The Mossbauer Effect in Ferric Stearate and Ferric Oleate

Ronald L. Wilson

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THE MOSSBAUER EFFECT IN
FERRIC STEARATE AND FERRIC OLEATE

by

Ronald L. Wilson

A Thesis
Submitted to the
Faculty of the School of Graduate
Studies in partial fulfillment
of the
Degree of Master of Arts

Western Michigan University
Kalamazoo, Michigan
August 1969
ACKNOWLEDGEMENTS

I wish to thank Mr. Jerry Boss and Miss Susan Stein for collecting and processing parts of the data that I have used here. I also wish to thank Prof. Joseph Kanamuller for very helpful discussions in the area of chemistry which started the investigation early in the right direction.

The people of the Computer Center of Western Michigan University were very helpful in every way and I wish to express my appreciation to them for the personal assistance they gave me as well as for the use of the physical facilities.

The person to whom I owe the most is my advisor, Dr. Larry D. Oppliger. His patient guidance, advice and counsel were sorely needed, thoroughly tested and greatly appreciated.

Ronald L. Wilson
MASTER'S THESIS

WILSON, Ronald Lee
THE MOSSBAUER EFFECT IN FERRIC STEARATE AND FERRIC OLEATE.

Western Michigan University, M.A., 1970
Physics, general

University Microfilms, A XEROX Company, Ann Arbor, Michigan
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INTRODUCTION

Nuclear Properties

The general aspects of the Mossbauer effect are described in many articles\textsuperscript{1,2}. Only those features required for the present study are discussed below.

The isomer shift

The s-electrons have a finite probability of being found in the nucleus. When an electron enters the nucleus the energy levels of the nucleus are changed; consequently, the absorption dips exhibited in a Mossbauer transmission spectrum are shifted in energy. This shift is known as the isomer shift and is given by

\[ IS = \frac{2}{\hbar} \pi Z e^2 (R^2 - R_g^2) \left( |\Psi(0)_a|^2 - |\Psi(0)_e|^2 \right), \]

where \( Z \) is the atomic number of the nucleus, \( e \) is the electronic charge, \( R \) and \( R_g \) are the radii of the excited and ground states respectively, and \( \Psi(0)_a \) and \( \Psi(0)_e \) are the total s-electron densities at the nucleus of the absorber and the emitter respectively.

The isomer shift is thus dependent on the s-electron density at the nucleus and the change in the radius of the nucleus. If one knows the radii of the excited state and ground state, then by noting the magnitude and direction of the isomer shift, one can compare the s-electron densities at the nuclear sites. This effect is often referred to as the chemical shift since chemical bonding can...
influence the s-electron density at the nucleus.

The isomer shift for iron is somewhat unusual. An increase in the s-electron density results in a decrease in the isomer shift. This is because the ground state has a larger radius than does the excited state, (i.e., \( R < R_e \)), hence an increase in the s-electron density at the absorbing nucleus results in a negative isomer shift.

Quadrupole splitting

If either the ground state or the excited state has an electric quadrupole moment and if the nucleus is located in a position where there is an electric field gradient (\( \text{grad } E \)), the absorption line seen in a Mossbauer spectrum will be split. Under favorable conditions this quadrupole splitting can be observed (see Fig. 13). The magnitude of the quadrupole splitting will be determined by \( Q(\text{grad } E) \), where \( Q \) is the quadrupole moment of the state. One can then determine the quadrupole moment if the electric field gradient is known or the electric field gradient if the quadrupole moment is known.

Iron has a ground state spin of \( 1/2^- \) and an excited state spin of \( 3/2^- \). Quadrupole splitting thus occurs only in the excited state, resulting in a relatively simple quadrupole spectrum for iron. Also, since the quadrupole moment (\( Q \)) of Fe-57 is well known, quadrupole splitting yields information about electric field gradients (\( \text{grad } E \)) in iron bearing compounds.

Magnetic hyperfine splitting

Magnetic splitting of the absorption lines occurs when at least
Figure 1. The decay scheme of Co-57.
one of the nuclear states has a magnetic dipole moment and when there is a magnetic field at the nuclear site. The magnitude of the splitting is given by $\mathcal{E} = g \mu_0 H$, where $\mathcal{E}$ is the magnitude of the splitting, $g$ is the nuclear g factor, $\mu_0$ is the nuclear magneton and $H$ is the magnitude of the magnetic field. This nuclear Zeeman effect can be observed when the splitting is greater than approximately twice the line width (full width a half maximum). For Fe-57 the line is narrow and one is often able to observe the nuclear Zeeman effect.

Since an excited state with spin $I$ will split into $2I + 1$ components, one can also determine the spin of the excited state assuming that the spin of the ground state is known and that the spectrum is not too complicated.

The excited state of iron would thus be split into $2(\frac{3}{2}) + 1 = 4$ components while the ground state would split into $2(\frac{1}{2}) + 1 = 2$ components. Using the selection rule ($\Delta m = 0, \pm 1$) one finds that six different transitions are possible between the excited state and the ground state of iron, therefore a magnetic field manifests itself as a sixfold splitting of the absorption line in iron.

Structure of Ferric Stearate and Ferric Oleate

Ferric stearate and ferric oleate might be thought to be quite similar based on the similarity between the stearate and the oleate. Both the stearate and the oleate are 18-carbon chains and the functional group in each case is the carboxyl group. In fact, the only
difference between the two is that the oleate has a carbon-carbon double bond between the ninth and tenth carbon atoms and the stearate does not. This double bond is so far from the functional group that one might guess that it would have no effect on the type or nature of the compounds (or complexes) formed. Thus one would expect to find the physical parameters at the iron site in ferric stearate and ferric oleate to be very similar.

Since the nuclear properties of Fe-57 are well known, one can use the Mossbauer effect to ascertain several things about the structure of the two molecules.

The relative s-electron densities at the iron sites can be found and this, in turn, can be related to the relative covalent nature of the bonding to the iron atom.

The quadrupole splitting indicates the magnitude of the electric field gradient and also the degree of symmetry about the iron site. This information is obviously very valuable when one is considering the molecular structure of compounds.

Since the magnetic moment is known, one can determine the magnetic field created by the unpaired 3d-electrons (or the core electrons which may be polarized by the outer electrons\(^4,5,6\)) and hence some idea as to the number of unpaired electrons. From this one can make inferences as to the splitting of the energy levels of the molecular orbitals.
APPARATUS

The Drive

Description

The drive is similar to that described by Kankeleit. It employs a negative feedback network to force the drive to follow a reference waveform. The operation of the drive is described below. A schematic diagram is shown in Fig. 2.

A signal generator sends pulses to the multichannel analyzer (MCA) at a precise frequency. Each pulse increments the address of the MCA (operated in the multiscaler mode) by one. While the address is any channel from 1 to 256 the MCA supplies a plus 1/4 volts output and while the address is any channel from 257 to 512, minus 1/4 volts. This resulting square wave is integrated by an integrating circuit and the resulting triangular reference voltage is used to regulate the velocity of the drive. This is explained in some detail in Appendix C. It is clear that the channel number will be a linear function of the velocity (see Fig. 3). Also, when the MCA is used in the multiscaler mode, as it is here, it has virtually zero dead time.

Velocity calibration of the drive

In the drive circuit there is a potentiometer (P2 in Appendix C) which determines the maximum voltage of the reference signal.
Figure 2. Schematic diagram of the drive circuit.
Key to Figure 2.

H. V. Supply - Power Designs, Model 2K-10.

SGA - Hamner Pulse Height Analyzer, Model N-686A.

MCA - Nuclear Data Model 180-M 512 channel memory unit plus Nuclear Data Model 180-F analog to digital converter.

Scope - Tektronix oscilloscope, Model 503. Used as a time base generator (see Appendix C).

Amp - Hamner, Model N-34QA.

PM tube - EMI-9536 photomultiplier tube.

X-tal - Harshaw Chem. Co. (Type HG) NaI(Tl) crystal 0.015" thick.

Absorber - the Mossbauer absorber, i.e., ferric oleate, Fe$_2$O$_3$, etc.

DC Power - A compound regulated DC power supply. Philbrick, Model PR-30CR.

Source - Co-57 in Pd.

Integrating Circuit - Circuit which integrates the square wave from the MCA to obtain a triangular reference voltage (see Appendix C for details).

Transducer - Sanborn Linear Velocity Transducer, Model LVsyn 6LV2.

Linear DC Amp - Linear amplifier to produce drive signal. Dana DC Amplifier, Model J520.

Drive Coil - Coil and magnet from speaker. North American Phillips, Co., Model AD 3701 AM.
Figure 3. A diagram of some of the wave forms in Fig. 2 and a diagram of the solid angle subtended by the source.
Figure 1. Magnetic splitting produced by a Fe$_2$O$_3$ absorber. The source is Co-57 in stainless steel. Reproduced from A. H. Muir, K. J. Ando and H. M. Coogan, Mossbauer Effect, Data Index, pp. 351.
Figure 5. Calibration curve.
and consequently the maximum velocity of the source. Since different velocity ranges were required to obtain a variety of data the potentiometer was calibrated in terms of the maximum velocity of the source.

Ferric oxide exhibits a hyperfine splitting which is well known (see Fig. 4) and it is often used for calibration purposes. Fig. 5 shows the calibration curve that was obtained using Fe$_2$O$_3$.

**Line width**

The measured line width of even an unsplit line is usually significantly broader than the natural line width reflecting imperfections in the drive, the finite spread of energies (or velocities) placed in a single channel and effects due to the finite thickness of the source and the absorber. Because of the finite spread of energies placed in a single channel one may not be able to fold the data in exactly the correct position, thus introducing another broadening effect. This last factor is thought to be minimal in this case for two reasons: 1) the spread of energies placed in a single channel, though finite, is small and 2) when the data were folded and fitted with the best theoretical curve, the least chi squared was found to be equally large when the fold was made one channel before and one channel after the chosen fold channel. Details of this are discussed on the next page.

Margulies and Ehrman$^9$ have calculated the ratio of the apparent (or measurable) line width ($\sigma_a$) to the natural line width ($\sigma$) caused by finite source and absorber thicknesses. If one applies
these calculations to this experiment, one obtains $10.6 \times 10^{-9}$ eV as the narrowest possible line width. The measured line width was $11.5 \times 10^{-9}$ eV. It seems clear that the apparatus introduces only a small amount of line broadening.

The solid angle effect

As the source moves it continuously subtends different solid angles as measured at the detector. Therefore, the number of counts in a particular channel will depend not only on the resonance absorption but also on the position of the source (or the absorber if it is the absorber which is moved) corresponding to that channel. The solid angle effect is virtually eliminated by the folding process. In order to understand this folding process one must observe that in any cycle a given velocity occurs twice; once nearer the detector than the equilibrium position and once farther from the detector than the equilibrium position. These two positions are symmetrically located with respect to the equilibrium position, therefore, by adding the number of counts in these symmetrically located channels, one effectively eliminates the solid angle effect. A justification of this process is given in Appendix D.

The channel after which the data was to be folded was expected to be near channel 256. To discover exactly which channel it should be, the data was folded after channels 255, 256 and 257 and then fitted with the best theoretical curve in each case. The accuracy of each fit was determined by the least squares method. The least
squares were found to be 639, 513 and 637 respectively. Channel 256 was therefore taken to be the best fold channel and all data were then treated in accordance with this finding.

Detection of the radiation

A NaI(Tl) crystal was used in conjunction with a photomultiplier tube to detect the radiation. The pulses from the photomultiplier tube were amplified and then analyzed using a single channel analyzer (SCA) to select the pulses corresponding to the 14.4 keV gamma ray. Only these pulses were stored in the MCA.

Setting the SCA window

A SCA was used to select only those pulses corresponding to the 14.4 keV gamma radiation. The window was set in the usual manner. Fig. 6 is a reproduction of the spectra as displayed on the screen of an oscilloscope showing the choice of window width and window position.

The Cryostats

The first cryostat

It was necessary to construct a cryostat so that the experiment could be performed at 77 °K since at this low temperature the recoil-free fraction is significantly larger.

A cross sectional view of the first cryostat constructed is shown in Fig. 7.
Figure 6. The setting of the SCA.
Figure 7. Cross sectional view of first cryostat.
Key to Figure 7.

1 - Styrofoam lid. Covered inside and outside with aluminum foil to form a moisture barrier.

2 - Styrofoam body. Covered inside and outside with aluminum foil to form a moisture barrier except in region 10.

3 - Flexible rubber seal to reduce warming of interior by convection.

4 - Drive rod extension. Made of 3/16 inch stainless steel tube turned down on lathe until walls were 0.010" thick to minimize heat loss by conduction and also to make the mass of moving parts as small as possible.

5 - Aluminum coupling ring. Ring epoxied to body and provided with set screw to make firm mechanical link between the body and the dewar.

6 - Cold finger. Made of 1/2 inch copper rod and extending to within 1/2 inch of the bottom of the dewar.

7 - Phosphor-bronze flat spring. Soldered to and carrying weight of the drive rod extension.

8 - Source holder with source inside.

9 - Absorber holder with absorber inside.

10 - Photomultiplier tube cavity.
One advantage of this cryostat is that both the source and the absorber are kept cold. Thus not only is the recoil-free absorption increased but also the recoil-free emission (or effective source intensity) is increased. However there are some disadvantages. The long extension of the drive rod made the drive more difficult to align. It also introduced the possibility of flexing of the drive rod.

The only physical link between the source and the body of the drive was through the styrofoam encasement. This puts a flexible medium between two components which should be coupled as rigidly as possible to eliminate any motion between the source and the absorber other than the desired motion produced by the drive.

A third disadvantage was that the dewar had to be filled through the hole which also contained the cold finger. For this reason it was necessary to remove the cryostat from the dewar each time the dewar was to be refilled, typically every one and one-half days. During this process the source and absorber would warm and the experiment could not proceed at maximum efficiency until they were recooled.

Finally, the copper box in which the absorber was located was made quite small so that the cooling of the absorber would be as efficient as possible. This made it very difficult to change absorbers.

These last two disadvantages did not directly affect the experimental results but they did add to the overall dissatis-
faction with the first cryostat.

The second cryostat

The second cryostat which was constructed eliminated all the disadvantages of the first one. However, it also failed to retain the one favorable aspect, that the absorber and the source were both cooled. Fig. 8 is a cross sectional view of the second cryostat.
Figure 8. Cross sectional view of second cryostat.
Key to Figure 8.

1 - Connecting flange. Cryostat bolts to this stainless steel flange.

2 - Liquid nitrogen enters cryostat here.

3 - Outer jacket. Made of thick walled stainless steel tube.

4 - Vacuum. To prevent heat from being conducted to inner jacket.

5 - Inner jacket. Made of thick walled stainless steel tube.

6 - Mylar window. Mounted in a piece of aluminum so that assembly is removable.

7 - Absorber holder and absorber.

8 - Mylar window. Epoxied into stainless steel block; not removable.

9 - Copper cold finger. Silver soldered to inner jacket to provide path for heat flow away from absorber.
RESULTS

Experimental Results

The source

The source was purchased from New England Nuclear Corp. and consisted of about 1 m curie of Co-57 diffused into a 0.001" Pd matrix.

Ferric oleate

At room temperature there was no resonance absorption apparent in ferric oleate (Fe O1). However, at liquid nitrogen temperature a measurable effect was observed. This is shown in Fig. 9-11.

The experimental data were fitted with a theoretical curve using the computer program described in Appendix A. Then, using the resonance absorption locations as determined by this program, the parameters of the fields at the iron site were calculated. These are listed in Table I.

Ferric stearate

A slight effect was observed at room temperature in the case of ferric stearate (Fe St). At liquid nitrogen temperature the effect was quite pronounced. These results are shown in Fig. 12 and Fig. 13. These data were treated as described above and the parameters which were calculated are listed in Table I.

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Figure 9. Mossbauer Spectrum of Co-57 in Pd source and ferric oleate absorber at room temperature.
Figure 10. Mossbauer spectrum of a ferric oleate absorber and Co-57 in Pd source at liquid nitrogen temperature. The four resonances in this spectrum are shown below to be due to magnetic splitting.

Figure 11. Mossbauer spectrum of ferric oleate absorber and Co-57 in Pd source at liquid nitrogen temperature showing the six resonances.
Figure 12. Mossbauer spectrum of ferric stearate absorber and Co-57 in Pd source at room temperature.
Figure 13. Mossbauer spectrum of ferric stearate absorber and Co-57 in Pd source at liquid nitrogen temperature.
Table I

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<th>Isomer Shift (mm/sec)</th>
<th>Magnetic Splitting (mm/sec)</th>
<th>Magnetic Field (kOe)</th>
<th>Quadrupole Splitting (mm/sec)</th>
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<tr>
<td>Fe St *</td>
<td>.07 ± .02</td>
<td>Not Resolved</td>
<td>--</td>
<td>.60 ± .10</td>
</tr>
<tr>
<td>Fe St **</td>
<td>.25 ± .04</td>
<td>Not Resolved</td>
<td>--</td>
<td>.75 ± .10</td>
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<tr>
<td>Fe 01 **</td>
<td>.33 ± .06</td>
<td>2.75 ± .30</td>
<td>4.00 ± 4.00</td>
<td>--</td>
</tr>
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</table>

* room temperature
** liquid nitrogen temperature

Discussion

Models for Fe St and Fe 01

Fig. 14 indicates the proposed model for Fe St. The bond resonance indicated by the dashed line allows the carboxyl groups to fulfill the requirement that iron have a coordination number of six. The resonance also has a stabilizing effect on the carboxyl bonding.
Fig. 15 indicates the proposed model for Fe O1. Again the requirement of a coordination number of six for iron is fulfilled. This time, however, the double bond is used as an electron source.

Figure 15. Ferric oleate indicating the use of the double bond as an electron source.

The most dramatic difference between the two complexes was the presence of a large magnetic field in the case of the Fe O1 and the essentially zero magnetic field of the Fe St. The magnetic field could conceivably be the result of one of the following: 1) the outer unpaired, nonbonding electrons, 2) the polarization of the core or inner electrons and 3) the nucleus itself.
Magnetic fields produced by nuclei are three orders of magnitude smaller than those produced by electrons and are too small to give rise to a field of 1400 kOe. It is anticipated that fields this large at the nucleus would be caused primarily by outer, unpaired electrons of the atom and to polarized electrons of the core. Watson and Freeman state that though such factors as covalent bonding, charge transfer and crystal field effects may have some effect, the dominant contribution to the effective magnetic field at the nucleus of Fe$^{3+}$ arises from the polarization of the core electrons by the outer, unpaired, nonbonding electrons. The field at the nucleus is thus considered to be due to the outer, unpaired, nonbonding electrons either directly or indirectly via polarization of the core electrons.

Nonbonding electrons generally occupy filled subshells and are thus paired and contribute nothing to the magnetic field. However, for Fe$^{3+}$ the 3d subshell has only 5 electrons and, therefore, is not filled. This provides the possibility of a significant magnetic field being produced by the 3d electrons which are not paired or by the polarization of the core electrons by the unpaired 3d electrons. Fig. 16 indicates the possible orientations of the 3d electrons in the Fe$^{3+}$ ion. The high spin case (Fig. 16.a) produces a large magnetic field, the intermediate spin case (Fig. 16.b) produces an intermediate magnetic field and the low spin case (Fig. 16.c) produces a correspondingly low magnetic field.

The widely differing magnetic fields observed experimentally would lead one to the conclusion that the high spin and low spin
Figure 16. Possible orientations of the nonbonding electrons in the ferric ion. The ↑ represents the spin of the nonbonding electrons and the ** represents orbitals used in hybridization. The hybridization column refers to the composition of the hybridization orbitals used to give Fe+++ a coordination number of 6.

Dark Color Light Color

Figure 17. Splitting of Molecular Orbitals. (Diagram is from reference 10, page 292)
cases represent Fe Ol and Fe St, respectively. The exclusion of the intermediate spin case is supported by Pauling's statement that this case is extremely unusual.

Further evidence for the high spin case and the low spin case is furnished by the colors of the substances. The ferric stearate is yellowish white indicating that most of the light that strikes it is reflected. The ferric oleate is dark reddish brown indicating that much of the light which strikes it is absorbed. This is interpreted to mean that the molecular orbitals are more widely split in the stearate than in the oleate; the wide splitting prohibiting optical absorption (see Fig. 17).

This is also the prediction one would make based on the proposed models. In the high spin case the bonding of the ligands to the iron is accomplished by the use of sp$^3$d$^2$ hybridized orbitals, whereas, in the low spin case, d$^2$sp$^3$ hybridized orbitals are used. In each case the hybridized orbitals are very similar; the only difference being that 4d orbitals are used in one case and 3d orbitals are used in the other. The sp$^3$d$^2$ orbitals would thus extend farther from the nucleus than would the d$^2$sp$^3$ orbitals.

One observes from the models that it is more difficult for the double bond of the Fe Ol to overlap the hybridized orbitals than for the resonant bond structure simply because size limits the approach of the carbon chain containing the double bond. Further, if the double bond is part of the same ligand which is attached via a carboxyl group, then there is a nine carbon (plus oxygen plus iron) ring formed. Rings of this size tend to be unstable due to
bond angle deformation. The resulting straightening tendency of the ring would tend to withdraw the electrons of the double bond from the bonding orbitals. The more stable complex of Fe O1 is thus formed with the high spin Fe$$^{3+}$$ and the sp$$^3$$ d$$^2$$ orbitals. Conversely, the more stable complex for the Fe St is that which is formed with the low spin Fe$$^{3+}$$ and the d$$^2$$ sp$$^3$$ orbitals. These conclusions, based on the proposed models, are in good agreement with the experimental results.

The case of the electric field gradient is not so clear cut. The difficulty lies not in the spectrum of the Fe St, which exhibits a readily interpretable effect, but in the spectrum of the Fe O1, which has a large magnetic splitting. When both a magnetic interaction and an electric quadrupole interaction occur, the spectrum may be quite complex and very difficult to interpret, depending upon the relative size and orientation of the fields$^{13}$. It is not clear from the data whether or not there is any electric quadrupole interaction in the case of Fe O1.

The bidentate bonding suggested for Fe St would most logically occur between adjacent corners of the octahedron characteristic of the iron. This being the case, there would result three identical ligands located in a plane with an angular separation of 120 degrees, producing an axially symmetric electric field. This axially symmetric field would, according to Boyle and Hall$^{14}$, produce a doublet which would have lines of equal intensities. The proposed model for Fe St thus predicts the results obtained experimentally.
Unfortunately the isomer shift does not give one much comparative information in this case. This is because the isomer shifts are relatively small and are probably produced by different mechanisms in the two cases.

In the transition metals an increase in the covalent nature of the bonding produces two opposing effects on the s-electron density at the nucleus. First the ls-electron density is increased, thus increasing the total s-electron density at the nucleus and second, the 3d-electron density is increased, thus shielding the nucleus from the 3s-electrons and decreasing the total s-electron density at the nucleus. Investigations reported by Danon15 indicate that in the high spin case the contribution of the ls-electrons dominates and that in the low spin case the shielding by the 3d-electrons is the dominant factor.

It is impossible to say whether the Fe St or Fe 01 forms bonds which have the greater degree of covalency since an increase in the covalent nature of one implies a relative decrease in the other, and the resulting isomer shifts will be in the same direction. It is impossible, then, to predict from the models the relative isomer shifts. However, since the shifts predicted by the models are in the same direction, one would be greatly surprised if the isomer shifts were considerably different, and so, to this extent, the predicted isomer shifts are consistent with those found experimentally.
Figure 18. Axial symmetry of ferric stearate. The dot in the center indicates the axis of symmetry.
CONCLUSIONS

The divergent results obtained for Fe St and Fe O1 were certainly unexpected and yet a reasonable explanation of these results was possible. Models for Fe St and Fe O1 (Fig. 14 and Fig. 15) were proposed which were based on the experimental results and, although it was not possible to prove conclusively that the experimental results were a necessary consequence of the models, in no case was there any inconsistency. In fact, all experimental findings could be inferred from the models.

Several aspects of the investigation could legitimately receive more intensive consideration. First among these would be to obtain chemically pure Fe St and Fe O1 to be used in place of the commercially produced substances used here. Second, the number of unpaired electrons in each compound could be inferred from the results of magnetic susceptibility experiments. The number of unpaired electrons found by this method could then be compared with the number of unpaired electrons in each of the proposed models. Finally, if a more intense source were used, it might be possible, due to the better statistics and reduced electronic drift, to detect electric quadrupole splitting in the Fe O1, thus further confirming or perhaps denying the model proposed for the Fe O1.
APPENDIX A

Computer Program

ZZDUP
*DELETWILSON
ZZFOR
*LDISKWILSON
*FANDK0808

O DIMENSION F(6), W(6), C(6), BG(6), STORE(6),
1 STORW(6), STORC(6), STORBG(6), DATA (256),
2 IDATA(512), DATSQ(256), ESQD(6)
O COMMON CHI2, STRCHI, E, W, C, BG, STORE, STORW,
1 STORC, STORBG, NO, K, DATA, WSQ4, DATSQ

500 READ 1, NRUN, MON, NDAY, NYEAR, VEL, NO
1 FORMAT (7X13, 10X12, 2(1X12), 25XF7.2, 17X12)
PUNCH 2, NRUN, MON, NDAY, NYEAR
2 FORMAT (10X6HRUN NO14, 30X6HDATA 12m2(1H/12),/
READ 3
3 O FORMAT (10X55H SOURCE INFO GOES HERE
1 )
PUNCH 3
READ 4
4 O FORMAT (10X55H ABSORBER INFO GOES HERE
1 )
PUNCH 4
VEL = VEL * 0.059
PUNCH 5, VEL
5 FORMAT (/10X16HVELOCITY/CHANNELF7.3, 8H MM/SEC
READ 6, IFOLD, BG(1)
6 FORMAT (21X13, 18XF8.0)
PUNCH 7, IFOLD
7 FORMAT (/10X22HFOLDED AFTER CHANNEL 14,/
READ 8, ( E(I), W(I), C(I) , I = 1,NO)
8 FORMAT (2F7.03, F7.5)
READ 9, IDATA
9 FORMAT (818)
IF (IFOLD - 256) 40, 40, 41
40 DO 100 I = 1, IFOLD
J = IFOLD + 1 - I
K = IFOLD + I
100 DATA(J) = IDATA(J) + IDATA(K)
K = IFOLD
GO TO 42
41 NN = 0
DO 101 K = IFOLD, 511

-36-
L = 512 - K
M = K + 1
N = IFOLD - NN
DATA (L) = IDATA(N) = IDATA(M)

101 NN = NN = 1
K = 512 - IFOLD

42 DO 43 J = 1,K
43 IDATA(J) = DATA(J)

45 SQRTBG = SQRTF(BG(1))
WAQ4 = (W(1)*W(1))/4.0

46 C(J) = C(J) * W(1)/6.28

48 DATSQ(J) = DATA(J)*DATA(J)
CALL CHISQD

CHI1ST = CHI2
STRCHI = CHI2
STORBG(1) = BG(1)

49 STORJ(J) = C(J)
II= 0
JJ = 0
DELL = 1.0

30 W(1) = W(1) + DELL
JJ = JJ + 1
WSQ4 = (W(1)*W(1))/4.0

300 C(J) = C(J) * W(1)/6.28
CALL CHISQD

DO 301 J = 1,N0
301 C(J) = C(J) * W(1)/6.28

31 II = II + 1
IF (II - 2) 33,34,34
33 IF (JJ - 1) 35,35,34

35 W(1) = W(1) - DELL
DELL =~- DELL
GO TO 30

34 W(1) = STORW(1) + 0.33333
WSQ4 = (W(1)*W(1))/4.0

341 C(J) = C(J) * W(1)/6.28
CALL CHISQD

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DO 342 J = 1,NO
342 C(J) = C(J) * 6.28/W(1)
IF ( (STRCHI - CHI2 - 1.0) 38,37,37
37 STRCHI = CHIZ
GO TO 400
38 W(1) = STORW(1) - 0.33333
WSQ4 = (W(1)*W(1))/4.0
DO 381 J = 1,NO
381 C(J) = C(J) * W(1)/6.28
CALL CHISQD
DO 382 J = 1, NO
382 C(J) = C(J) * 6.28/W(1)
IF ( (STRCHI - CHI2) - 1.0 ) 39,37,37
39 W(1) = STORW(1)
400 DO 410 J = 1,NO
410 C(J) = C(J) * W(1)/6.28
W(J) = W(1)
WSQ4 = (W(1)*W(1))/4.0
CALL DELTA (C, STORC, NO, 0.009
CALL DELTA (E, STORE, NO, 1.0)
CALL DELTA (BG, STORBG, 1, 3000.)
DO 420 J = 1,NO
420 C(J) = C(J) * 6.28/W(1)
PUNCH 302, CHIST
302 FORMAT (///10X19HFIRST CHI SQUARED = F7.1)
PUNCH 303, STRCHI
303 FORMAT (//10X19HLAST CHI SQUARED = F7.1,/) 
PUNCH 304, STORBG(1)
304 FORMAT (10X19HBACKGROUND = F8.0,////) 
PUNCH 305, (I,E(I),I,W(I),I,C(I), I = 1,NO)
305 0 FORMAT (10X1HEI1,2H =F7.1, 7X1HWI1,2H =F5.1, 
1 7X1HCI1,2H =F6.3,/) 
47 PUNCH 306, (J, IDATA(J) , J = 1,K)
306 FORMAT (10X13,18,17,18,17,18,17,18,17,18,/) 
308 GO TO 500
END
SUBROUTINE DELTA (A, STORA, N, DEL)

C DIMENSION E(6), W(6), C(6), BG(6), STORE(6),
D STORW(6), STORC(6), STORB(6), DATA(256), A(6),
F STORA(6), DATSQ(256)

C COMMON CHI2, STRCHI, E, W, C, BG, STORE, STORW,
G STORC, STORB, NO, K, DATA, WSQ4, DATSQ

DO 56 J = 1,N
II= 0
JJ = 0
DELL = DEL
50 A(J) = A(J) + DELL
JJ = JJ + 1
CALL CHISQD
IF ((STRCHI - CHI2 - 1.0) > 1.0) 51,52,52
52 STRCHI = CHI2
STORA(J) = A(J)
GO TO 50
51 II= II+1
IF (II- 2) 53,54,54
53 IF (JJ - 1) 55,55,54
55 A(J) = A(J) - DELL
DELL = - DELL
GO TO 50
54 A(J) = STORA(J) + DEL/3.0
CALL CHISQD
IF ((STRCHI - CHI2) - 1.0) 58,57,57
57 STRCHI = CHI2
GO TO 56
58 A(J) = STORA(J) - DEL/3.0
CALL CHISQD
IF ((STRCHI - CHI2) - 1.0) 59,57,57
59 A(J) = STORA(J)
CONTINUE
RETURN
END
SUBROUTINE CHISQD
0 DIMENSION E(6), W(6), C(6), BG(6), STORE(6),
1 STORW(6), STORC(6), STORBG(6), DATA(256),
2 DATSQ(256), ESQD(6)
0 COMMON CHI2,STROH, E, W, C, BG, STORE, STORW,
1 STORC, STORBG,NO, K, DATA, WSQ4, DATSQ
CHI2 = 0.0
DO 200 J = 1, NO
200 ESQD(J) = E(J)*E(J)
DO 201 J = 1, K
XJ = J
SUM = 0.0
DO 202 I = 1, NO
202 SUM = SUM = C(I)/(XJ*(XJ - 2.0*E(I)) + ESQD(I)
1 + WSQ4 )
CALINT = BG(1) - BG(1)*SUM
201 CHI2 = CHI2 + (CALINT*(CALINT - 2.0*DATA(J))
1 + DATSQ(J))/BG(1)
PUNCH 1000, CHI2
1000 FORMAT (F10.1)
RETURN
END
Explanation of the Computer Program

The program is written in Fortran IID language and is stored on a disk to facilitate its use. The program folds the raw data and either punches it out (sense switch 1 in the 'on' position) or it fits the data with the best theoretical curve (sense switch 1 in the 'off' position) using the chi squared criterion. The program varies the energy position of each absorption dip (E), the intensity, expressed as a decimal, of each absorption dip (C) and the background (BG) individually but the energy widths of the absorption dips (W) together. The amount by which the program varies each parameter can be changed. For the case of E, C and BG this is accomplished by changing the last variable in the appropriate Call Delta statement. For W the value of Dell in statement $l_{9} + 0.03$ must be changed.

The uncertainties that the program introduces are given below.

For E: $\pm 1/6$ Dell$^{*}$ channels (presently $\pm 1/6$ channels).
For W: $\pm 1/6$ Dell$^{**}$ channels (presently $\pm 1/6$ channels).
For C: $\pm 1/6$ Dell$^{*}$ (presently $\pm 0.1\%$).
For BG: $\pm 1/6$ Dell$^{*}$ counts (presently $\pm 500$ counts).

The input must be as follows.

The first card must contain the run number (NRUN), the month (MON), the day (NDAY), the year (NYEAR), the velocity per channel

$^*$ This Dell is in the appropriate Call Delta statement.
$^{**}$ This Dell is in the body of the program.

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in mm/sec. (VEL) and the number of absorption dips that the data contains (NO).

The second card must contain information about the source.
The third card must contain information about the absorber.
The fourth card must contain the number of the channel after which the data is to be folded (IFOLD) and an estimate of the background (BG(1)).

The next 'NO' cards (one for each absorption dip) each contains an estimate of the position of an absorption in channels (E), an estimate of the width of the absorption in channels (W), and an estimate of the intensity of the absorption written as a decimal fraction (C).

The last 64 cards contain the raw data.

For a typical output see Appendix B.
### Typical Output of Computer Program

**RUN NO 13**

DATA 5/15/66

**SOURCE** FE IN PD AT ROOM TEMP MOVING

**ABSORBER** FERRIC OXIDE AT ROOM TEMP

**VELOCITY/CHANNEL** 0.000 MM/SEC

**FOLDED AFTER CHANNEL** 256

**FIRST CHI SQUARED** = 331.1

**LAST CHI SQUARED** = 267.7

**BACKGROUND** = 389000

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APPENDIX C

The Drive

A reference voltage which varies linearly with time was needed to govern the motion of the source. In order to obtain this voltage, the circuit shown below was constructed.

![Circuit Diagram]

R1 - 100K
R2 - 10K
R3 - 500K
R4 - 15K
R5 - 100K
R6 - 0K
P1 - 1 Meg pot
P2 - 100K 10 turn pot

Z1 - 1N1511, 8.2 V Zener (4)
Z2 - 1N1509, 5.6 V Zener (2)
OA-1, 2 & 3 - Philbrick No. P 65A Operational Amplifier
OA-4 - Philbrick No. P 66A Operational Amplifier

Figure 19. A schematic diagram of the integrating circuit.
The address of the MCA is advanced from one channel to the next by a positive pulse of about 6 to 8 volts which is obtained from the sweep circuit of a Tektronics 503 oscilloscope. The MCA provides a square wave as it sweeps through the 512 channels: +1/4 volts while the address is any channel from 1 to 256, -1/4 volts while the address is any channel from 257 to 512. This square wave is integrated by the circuit shown in Fig. 19. The result is a triangular wave with the same period as the square wave. One thus has a reference voltage which varies with time precisely as one wants the velocity of the source to vary with time. The velocity is forced to vary as the reference voltage varies via a feedback network.

A coil and a velocity transducer core are rigidly fixed to the drive shaft. The drive coil moves the shaft and the transducer monitors the movement of the drive shaft and all that is attached to it. The voltage produced by the transducer is, of course, proportional to the velocity of the drive shaft.

As long as the velocity of the drive shaft changes with time exactly as the reference voltage the difference between the reference voltage and the transducer induced voltage is zero, hence there is no driving signal. Any deviation from this produces a finite voltage difference which is amplified by the linear DC amplifier and applied to the drive coil.

The linear DC amplifier is a Dana Amplifier Model 3520, the transducer is a LVsyn Transducer Model 6LV2, and the drive coil
(with its magnet) is from a North American Philips, Company Model AD 3701 AM, 8 ohm speaker.
APPENDIX D

Mathematical Justification of Fig. 3.d

Let \( R \) be the distance from the detector to the equilibrium position of the source and \( x \) be the displacement of the source from this equilibrium position. The solid angle (\( \Omega \)) subtended by the source of area \( A \) is then given by

\[
\Omega = \frac{A}{(R + x)^2} = \frac{A}{R^2} \left(1 + \frac{x}{R}\right)^{-2}.
\]

But since \( x/R \ll 1 \), we have

\[
\Omega = \frac{A}{R^2} \left(1 - 2\frac{x}{R} + 3\left(\frac{x}{R}\right)^2 - 4\left(\frac{x}{R}\right)^3 + \ldots\right),
\]

therefore, to a first order approximation, \( \Omega \) depends linearly on \( x \). Hence

\[
\Omega = \frac{A}{R^2} \left(1 - 2\frac{x}{R}\right).
\]

Points of inflection of \( \Omega \) occur when points of inflection of \( x \) occur, i.e., when

\[
\frac{dx}{dt} = 0 \quad \text{but} \quad \frac{dx}{dt} = v,
\]

where \( v \) is the velocity of the source; therefore, the maxima and minima of \( \Omega \) occur when \( v = 0 \). It is apparent that a minimum occurs when \( v \) is in transition from a negative value to a positive value and a maximum occurs during the transition from a positive value to a negative value.
BIBLIOGRAPHY