of the samples was analyzed using a microbeam probe and was found to be acceptable. In addition, metallographic analysis showed no concentration gradients, precipitates, or inclusions.

According to the Fe-W equilibrium diagram, slow cooling of the alloys could result in precipitation of WFe₅, W₂Fe₇, or W₄Fe₇. With the rapid quenching, however, none of these phases appeared. As a check, a sample was prepared in which the most abundant phase was WFe₅. The W spectrum at 4.2°K showed no evidence of magnetic hyperfine splitting.

III. RESULTS AND DISCUSSION

A. W¹⁸² Measurements

The zero-external-field spectrum for the 0.5% W-Fe alloy is shown in Fig. 1. The spectra for all the alloys were computer fitted with five equally spaced and equally intense lines, i.e., a pure magnetic interaction [Eq. (1)]. Since the alloys in this composition range are cubic, we did not include a quadrupole term in the interaction Hamiltonian and indeed obtained satisfactory fits without such a term, although a cubic lattice symmetry is not enough to guarantee the absence of quadrupole effects. The existence of the magnetization axis in a ferromagnetic system lowers the symmetry, and a localized electric field gradient could appear. Such effects have not, however, been observed in systems of this type.

The theoretical curve in Fig. 1 was fit to the data by a least-squares analysis, and the computer program was allowed to vary three parameters: the strength of the interaction Hamiltonian and indeed obtained satisfactory fits without such a term, although a cubic lattice symmetry is not enough to guarantee the absence of quadrupole effects. The existence of the magnetization axis in a ferromagnetic system lowers the symmetry, and a localized electric field gradient could appear. Such effects have not, however, been observed in systems of this type.

The resolution is improved in an external longitudinal magnetic field, because only the ∆m = ±1 lines are observed along the external field direction. The alloys at the ends of the series, 0.5 and 5.0 at.%, were studied in the external field; the absorption spectrum for the 0.5 at.% alloy in a longitudinal magnetic field of 22 kOe is shown in Fig. 2. The solid curve is a computer-calculated least-squares fit to the data, the computed linewidth is 2.5 mm/sec, and the splitting is 3.10 mm/sec. The 5.0 at.% alloy in the same external field gave a slightly smaller splitting (see Fig. 3) and linewidths of 3.2 mm/sec.

An independent measurement of the magnetization of a piece of the alloy used in the external field Mössbauer experiments¹⁹ showed that the magnetization was completely saturated for H₀ = 12 kOe. Because of the shape dependence of the demagnetizing effects, all measurements were carried out with H₀ ≥ 20 kOe. It is worth remarking here that if the sample is not completely polarized, the hyperfine interaction may appear to be nonlinearly dependent on the external field, because in addition to changes in the hyperfine splitting, the intensity of the ∆m = ±2 and 0 lines will decrease as the domains rotate with increasing H₀; this is especially important if the lines are not well resolved.¹¹

* S. Foner (private communication).
¹¹ In a thin (0.001 in.) iron foil, H₀ is 21.7 kOe, and observations of the relative intensities of the well-resolved hyperfine lines for the 14.4 keV transition in Fe⁹⁵ show that about 30 kOe of applied field is required to fully polarize the foil perpendicular to its plane, the extra ~9 kOe being necessary to overcome the anisotropy energy of the domains in the foil.
Table I. Experimental values of the magnetic-dipole moment of the 100-keV state in W^{182}.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \mu ) (( \mu_N ))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulomb excitation</td>
<td>+0.403(36)</td>
<td>b</td>
</tr>
<tr>
<td>Coulomb excitation time</td>
<td>+0.498(48)</td>
<td>c</td>
</tr>
<tr>
<td>Differential perturbed angular correlation</td>
<td>+0.672(88)</td>
<td>e</td>
</tr>
<tr>
<td>Integral reversed field Mossbauer scattering</td>
<td>+0.466(54)</td>
<td>f</td>
</tr>
<tr>
<td>Mössbauer effect</td>
<td>+0.532(18) (assumes ( H_M = -630 ) kOe)</td>
<td>g this work</td>
</tr>
</tbody>
</table>

\( g_\text{hf} = 0.22 \pm 0.02 \)

or

\( \mu = (0.44 \pm 0.04) \mu_N \).

The value is compared in Table I with the results of measurements by other techniques. As discussed in Sec. II A, the sign of the hyperfine field relative to the magnetization direction and hence the external field may be determined from the slope in Fig. 3. Since the sign of \( g_\text{hf} \) is positive, the observed negative slope implies that the hyperfine field is negative.

The magnitude of the hyperfine field may be obtained by extrapolating the line in Fig. 3 to \( H = 0 \). The value obtained by this procedure is \( H_M \) (intercept) 750±66 kOe. To obtain the most accurate value of \( H_M \) from these measurements, we use the mean value of \( g(2+) \) determined by all methods (see Table I), i.e., angular correlation, Coulomb excitation, integral reversed field Mössbauer scattering method, and the present experiment. This gives \( g_\text{hf} = 0.233 \pm 0.015 \), from which

\[ H_M = -708 \pm 25 \text{ kOe} \]

The quoted error includes estimated errors in the theoretical fitting procedure, the statistical error in the data, and also the possible systematic error in the value of \( H_{DM} \) in Eq. (4).

B. Comparison with Other Measurements

Table II gives the value for the hyperfine field at tungsten iron determined by various methods. The measurement by NMR was quoted in Ref. 12; no details of the measurement were given. In the nuclear alignment experiment, the anisotropies of the 482 (\( E2 \)) and 686 (\( E1 \)) \( \gamma \) rays in Re^{187} following the decay of 24-h W^{182} (\( I = \frac{3}{2} \)) in iron were studied as a function of temperature for temperatures between 0.01 and 1.0 K; the maximum anisotropies were \( \sim 3.0 \) and \( \sim 6.5\% \) for the 482- and 686-keV \( \gamma \) rays, respectively. From the temperature variation, Kul’kov et al.\(^{13} \) derived \( \mu H_M = (0.38 \pm 0.06) \times 10^{-17} \), and assuming \( \mu (W^{187}) = 0.7 \) (by analogy with the known moment of Os^{189}), they obtained \( H_M = (1.1 \pm 0.15) \times 10^{10} \) e.

The values of the hyperfine field by the Mössbauer effect and by NMR overlap because of the uncertainty in the W^{182} nuclear moment, which has not been determined to better than \( \sim 10\% \) by any direct method (the errors quoted in Table II for our measurements and the measurements of Agresti et al.\(^{4} \) are errors in the measurement of the splitting).

It is worth noting that there is a possibility of a sizable hyperfine anomaly, which would account for a difference between the NMR and the Mössbauer results. The NMR investigation measures the hyperfine interaction with W^{182}, a nucleus consisting of an odd neutron in an \( s_1/2 \) orbit, while the Mössbauer measurements use the first rotational state in W^{182}, and a substantial difference in the spatial distribution of the magnetic moment in the two cases would not be unexpected.

Two independent measurements\(^{2,4} \) of the tungsten hyperfine field in iron have been made by the Coulomb excitation and recoil implantation—perturbed angular correlation method (impact technique) in which W nuclei, Coulomb excited into the 2+ state by an O^{16} beam, were implanted by recoil into a polarized iron foil catcher, and the rotation of the correlation between the deexcitation \( \gamma \) rays and the backscattered oxygen

\[ 13 \text{ D. A. Shirley and G. A. Westenhager, Phys. Rev. 138, A170 (1965).} \]

ions was measured. The results of the two groups are in reasonable agreement with each other. In the experiments of Gilad et al., the rotation of the correlation for W184 and W186 recoiled into a Cu matrix was used as a "calibration"; in this case, the rotation was supposed to be due to the external field, and hence the hyperfine fields in the other matrixes were derived by comparing the \( \omega \)r values. These measurements were made at room temperature, whereas the Mössbauer data and NMR data were taken at 4.2°K.

C. Fe57 Measurements

The effects of impurities on the magnetic properties of iron metal have been investigated by NMR, Mössbauer effect, neutron diffraction, and bulk magnetization techniques. In the NMR and Mössbauer experiments using Fe57, the measurements yield a quantity related to the distribution of electronic moments, namely, the distribution of hyperfine fields. But as has been emphasized by various authors, the moment at a site and the hyperfine field at the same site are not simply related because of the complex balancing of terms which result in the net hyperfine interaction. Recently, the moment distributions about impurities in iron have been calculated from neutron scattering experiments, and one obtains a value for the moment at the impurity site and also a value for the average moment on the first and second nearest-Fe-neighbor sites to the impurity.

We have measured the hyperfine spectra for the WFe alloys using a Co57 in Cr source at room temperature; using a thin Fe metal absorber, a linewidth of 0.21 mm sec\(^{-1}\) was observed. The structures of one of the outer \( \Delta m = \pm 1 \) lines, for the various alloys, are shown in Fig. 4. We summarize the results as follows: (a) The main Fe hyperfine line is unshifted, or only slightly shifted, to higher frequency, compared to pure Fe; (b) there are concentration-dependent low-field satellites on the main hyperfine line; and (c) the spectra are reasonably symmetric, i.e., there are no large isomer shifts or quadrupole effects. The low-field satellites are unresolved, but it is possible to obtain a satisfactory fit to the shape of the line by postulating that iron atoms, which are first nearest neighbor and second nearest neighbor to the W impurity, are shifted by \( \sim 9 \) and \( \sim 12\% \) to lower field, respectively, and that the linewidth corresponds to that of the main iron line. The spectra are similar to those obtained for ReFe, except that no large isomer shifts are observed.

\[ H_{1n,2nn} = a \mu_L + b \sum \mu_{1nn,2nn} \]  

where \( \mu_{1nn,2nn} \) is the average moment on the first and second nearest-neighbor sites from neutron diffraction, \( \mu_L \) is the local moment on the impurity site, and \( H_{1nn,2nn} \) is the average hyperfine field for the first and second nearest-neighbor sites. They found good agreement for the whole series for \( a = 90 \) kOe/\( \mu_B \) and \( b = 6 \) kOe/\( \mu_B \); that is, they determined an empirical relationship between the moment distribution and the hyperfine fields at the Fe sites. These measurements and the two-parameter fit do not confirm the distribution of moments obtained from the neutron data, but the internal consistency, also with \( d\mu/dc \) measurements, is satisfactory.

Returning to WFe alloys, the values of \( \mu \) obtained from neutron diffraction studies of dilute WFe alloys \( \mu_L = -0.6 \), and \( \mu_{1nn,2nn} = 2.15 \), when used in Eq. (6), yields \( \Delta H_{1nn,2nn} \approx 8\% \), in fair agreement with the experimental value of \( \sim 10\% \). We conclude from this agreement that the Mössbauer measurements in WFe...
are consistent with the moments derived from the neutron diffraction data and use these moments to briefly discuss the hyperfine field at the W impurity site.

D. W Hyperfine Field in Fe

Hyperfine interactions at transition-metal impurities in iron have been discussed previously.\textsuperscript{15,20} There are several sources of these interactions which give contributions of different signs. Two sources, conduction electron polarization and core polarization, are considered to dominate, and the others are usually neglected as being small by comparison. The core polarization contribution arises only if there is a local moment at the impurity site and gives an effective hyperfine field which is antiparallel to the direction of the local moment. The conduction electron polarization contribution gives an effective hyperfine field which is found to be antiparallel to the net host magnetization. One may fit the observed fields for the 5d transition elements in iron with an equation of the form\textsuperscript{15,19}

\[ \text{H}_{\text{imp}} = A \mu_{\text{imp}} - B(z) \mu_{\text{host}}, \]  

(7)

where \( A \) is a constant (in kOe/spin moment), \( \mu_{\text{imp}} \) is the localized moment at the impurity site, \( B(z) \) is a constant for each element, and \( \mu_{\text{host}} \) is the host moment. The latter should be a good approximation to the moment for the first and second neighbors. \( A \) is taken as a constant independent of \( z \) by analogy with the 3d and 4d transition metal atoms; as discussed by Watson and Freeman,\textsuperscript{21} experiment and theory show constant values for all the elements in these series. Unfortunately, no calculations exist for the 5d transition metal atoms, and because of the complex balance of large contributions, it is not possible to extrapolate from 3d and 4d values. \( B(z) \) has been extensively discussed by Shirley and Westenbarger;\textsuperscript{18} it is proportional to the 6s electron hyperfine field in the free atom (which changes by a factor of \( \sim 2 \) going from W to Au). The proportionality is usually taken to be independent of \( Z \),\textsuperscript{12} however, it must be noted that some of the Mössbauer results\textsuperscript{13,19} show isomer shifts at the 1nn and 2nn sites, which may be related to charge transfer effects which tend to reduce the validity of this assumption. The hyperfine field for Pb in Fe is positive,\textsuperscript{22} and it is clear that Eq. (7) breaks down for Pb; in fact, additional contributions may be important even for Pt.

The neutron diffraction results\textsuperscript{18} show no localized moment for Os or Ir in Fe; hence, \( A = 0 \) in Eq. (7) for these elements allows us to determine \( B(z) \) and, from the known \( z \) dependence of \( B(z) \),\textsuperscript{12} to derive the value of \( B \) for W. Fixing \( B(\text{Os}) = 545 \) kOe/\( \mu_B \) and \( B(\text{Ir}) = 605 \) kOe/\( \mu_B \) gives \( B(\text{W}) = 406 \) kOe/\( \mu_B \). From the measured hyperfine field, one gets \( A(W) \approx -400 \) kOe/\( \mu_B \). As discussed above, we expect this value of \( A \) to apply to all the 5d transition solutes. This value for the core polarization may be compared with recent estimates\textsuperscript{23} based on EPR measurements in W,\textsuperscript{24} which indicates a core polarization of about \( -400 \) kOe per unpaired spin. The agreement is perhaps fortuitous.

E. Conclusion

We have shown that the hyperfine field for tungsten in iron as determined by the static techniques is independent of concentration over a limited range, that the effect of the W impurity on its Fe neighbors could be correlated with effects observed in similar alloy systems and with neutron diffraction measurements, and conclude that the conflict between the two sets of measurements of the internal field \( H_{\text{w}}(\text{Fe}) \) must be resolved in favor of the Mössbauer-NMR results. The low value of \( H_{\text{w}}(\text{Fe}) \) deduced from implantation experiments must therefore result from as yet unaccounted for phenomena. Gilad et al.\textsuperscript{25} already showed that a static quadrupole interaction cannot be invoked. The transient field effects discovered by Borcher et al.\textsuperscript{24} can account for no more than a few percent of the discrepancy in this case. Other phenomena, however, which have resulted in significant reduction in observed precessions in impact-technique experiments on long lived states, may be of importance here. In particular, we mention (1) the possibility of an insufficient strength of polarizing field\textsuperscript{26} and (2) the possibility of relaxation effects. Either or both could account for the discrepancy, but neither has been explored in this case.

ACKNOWLEDGMENT

The authors are pleased to acknowledge useful discussions with H. Bernas, N. A. Blum, I. A. Campbell, S. Foner, A. J. Freeman, R. Kalish, E. Kankeleit, and D. E. Murnick. J. W. Williams designed and constructed the superconducting magnet, and W. B. Mosby provided technical assistance.