A Mössbauer Study of Temperature-Dependent Intervalence Charge Transfer in Ilvaite

by

Daniel Arthur Nolet

S.B., Massachusetts Institute of Technology, (1977)

Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science at the Massachusetts Institute of Technology (May, 1977)

Signature of Author

Department of Earth and Planetary Sciences, May, 1978

Certified by

Thesis Supervisor

Accepted by

Chairman, Departmental Committee
A MOSSBAUER STUDY OF TEMPERATURE-DEPENDENT
INTERVALENCE CHARGE TRANSFER IN ILVAITE

by

Daniel Arthur Nolet

Submitted to the Department of Earth and Planetary Sciences on May 12, 1978 in partial fulfillment of the requirements for the Degree of Master of Science.

Abstract

The mixed valence compound ilvaite, CaFe$_{2}^{2+}$Fe$_{3}^{3+}$Si$_{2}$O$_{8}$ (OH), is reputed to show strongly temperature-dependent Fe$^{2+}$-Fe$^{3+}$ charge transfer. Previous studies report the resolution of discrete valence states below 320ºK. The ilvaite structure is especially conducive to charge transfer. Fe(A) octahedra share edges to form double chains parallel to c. Fe(B) octahedra share edges with four Fe(A) octahedra. The Mössbauer spectra of a suite of naturally occurring ilvaites at temperatures from 80 to 575ºK were recorded. A constrained fitting procedure resolved doublets assigned to Fe$^{2+}$(A), Fe$^{2+}$(B), Fe$^{3+}$(A), Fe$^{2+}$(A)-Fe$^{3+}$(A) \( \perp \) c and Fe$^{2+}$(A)-Fe$^{3+}$(A) \( \parallel \) c. The temperature dependence of the charge transfer doublets indicates that, contrary to prior work, a gradual transition from discrete valence states to intervalence charge transfer takes place (with the appearance of charge transfer peaks) over a broad temperature range and transfer is incompletely quenched at 80ºK. Models for charge transfer mechanisms have been explored and necessary variables discussed.

Thesis Supervisor: Roger G. Burns
Title: Professor of Mineralogy and Geochemistry
ACKNOWLEDGEMENTS

Several samples employed in this study were provided by the Harvard Mineralogical Collection and I am very grateful to Dr. Clifford Frondel for his generosity. I would like to thank Dr. Alan Parkes for his assistance in microprobe analysis and Peter Cunningham for electronics consultation. Also thanks are due Roxanne Regan for assistance in many things, not least in typing this manuscript. Useful discussions, devil's advocacy, and much support and love came from Margery Osborne and Kay Parkin. I owe the greatest debt to Dr. Roger Burns who introduced me to Mössbauer spectroscopy, supported and encouraged me throughout my research, and provides an example of a scientist: one who measures, probes, and analyzes the curious things of the world, in a harsh scientific environment and yet is above all a person -- considerate, caring, and gentle.

This thesis is dedicated to my friend and wife, Teresa. Her support, personally and scientifically, has been enormous. May she always remain a sign of Presence in this world.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>2</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>3</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>4</td>
</tr>
<tr>
<td>LIST OF FIGURES AND TABLES</td>
<td>5</td>
</tr>
<tr>
<td>CHAPTER 1</td>
<td>8</td>
</tr>
<tr>
<td>1.1 Statement of the Problem</td>
<td>8</td>
</tr>
<tr>
<td>1.2 Occurrence and Paragenesis</td>
<td>11</td>
</tr>
<tr>
<td>1.3 Structure</td>
<td>16</td>
</tr>
<tr>
<td>1.4 Previous Mössbauer Work</td>
<td>25</td>
</tr>
<tr>
<td>1.5 Experimental Plan</td>
<td>27</td>
</tr>
<tr>
<td>CHAPTER 2</td>
<td>30</td>
</tr>
<tr>
<td>2.1 Microprobe Analyses</td>
<td>30</td>
</tr>
<tr>
<td>2.2 Unfit Mössbauer Spectra</td>
<td>32</td>
</tr>
<tr>
<td>2.3 Mössbauer Fitting Procedures</td>
<td>40</td>
</tr>
<tr>
<td>CHAPTER 3</td>
<td>52</td>
</tr>
<tr>
<td>3.1 Final Mössbauer Parameters</td>
<td>52</td>
</tr>
<tr>
<td>3.2 Site Occupancy</td>
<td>64</td>
</tr>
<tr>
<td>3.3 Electron Hopping - A Model</td>
<td>66</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>80</td>
</tr>
<tr>
<td>APPENDICES</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES AND TABLES

FIGURE 1. PROJECTION OF THE ILVAITE STRUCTURE \( \perp c \) (Beran and Bittner, 1974) 18
FIGURE 2. PROJECTION OF THE ILVAITE STRUCTURE \( \perp b \) 19
FIGURE 3. PROJECTION OF ONE UNIT OF Fe(A) OCTAHEDRAL CHAINS 22
FIGURE 4. UNFIT MöSSBAUER SPECTRUM OF IL 9 300°K 33
FIGURE 5. UNFIT MöSSBAUER SPECTRUM OF IL 8 300°K 34
FIGURE 6. UNFIT MöSSBAUER SPECTRUM OF IL 5 300°K 35
FIGURE 7. MöSSBAUER TEMPERATURE PROFILE OF IL 7 80-390°K 37
FIGURE 8. MöSSBAUER TEMPERATURE PROFILE OF IL 3 80-390°K 38
FIGURE 9. MöSSBAUER TEMPERATURE PROFILE OF IL 4 80-390°K 39
FIGURE 10. FIT HIGH VELOCITY REGION OF THE MöSSBAUER SPECTRUM OF IL 3 80°K 43
FIGURE 11. FIT HIGH VELOCITY REGION OF THE MöSSBAUER SPECTRUM OF IL 3 200°K 44
FIGURE 12. FIT HIGH VELOCITY REGION OF THE MöSSBAUER SPECTRUM OF IL 3 320°K 45
FIGURE 13. FIT HIGH VELOCITY REGION OF THE MöSSBAUER SPECTRUM OF IL 3 340°K 46
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 4</td>
<td>Mössbauer Parameters from IL 3 Temperature Profile</td>
<td>53</td>
</tr>
<tr>
<td>Table 5</td>
<td>Regression Fit Parameters for Functions Fit to Figures 18 and 19</td>
<td>56</td>
</tr>
</tbody>
</table>
1.1 **Statement of the Problem**

In recent years much interest has been shown concerning intervalence compounds. Many of these compounds exhibit properties such as anomalous color, electrical conductivity, and magnetic ordering, not directly attributable to electronic transitions of a single cation. Various charge transfer mechanisms have been proposed to account for these properties. Of greatest interest in geological materials are $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$, $\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$, $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$, all homonuclear charge transfers, and various heteronuclear $\text{Fe} \rightarrow \text{Ti}$ and $\text{Fe} \rightarrow \text{Mn}$ charge transfers. Robin and Day (1967) have proposed a classification system for intervalence compounds. Class I compounds are those which show no charge transfer and whose properties are the sum of the properties of their components. Class III compounds, on the other hand, show charge transfer to the extent that it is impossible to resolve discrete valence states and the compound is best characterized by an "averaged" oxidation state with anomalous properties. Class II compounds exhibit an intermediate range of properties and various degrees of "mixing" of oxidation states.
Ilvaite, $\text{CaFe}_{2}^{2+}\text{Fe}^{3+}\text{Si}_{2}\text{O}_{8}$(OH) is regarded as a Class II compound (Gerard and Grandjean, 1971; Grandjean and Gerard, 1975). It is of particular interest that the amount of "mixing" is believed to be strongly temperature dependent. The aim of the current investigation is to examine the effects of composition and temperature on a suite of naturally occurring ilvaites and to explore the implications of the results for models of inter-valence charge transfer systems.

Principal use was made of the technique of Mössbauer spectroscopy. The Mössbauer effect allows the resolution of tiny energy differences in $^{57}\text{Fe}$ atomic environments due to differences in oxidation state, coordination number, and site symmetry. Mössbauer spectroscopy measures transitions between nuclear quantum levels analogous to electronic quantum levels. Gamma-rays of appropriate energy to excite $^{57}\text{Fe}$ nuclei are provided by $^{57}\text{Co}$ radioactive decay. These $\gamma$-rays are absorbed and re-emitted, setting up resonance in the sample. Slight energy differences between nuclei due to different electronic environments are compensated for by providing the $\gamma$-ray source with a constant acceleration Doppler shift energy and "sweeping" an energy spectrum.
Common iron species in minerals exhibit two typical Mössbauer parameters, isomer shift and quadrupole splitting. Isomer shift is the location of the midpoint of the spectrum of the absorbing species with respect to some zero of energy. Our spectra are reported relative to iron foil (Fe metal) calibration. Quadrupole splitting is the energy separation of the two peaks which typically occur in $^{57}$Fe absorbers due to transitions from a nuclear ground state with nuclear angular momentum of $\pm 1/2$, to a split excited state with nuclear angular momenta of $+1/2$ and $+3/2$. This doublet spectrum, offset from zero energy, is typical of all $^{57}$Fe absorbers, except those which are magnetically ordered. In such a case, the $\pm$ degeneracy of the nuclear levels is lifted and a six peak spectrum results. Since the lifetime of the Mössbauer transition is on the order of $10^{-7}$ sec, the excited nucleus "sees" only electronic states which are long-lived compared to $10^{-7}$ sec. Short-lived states which occur with sufficient frequency may, however, be observable as "averaged" between the ground and excited states, though the excited state can correctly be said to be absent from the Mössbauer spectrum. For a more complete discussion of Mössbauer theory and parameters,
including some geochemical and inorganic chemical applications, see Bancroft (1973).

1.2 Occurrence and Paragenesis

The name ilvaite comes from the Latin for Elba, referring to the type locality of the mineral, a skarn at Capo Calamita on the island of Elba, Italy. Ilvaite, also called "lievrite" for M. Lelievre, its discoverer, occurs mainly as a late-stage hydrothermal alteration product in skarn deposits. Mineral samples used in this study are listed in Table 1, along with several other locations where ilvaite has been reported.

Skarns are formed in contact metasomatic zones, replacing limestones or dolomites near granitic intrusives, and have world-wide occurrence in space and time. Interest in skarn deposits has been great for many years due to their economic value as ore sources. Burt (1972) gave a list of elements currently recovered from skarn deposits:
TABLE 1. LOCATION INDEX FOR ILVAITE SAMPLES

<table>
<thead>
<tr>
<th>IL</th>
<th>Location Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ELBA, ITALY (MIT COLLECTION)</td>
</tr>
<tr>
<td>2</td>
<td>ELBA, ITALY (UNIVERSITY OF CAMBRIDGE #1413)</td>
</tr>
<tr>
<td>3</td>
<td>ELBA, ITALY (WILKE, PALO ALTO, CA.)</td>
</tr>
<tr>
<td>4</td>
<td>SANTA EULALIA, MEXICO (MIT COLLECTION)</td>
</tr>
<tr>
<td>5</td>
<td>SANTA EULALIA, MEXICO (MIT COLLECTION)</td>
</tr>
<tr>
<td>6</td>
<td>SIORAR SUIT, GREENLAND (HARVARD 86189)</td>
</tr>
<tr>
<td>7</td>
<td>DANNEMORA, SWEDEN (HARVARD 85091)</td>
</tr>
<tr>
<td>8</td>
<td>SERIPHOS, GREECE (HARVARD 93753)</td>
</tr>
<tr>
<td>9</td>
<td>LACEY MINE, IDAHO (HARVARD 106085)</td>
</tr>
<tr>
<td>10</td>
<td>HANOVER, NEW MEXICO (HARVARD 91858)</td>
</tr>
<tr>
<td>11</td>
<td>TETJUKE, USSR (HARVARD 114518)</td>
</tr>
</tbody>
</table>


- NORANDA, QUEBEC
- TYRNYAUZ, USSR
- DASHKESAN, USSR
- BALKHASH (KARATAS ORE DEPOSIT), USSR
- POIANA RUSCA, ROMANIA
- BINNTAL, SWITZERLAND
- SAN LEONE, SARDINIA
- HORNSEELBACH, GERMANY
- LIVORNO, ITALY
\begin{tabular}{ll}
C & graphite \\
W & scheelite \hspace{1cm} \text{CaWO}_4 \\
Mo & molybdenite \hspace{1cm} \text{MoS}_2 \\
& powellite \hspace{1cm} \text{CaMoO}_4 \\
Sn & cassiterite \hspace{1cm} \text{SnO}_2 \\
Be & helvite \hspace{1cm} \text{(Mn,Fe,Zn)}_8\text{(BeSiO}_4\text{)}_6\text{S}_2 \\
& chrysoberyl \hspace{1cm} \text{BeAlO}_4 \\
Fe & magnetite \hspace{1cm} \text{Fe}_3\text{O}_4 \\
& specular hematite \hspace{1cm} \text{Fe}_2\text{O}_3 \\
Cu & chalcopyrite \hspace{1cm} \text{CuFeS}_2 \\
& bornite \hspace{1cm} \text{Cu}_5\text{Fe}_2\text{S}_4 \\
& cubanite \hspace{1cm} \text{CuFe}_2\text{S}_3 \\
Zn & sphalerite \hspace{1cm} \text{ZnS} \\
\end{tabular}

Of rarer occurrence but still recoverable are elements from the following list:

\begin{tabular}{ll}
Pb & galena \hspace{1cm} \text{PbS} \\
Au & with arsenides, sulfides \\
Ag & with galena \\
As & arsenopyrite \hspace{1cm} \text{FeAsS} \\
Bi & bismuthinite \hspace{1cm} \text{Bi}_2\text{S}_3 \\
Sb & stibnite \hspace{1cm} \text{Sb}_2\text{S}_3 \\
Ba & barite \hspace{1cm} \text{BaSO}_4 \\
& witherite \hspace{1cm} \text{BaCO}_3 \\
\end{tabular}

Impressive beyond the size and scope of the above lists, is a list of those elements which are concentrated in skarn deposits but rarely recovered. These include Mn, B, F, Ti, V, P, Cr, Ni, Co, Hg, Pt, U, Nb, Th, and the rare earth elements. The size of skarn resources is also
an economic consideration; while an individual deposit may be small in areal extent, metasomatic concentration may have greatly enriched a given element. Iron Mountain deposits (southwestern Utah) have Be reserves of 30,000 tons with ore containing 0.4% Be (average crustal abundance of Be is 2.8 ppm).

Many theories have been advanced to explain the formation of skarn deposits. The most widely accepted of these is the infiltration-diffusion theory of Korzhinsky (1948, 1950). The theory postulates the establishment of an unstable chemical system at the intrusive-carbonate contact. This instability is due to high concentrations of Ca on one side of the contact and of Si, Al, Mg, Fe, Na, and K on the other side. The system is then opened to hot aqueous solutions along planes of high porosity and low resistance. Concentration gradients are set up as the system proceeds toward the ultimate goal of uniform composition throughout the areas in contact with the fluids.

Conditions of skarn formation have been estimated by many geologists from field evidence and mineral stability experiments. Most authors agree that skarns are formed by hypabyssal (shallow) intrusives and Smirnov (1976)
gives a range of 500-2000 meters which likely covers the majority of skarn deposits. The thermal history of skarns is complex, beginning with thermal metamorphism from contact with a hot intrusive, through hydrothermal metasomatism and ore emplacement, to late-stage metamorphism (normally retrograde hydration reactions). Burt (1972) gives as estimates for these stages:

- 700-900°C Solidification of the intrusive
- 500-700°C Contact metamorphism
- 400-600°C Hydrothermal metasomatism (skarn formation)
- 300-500°C Ore emplacement
- 200-400°C Late-stage metamorphism

Smirnov (1976) gives a thermal range of 100-900°C, based on experimental measurement of garnet and hedenbergite stabilities and fluid inclusions in skarn minerals.

Burt (1971, 1972) has done extensive work on the stability of ilvaite and another hydrous phase, babingtonite, Ca$_2$Fe$^{2+}$Fe$^{3+}$Si$_5$O$_{14}$(OH), in Ca-Fe-Si skarns. Ilvaite in such skarns is formed primarily by late-stage hydrothermal alteration and retrograde metamorphism of hedenbergite. Relevant reactions are:

$$7 \text{Hed} + \frac{1}{2} \text{H}_2\text{O} + \frac{5}{4} \text{O}_2 = \text{Ilv} + 6 \text{Qtz} + 2 \text{And}$$

$$3 \text{Hed} + 2 \text{CO}_2 + \frac{1}{2} \text{H}_2\text{O} + \frac{1}{4} \text{O}_2 = \text{Ilv} + 2 \text{Cal} + 4 \text{Qtz}$$
Occasionally, however, ilvaite can appear as a primary constituent of the zoned skarn, i.e. as a direct product of metasomatism (e.g. Elba and Sardinia, Bartholome and Dimanche, 1967). Ilvaite occurs in many different assemblages, of which the most common are:

- Ilvaite, hedenbergite, andradite
  - Hanover, New Mexico
  - South Mountain, Idaho
  - Shasta, California
- Ilvaite, quartz
  - Santa Eulalia, Mexico
- Ilvaite, quartz, andradite
  - South Mountain, Idaho
  - Hanover, New Mexico
  - Yaguki, Japan
- Ilvaite, quartz, andradite, magnetite, babingtonite
  - San Leone, Sardinia
- Ilvaite, quartz, calcite, magnetite, hedenbergite, ferroactinolite
- Ilvaite, pyrrhotite, sphalerite, hedenbergite, knebelite
  - Santa Eulalia, Mexico
  - Lima, Peru

1.3 Structure

Early structural work on ilvaite was done by von Gossner and Reichel (1932) who placed ilvaite in the orthosilicates. Takeuchi (1948) agreed with this determination, proposing a structure based on an $\text{SiO}_4$ framework of isolated tetrahedra linked by $\text{Fe}^{2+}\text{O}_6$.
octahedra, with Fe$^{3+}$ in an unusual 5-coordinate site surrounded by four O$^{2-}$ and one OH$^-$.  

The first work placing ilvaite in the sorosilicate class was done by Belov and Mokeeva (1954). A recent structural refinement by Beran and Bittner (1974) confirmed the unambiguous existence of Si$_2$O$_7$ groups in the ilvaite structure, and provides the primary structural reference for this work. Krause (1960) performed UV absorption analysis of ilvaite and Hanisch (1967) verified the OH assignment by the OH stretching frequency in the infrared.

The structure of ilvaite (Pbnm - D$_{2h}^{16}$, a = 8.82Å, b = 13.07Å, c = 5.86Å, Z = 4 CaFe$_2^{2+}$Fe$_2^{3+}$Si$_2$O$_8$(OH)) is characterized by isolated Si$_2$O$_7$ groups linking together double chains of Fe(A) octahedra parallel to c. This framework then provides the ligands for the octahedral Fe(B) site and the seven-coordinate Ca site. Figure 1 shows a projection of the unit cell perpendicular to c. Figure 2 illustrates the FeO$_6$ chains and Fe(B) and Ca sites in a projection perpendicular to b (note the Si sites have been deleted for clarity).

The coordination polyhedra are all distorted from highest symmetry. Fe(A) can be modelled as a nearly
Figure 1. Projection of the ilvaite structure \( \perp c \), showing \( \text{Si}_2\text{O}_7 \) groups (Beran and Bittner, 1974).
Figure 2. Projection of the ilvaite structure \( \perp b \), showing Fe(A) double chains and Fe(B) sites. Si sites have been deleted for clarity.
regular octahedron with a range of M-O distances from 2.006 to 2.172Å, averaging 2.081 ± .058Å. Fe(B) displays tetragonal distortion with four long planar and two short apical M-O distances approximately 2.266Å and 2.039Å, respectively, with a mean of 2.190 ± .129Å and planar O(2) - Fe(B) - O(4) angles of 162.9°. It should also be noted that the Fe(B) site is on the average larger than the Fe(A) site. The seven-coordinate Ca site has a mean M-O distance of 2.411 ± .053Å and is comparable to Ca coordination polyhedra in the minerals titanite (mean Ca-O distance of 2.459Å, Mongiogi and Riva di Sanseverino, 1968), zoisite and clinozoisite (2.461 to 2.67Å, Dollase, 1968). Table 2 gives relevant interatomic distances for the metal-oxygen coordination polyhedra and Figure 3 shows the intermetallic distances for one unit of the octahedral chain.

Several theories have been proposed to describe the distribution of Fe²⁺ and Fe³⁺ over the two Fe sites. Belov and Mokeeva (1954) proposed a scheme with Fe²⁺ occupying Fe(A) (eight sites per unit cell) and Fe³⁺ occupying Fe(B) (four sites per unit cell). Beran and Bittner (1974) proposed occupation of Fe(B) by Fe²⁺ and a statistical distribution of Fe²⁺ and Fe³⁺ over Fe(A).
TABLE 2. INTERATOMIC DISTANCES IN ILVAITE

<table>
<thead>
<tr>
<th></th>
<th>Fe(A)</th>
<th>Fe(B)</th>
<th>Ca</th>
<th>Si(1)</th>
<th>Si(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(1) 2.172Å</td>
<td>O(1) 2.120Å</td>
<td>O(2) 2.399Å</td>
<td>O(2) 1.628Å</td>
<td>O(3) 1.658Å</td>
</tr>
<tr>
<td></td>
<td>O(2) 2.060</td>
<td>O(2) 2.246 (2x)</td>
<td>O(3) 2.411</td>
<td>O(5) 1.640</td>
<td>O(4) 1.658Å</td>
</tr>
<tr>
<td></td>
<td>O(2) 2.044</td>
<td>O(4) 2.285 (2x)</td>
<td>O(4) 2.461 (2x)</td>
<td>O(6) 1.598</td>
<td>O(4) 1.619 (2x)</td>
</tr>
<tr>
<td></td>
<td>O(3) 2.088</td>
<td>O(6) 1.957</td>
<td>O(5) 2.440</td>
<td>O(6) 1.619</td>
<td>O(5) 1.666</td>
</tr>
<tr>
<td></td>
<td>O(4) 2.116</td>
<td>O(7) 2.006</td>
<td>O(7) 2.306</td>
<td>Average 1.624 + .018Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O(7) 2.006</td>
<td>Average 2.190 + .129Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Average 2.081 + .058Å</td>
<td>Average 2.411 + .053Å</td>
<td></td>
<td>Average 1.641 + .025Å</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3. Projection of one unit of Fe(A) double chain showing possible Fe-Fe edge-shared interactions and metal-metal distances.
(Beran and Bittner (1974) also advanced and rejected the theory of complete statistical distribution of Fe$^{2+}$ and Fe$^{3+}$ over both sites.) The case for the latter model is supported by a compilation of Fe$^{2+}$-O and Fe$^{3+}$-O distances for octahedral iron in silicates by Ghose (1969) who gave a mean Fe$^{2+}$-O distance of 2.135Å and Fe$^{3+}$-O distance of 2.025Å. Beran and Bittner's (1974) own compilation yielded a mean Fe$^{2+}$-O distance of 2.155Å and Fe$^{3+}$-O distance of 2.014Å, for six-coordinate iron in silicates and sulfates. The average M-O distance for Fe(B) agrees well with the values for octahedral Fe$^{2+}$, especially for values of silicates with similar components, e.g.

babingtonite, Ca$_2$Fe$^{2+}$Fe$^{3+}$Si$_5$O$_{14}$(OH), with a mean Fe$^{2+}$-O distance of 2.169Å (Araki and Zoltai, 1972). The average Fe(A)-O distance lying between the pure Fe$^{2+}$-O and Fe$^{3+}$-O distances supports an intermediate statistical population of Fe(A). Haga and Takeuchi (1976) performed a neutron diffraction study on an ilvaite sample from the Kamioka Mine, Japan and using Fourier mapping techniques derived a site occupancy of:

\[
\begin{align*}
&\text{Fe(A)} & \text{Fe}^{2+} & 0.478 \\
& & \text{Fe}^{3+} & 0.514 \\
& & \text{Mn} & 0.006 \\
&\text{Fe(B)} & \text{Fe}^{2+} & 0.815 \\
& & \text{Mn} & 0.185
\end{align*}
\]
confirming Beran and Bittner's (1974) assignments. Site occupancies derived from the Mossbauer spectra will be discussed in Section 3.2.

The structural possibilities for \( \text{Fe}^{2+} - \text{Fe}^{3+} \) charge transfer are many as can be seen in Figure 3. \( \text{Fe(A)} \) octahedra form a double chain by edge-sharing both in the xy-plane and along the z-axis. In the z-direction there are two M-M distances (2.83 and 3.03 Å) as each pair of \( \text{Fe(A)} \) octahedra does not lie flat in the xy-plane but is skewed with one \( \text{Fe(A)} \) down (closer to the \( \text{Fe(A)} \) in the chain below it) and one \( \text{Fe(A)} \) up (closer to the site above it). This distortion provides room for the large Ca site in the "hollow" created by the elongated \( \text{Fe(A)} - \text{Fe(A)} \) pair. Also available for electron transfer are \( \text{Fe(A)} - \text{Fe(B)} \) pairs sharing edges. Each \( \text{Fe(B)} \) site shares edges with four \( \text{Fe(A)} \) sites, with M-M distances varying slightly (3.15 to 3.25 Å).

The intermetallic distances in ilvaite are well within the range cited for minerals known to show inter-valence charge transfer transitions (Loeffler et al., 1976; Burns et al., 1977). Loeffler et al. (1976) argue that, all other factors being equal, inter-valence charge transfer occurs preferentially along short metal-metal
distances. Therefore, in ilvaite, \( \text{Fe}(A)^{2+} - \text{Fe}(A)^{3+} \) might be expected to predominate over \( \text{Fe}(B)^{2+} - \text{Fe}(A)^{3+} \). Hush (1967) and Day (1976) also advance the argument, on theoretical grounds, that intervalence charge transfer occurs preferentially between sites of similar symmetry. Again, this leads to the expectation that in ilvaite \( \text{Fe}(A)^{2+} - \text{Fe}(A)^{3+} \) predominates over \( \text{Fe}(B)^{2+} - \text{Fe}(A)^{3+} \).

1.4 Early Mössbauer Work

Previous Mössbauer measurements of ilvaites were made by Herzenberg and Riley (1969), Borshagovskii et al. (1971), Gerard and Grandjean (1971), and Grandjean and Gerard (1975). Herzenberg and Riley analyzed the spectrum in terms of three quadrupole doublets assigned to ferrous doublets assigned to ferrous iron in two crystal sites and ferric iron in a distorted site. They reported Mössbauer parameters with isomer shifts of 1.07, 0.98, and 0.51 mm/sec and quadrupole splittings of 2.36, 2.18, and 1.24 mm/sec, respectively. They used their study to support the Belov and Mokeeva (1954) structure determination and concluded that the ferric iron site should be distorted to produce large quadrupole splitting analogous to epidote (Bancroft et al., 1967). Herzenberg and Riley also reported an asymmetry in
absorption intensities with total high velocity absorption greater by about ten percent than total low velocity absorption. They suggest this asymmetry has only a minor effect on fitting.

Borshagovskii et al. (1971) studied Mn substitution in ilvaite by Mössbauer spectroscopy. Interested mainly in the temperature variation of the Curie point with composition, they resolved only two doublets in the six ilvaites studied, assigned to Fe\textsuperscript{2+} (octahedral) and Fe\textsuperscript{3+} (octahedral). In the range of Mn compositions 0 to 12%, it was found that the Curie point was raised with increasing Mn, until magnetic order could be observed at 80K for samples with 12% Mn.

Gerard and Grandjean (1971) published data on the "electron-hopping process" in ilvaite. They recorded the Mössbauer spectrum of an ilvaite sample from Livorno, Italy over the temperature range of 4.2K to 520K, fitting the spectrum to three doublets assigned to two ferrous and one ferric iron sites. Their attention was drawn to the temperature range 300K to 350K, where an additional absorption is readily apparent between the high velocity ferrous and high velocity ferric peaks. Gerard and Grandjean concluded that "one of the two
ferrous ions undergoes a change which gives it a ferric character." In other words, one high velocity ferrous peak moves to lower velocity with increasing temperature until at 370°K it overlaps with the ferric high velocity peak. Gerard and Grandjean attributed this movement to rapid transfer of an electron from Fe$^{2+}$ to Fe$^{3+}$ and compared the process to electron transfer on the B sites of magnetite at high temperature.

1.5 Experimental Plan

In order to derive an experimental plan, the question asked was, "What was the status of knowledge of inter-valence charge transfer in ilvaite prior to this research?" Structural data gives site preferences of Fe$^{3+}$ for Fe(A) and Mn for Fe(B) which reduce the charge transfer possibilities to Fe$^{2+}$(A)→Fe$^{3+}$(A) $\parallel$ c and $\perp$c and Fe$^{2+}$(B)→Fe$^{3+}$(A) $\perp$c. The fitting of Mössbauer spectra by Gerard and Grandjean (1971) and Grandjean and Gerard (1975) is highly suspect due to the poor quality of the published spectra and the lack of any published fitting parameters such as line widths or $\chi^2$. These authors' interpretations of electron transfer as "assuming a ferric character" are also suspect on mechanistic grounds. Borshagovskii et al.
(1971) did not deal with the effects of Mn substitution on the charge transfer process but rather concerned themselves with variations in the Curie temperature and magnetic ordering. Therefore, we know only that inter-valence charge transfer has been ascribed to ilvaite, that the ilvaite structure is highly conducive to electron delocalization, and that a phenomenon occurs in the Mössbauer spectrum of ilvaite with increasing temperature (i.e. between 300 and 350°C).

The questions which this research attempts to answer are:

1) How does one fit the Mössbauer spectrum of ilvaite in a self-consistent manner for a suite of specimens encompassing a range of temperatures, compositions, and formation conditions?

2) What can be said about the site occupancies and ferrous/ferric ratios derived from Mössbauer measurement as opposed to chemical or x-ray determinations?

3) What are the implications for and restrictions placed upon models of the charge transfer mechanism in ilvaite by the temperature variation of the observed Mössbauer parameters?

To achieve answers to these questions, the following
experimental plan was adopted. First, a suite of natural 
ilvaites was assembled and chemically analyzed to determine 
the range of cation substitutions. Second, the suite of 
ilvaites was measured by Mössbauer spectroscopy at room 
temperature and spectra fit to component peaks, attempting 
to obtain consistency over the compositional range. 
Finally, temperature profiles of the Mössbauer spectra 
of several samples of differing compositions were obtained 
at temperatures above and below room temperature and fit 
to determine temperature variations of Mössbauer parameters. 
Once these results were obtained, theoretical implications 
for questions 2 and 3 above were explored and conclusions 
drawn.
CHAPTER 2

2.1 Microprobe Analyses

The suite of samples of Table 1 were analyzed by a Materials Analysis Corp. electron microprobe maintained by the MIT Department of Earth and Planetary Sciences. Handpicked crystallites were mounted in an epoxy matrix and polished with .5μ corundum grit. Thin carbon coating of the samples assured high conductivities. The data were corrected using GEOLAB correction factors and mineral standards maintained by the facility. Table 3 gives the compositions in weight percent of oxides. The microprobe is unable to distinguish ferrous and ferric iron and thus all iron is reported as FeO. When total weight percentages are corrected for Fe₂O₃ and FeO (by estimates based on stoichiometry) and for the (OH)⁻ also not analyzed and present in the stoichiometric formula, all totals came to equal 100 ± 1 wt.%.

Mn contents of the suite vary from 6.44 wt.% MnO in Il 7 to 0.30 wt.% MnO in Il 8. On the basis of Mn content and after examination of the room temperature Mössbauer spectra, Il 3, Il 4, and Il 7 were chosen as candidates for temperature variant Mössbauer study.
<table>
<thead>
<tr>
<th></th>
<th>IL 1</th>
<th>IL 2</th>
<th>IL 3</th>
<th>IL 4</th>
<th>IL 5</th>
<th>IL 6</th>
<th>IL 7</th>
<th>IL 8</th>
<th>IL 9</th>
<th>IL 10</th>
<th>IL 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>28.86</td>
<td>29.90</td>
<td>29.32</td>
<td>27.18</td>
<td>28.02</td>
<td>29.74</td>
<td>29.78</td>
<td>29.60</td>
<td>29.56</td>
<td>29.71</td>
<td>29.88</td>
</tr>
<tr>
<td>TiO₂</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.01</td>
<td>.01</td>
<td>.01</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
</tr>
<tr>
<td>SnO₂</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>.07</td>
<td>.07</td>
<td>.07</td>
<td>.05</td>
<td>.10</td>
<td>.07</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>.34</td>
<td>.21</td>
<td>.28</td>
<td>.27</td>
<td>.16</td>
<td>.21</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>.28</td>
<td>.78</td>
<td>.63</td>
<td>.10</td>
<td>.10</td>
<td>.16</td>
<td>.28</td>
<td>.91</td>
<td>.35</td>
<td>.08</td>
<td>.16</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>.00</td>
<td>.00</td>
<td>.04</td>
<td>.07</td>
<td>.03</td>
<td>.04</td>
<td>.02</td>
<td>.00</td>
<td>.04</td>
<td>.04</td>
<td>.04</td>
</tr>
<tr>
<td>FeO</td>
<td>51.88</td>
<td>51.35</td>
<td>51.00</td>
<td>51.48</td>
<td>50.64</td>
<td>51.02</td>
<td>45.97</td>
<td>51.87</td>
<td>49.05</td>
<td>46.83</td>
<td>48.61</td>
</tr>
<tr>
<td>MgO</td>
<td>.10</td>
<td>.16</td>
<td>.11</td>
<td>.12</td>
<td>.08</td>
<td>.08</td>
<td>.22</td>
<td>.20</td>
<td>.02</td>
<td>.62</td>
<td>.02</td>
</tr>
<tr>
<td>MnO</td>
<td>1.23</td>
<td>.97</td>
<td>1.49</td>
<td>4.08</td>
<td>4.79</td>
<td>2.11</td>
<td>6.44</td>
<td>.30</td>
<td>4.08</td>
<td>5.49</td>
<td>4.30</td>
</tr>
<tr>
<td>Na₂O</td>
<td>.10</td>
<td>.00</td>
<td>.06</td>
<td>.09</td>
<td>.00</td>
<td>.00</td>
<td>.06</td>
<td>.00</td>
<td>.00</td>
<td>.00</td>
<td>.01</td>
</tr>
<tr>
<td>WO₃</td>
<td>.00</td>
<td>.20</td>
<td>.02</td>
<td>.00</td>
<td>.13</td>
<td>.00</td>
<td>.08</td>
<td>.08</td>
<td>.05</td>
<td>.00</td>
<td>.18</td>
</tr>
<tr>
<td>TOTAL</td>
<td>95.39</td>
<td>96.05</td>
<td>95.50</td>
<td>94.41</td>
<td>94.84</td>
<td>96.23</td>
<td>95.32</td>
<td>95.84</td>
<td>95.61</td>
<td>94.96</td>
<td>95.33</td>
</tr>
</tbody>
</table>

* Element not analyzed
2.2 Mössbauer Spectra

Mössbauer spectra were recorded on an Austin Associates spectrometer with a 50 millicurie $^{57}$Co source in a palladium matrix. Each spectrum was recorded on 512 channels of a 1024 channel multichannel analyzer and the spectrum allowed to acquire greater than $10^6$ counts per channel. Low temperature runs were made employing a "cold finger" arrangement of mounting samples on a copper rod suspended in a reservoir of liquid nitrogen (80°K) or dry-ice/trichloroethylene (200°K). High temperature spectra were recorded by means of a Ranger Electronics furnace and temperature controller designed for Mössbauer work and calibrated with a chrome-alumel thermocouple and external ice point reference.

Unfit Mössbauer spectra at room temperature are shown in Figures 4 - 6. Figure 4 shows a typical ilvaite spectrum with resolution of two ferrous components (at about 2 mm/sec) and one ferric component (about 1.2 mm/sec) at high velocity and strong overlap of the low velocity components (near 0 mm/sec) of all three doublets. Il 8 shown in Figure 5 displays some variation with the innermost high velocity ferrous peak appearing as only a
Figure 4. Unfit Mössbauer spectrum of IL 9 300°K. Two ferrous components resolved at about 2.2 mm/sec.
Figure 5. Unfit Mössbauer spectrum of IL 8 300°K. Ferrous shoulder at 2.1 mm/sec and increased absorption at 1.5 mm/sec.
Figure 6. Unfit Mössbauer spectrum of IL 5 300°K.
Large broad absorption centered near 1.5 mm/sec.
shoulder and some significant absorption in the 1.5 mm/sec region under the minimum between ferrous and ferric in the high velocity region. Again low velocity components are strongly overlapped. Figure 6 shows yet another ilvaite specimen (Il 5) at room temperature. Here only one high velocity ferrous component can be resolved and a large broad absorption is seen centered near 1.5 mm/sec, at higher velocity than the previous position for ferric iron absorption (about 1.2 mm/sec). The low velocity region remains overlapped.

Obviously, the variation in room temperature Mössbauer spectra is extreme and fitting procedures must account for the variations in changing positions, widths, or intensities of absorbing species. In order to obtain another view of the variation in spectral profiles, Mössbauer spectra of three specimens were run over a range of temperatures and are shown in Figures 7-9.

It is readily apparent in Figure 7 (Il 7) that the resolution of two ferrous components at 300°K is lost with increasing temperature as the inner ferrous doublet decreases in intensity concurrent with increased absorption in the 1.4-1.5 mm/sec region. Figure 8 shows the temperature profile of Il 3 in which the 300°K spectrum
Figure 7. Mössbauer temperature profile of IL 7. Note changes in the high velocity profile with increasing temperature.
Mössbauer temperature profile of I.3. Note changes in the high velocity profile with increasing temperature.
Figure 9. Mössbauer temperature profile of II.4. Note changes in the high velocity profile with increasing temperature.
has a shoulder in the high velocity ferrous region (cf. Il 8, Figure 5). This sample shows similar variation to Il 7 (Figure 7) with increasing temperature and greater resolution of a new peak at 390°K centered about 1.5 mm/sec. The room temperature spectrum of sample Il 4 in Figure 9 shows significant absorption around 1.4-1.5 mm/sec and only one ferrous component at high velocity. Again, at 390°K, a separate peak about 1.3-1.4 mm/sec is clearly resolved.

2.3 Spectral Fitting Procedures

Given the variations of spectral profiles in Figures 4 - 9, it becomes necessary to describe these effects in terms of component peak parameters and their variations. We have used a program written by A.J. Stone (Stone et al., 1969) and modified by F.E. Huggins which fits a sum of Lorentzian lines using the Gauss non-linear regression procedure and allowing a variety of constraint packages.

The first attempts to fit the spectra were based on the following assumptions: 1) Since there is no evidence for magnetic ordering, all Fe species will absorb as quadrupole doublets; 2) Components of a doublet can be expected to be equal in width and intensity to a reasonable
approximation; 3) All ferrous species can be expected
to be equal in width to a reasonable approximation;
4) Criteria for goodness of fit are convergence, reduction
of $\chi^2$, consistency between samples and temperatures, and
crystallochemical reasoning. Assumptions 1 and 2 are
supported by theoretical considerations of Mössbauer
absorbers (Bancroft, 1973) which predict quadrupole
doublets of equal width and intensity for non-magnetically
ordered species. Assumptions 2 and 3 are based on
Mössbauer practice and common values found over a wide
range of minerals. Assumption 4 is supported by statisti-
cal arguments for convergence and chi-squared reduction
and by geochemical evidence for consistency. Work is in
progress to verify fits as well by Ruby's MISPIT param-
eter (Ruby, 1973).

Due to the extreme overlap in the low velocity region,
initial fitting attempts were made on the high velocity
evelope only. Three peaks corresponding to one ferric
and two ferrous species were postulated and additional
peaks added to take up excess area. Resolution of more
than three peaks was further justified by significant
decreases in $\chi^2$. It was found that two such additional
peaks were required to fit all spectra. More than two
such peaks made convergence difficult and did not reduce $\chi^2$. Figures 10 - 13 show high velocity fits for IL 3 at various temperatures. These fitted spectra point out the gross variation in peak parameters with temperature. The correlation diagram in Figure 14 shows the consistency of the positions of the five high velocity peaks for the suite of specimens at room temperature. Constraints employed during this stage of fitting were ferrous widths held equal and widths of the two additional peaks held equal.

Having now located the positions, widths, and intensities of the high velocity peaks, their low velocity components were added to each doublet. Initial positions and intensities in the low velocity region were constrained to estimated values and allowed to converge before releasing these constraints. Final fits were obtained holding all ferrous widths equal, both ferric widths equal, and all additional peak widths equal. Intensities, originally held to estimates and later constrained in pairs, were freed, except for the tightly overlapped low velocity areas which required constraints to avoid divergence. Figures 15 - 17 show full ten peak,
Figure 10. High velocity region of IL 3 80°K Mössbauer spectrum fit to five peaks.
Figure 11. High velocity region of IL 3 200°K Mössbauer spectrum fit to five peaks.
Figure 12. High velocity region of IL 3 320\,K Mössbauer spectrum fit to five peaks.
Figure 13. High velocity region of IL 3 340°K Mössbauer spectrum fit to five peaks.
Figure 14. Correlation diagram for the positions of the five high velocity Mössbauer peaks over the suite of samples, all at 300°C.

Position (mm/sec)

2.2
2.0
1.8
1.6
1.4
1.2

Specimen Number

1 2 3 7 8 9 10 11

Fe²⁺(B)
Fe²⁺(A)
Fe-Fe CT(xy)
Fe-Fe CT(z)
Fe³⁺
Figure 15. Full ten peak five doublet fit for the Mössbauer spectrum of IL 3 80°K.
Figure 16. Full ten peak five doublet fit for the Mössbauer spectrum of IL 3 300°K.
Figure 17. Full eight peak four doublet fit for the Mössbauer spectrum of IL 3 390 K.
five doublet fits for Il 3 at several temperatures. Figure 15 at 80°K shows a low intensity for both additional peaks. These peaks can be seen to gradually increase in intensity relative to the ferric and innermost ferrous doublets as temperature increases. Finally at 390°K, the innermost ferrous doublet lies below the resolution of the Mössbauer effect and only one ferrous doublet can be fit.
3.1 Final Mössbauer Parameters

All spectra taken were fit according to the above procedure, resulting in ten peak, five doublet fits. Table 4 gives fitting parameters for the Il 3 temperature profile, including positions, widths, isomer shifts, quadrupole splittings, and $\chi^2$. Appendix 1 shows fit spectra from a range of samples and temperatures.

It becomes obvious, upon inspection of the fitted spectra, just how the electron transfer process varies with temperature and composition. The variation is best illustrated by plotting Mössbauer parameters versus temperature. Figure 18 shows such a plot for the positions of the Il 3 temperature profile peaks. Peak positions vary in a near linear fashion and lines were calculated by a least squares program. Correlation coefficients for the lines are given in Table 5.

Figure 19 shows the variation of line widths with temperature. It has been reported that widths of peaks associated with intervalence charge transfer in magnetite decrease with increasing temperature, i.e. show inverse temperature variation to "pure" ferrous and ferric species.
TABLE 4. MOSSBAUER PARAMETERS FROM IL 3 TEMPERATURE PROFILE

<table>
<thead>
<tr>
<th>POSITIONS (mm/sec)</th>
<th>80°K</th>
<th>200°K</th>
<th>300°K</th>
<th>320°K</th>
<th>340°K</th>
<th>390°K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺</td>
<td>.297</td>
<td>-.230</td>
<td>-.189</td>
<td>-.170</td>
<td>-.180</td>
<td>-.149</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>.161</td>
<td>-.133</td>
<td>-.131</td>
<td>-.135</td>
<td>-.119</td>
<td></td>
</tr>
<tr>
<td>Fe²⁺⁺Fe³⁺⁺</td>
<td>-.113</td>
<td>-.085</td>
<td>-.039</td>
<td>-.037</td>
<td>-.030</td>
<td>-.019</td>
</tr>
<tr>
<td>ISOMER SHIFT (mm/sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-10</td>
<td>1.069</td>
<td>1.032</td>
<td>1.030</td>
<td>1.018</td>
<td>1.000</td>
<td>.989</td>
</tr>
<tr>
<td>2-9</td>
<td>1.088</td>
<td>1.004</td>
<td>.940</td>
<td>.887</td>
<td>.864</td>
<td></td>
</tr>
<tr>
<td>3-8</td>
<td>1.021</td>
<td>.910</td>
<td>.860</td>
<td>.829</td>
<td>.797</td>
<td>.796</td>
</tr>
<tr>
<td>4-7</td>
<td>.787</td>
<td>.771</td>
<td>.760</td>
<td>.735</td>
<td>.693</td>
<td>.668</td>
</tr>
<tr>
<td>5-6</td>
<td>.649</td>
<td>.647</td>
<td>.657</td>
<td>.640</td>
<td>.637</td>
<td>.635</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>WIDTHS (mm/sec)</th>
<th>Fe²⁺</th>
<th>Fe³⁺</th>
<th>Fe²⁺⁺Fe³⁺⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>.228</td>
<td>.261</td>
<td>.482</td>
<td></td>
</tr>
<tr>
<td>.254</td>
<td>.378</td>
<td>.247</td>
<td></td>
</tr>
<tr>
<td>.284</td>
<td>.361</td>
<td>.240</td>
<td></td>
</tr>
<tr>
<td>.301</td>
<td>.448</td>
<td>.249</td>
<td></td>
</tr>
<tr>
<td>.303</td>
<td>.431</td>
<td>.244</td>
<td></td>
</tr>
<tr>
<td>.290</td>
<td>.465</td>
<td>.241</td>
<td></td>
</tr>
</tbody>
</table>

QUADRUPOLE SPLITTING (mm/sec)

| 1-10 | 2.732 | 2.525 | 2.439 | 2.376 | 2.361 | 2.275 |
| 2-9  | 2.497 | 2.274 | 2.141 | 2.043 | 1.966 |       |
| 3-8  | 2.268 | 1.989 | 1.799 | 1.732 | 1.653 | 1.630 |
| 4-7  | 1.661 | 1.584 | 1.539 | 1.506 | 1.406 | 1.346 |
| 5-6  | 1.153 | 1.143 | 1.094 | 1.104 | 1.036 | 1.050 |
| X²   | 1.445 | 1.285 | 2.001 |       |       | 1.044 |
Figure 16. Positions of the peaks of the II 3 temperature regression-calculated lines (Table 5).
Figure 19. Widths of the peaks of the IL 3 temperature profile versus temperature. Fe$^{2+}$, Fe$^{3+}$ fit to regression calculation lines; Fe$^{2+}$→Fe$^{3+}$ charge transfer fit to $1/\Gamma = e^{-\varepsilon/kT}$ (Sawatzky et al., 1969) (Table 5).
TABLE 5. REGRESSION FITS FOR FUNCTIONS IN FIGURES 18 and 19

Figure 18 - All lines fit to \( y = a_1 x + a_0 \)

<table>
<thead>
<tr>
<th>Peak</th>
<th>80°K Position (mm/sec)</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>Correlation Coefficient ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 1 \text{ Fe}^{2+} \Delta )</td>
<td>-0.297</td>
<td>-0.330</td>
<td>0.0005</td>
<td>0.991</td>
</tr>
<tr>
<td>( 2 \text{ Fe}^{2+} \Delta )</td>
<td>-0.161</td>
<td>-0.167</td>
<td>0.0001</td>
<td>0.892</td>
</tr>
<tr>
<td>( 3 \text{ Fe}^{2+} + \text{Fe}^{3+} )</td>
<td>-0.113</td>
<td>-0.142</td>
<td>0.0003</td>
<td>0.991</td>
</tr>
<tr>
<td>( 4 \text{ Fe}^{2+} + \text{Fe}^{3+} )</td>
<td>-0.043</td>
<td>-0.049</td>
<td>0.0001</td>
<td>0.952</td>
</tr>
<tr>
<td>( 5 \text{ Fe}^{3+} )</td>
<td>0.075</td>
<td>0.059</td>
<td>0.0001</td>
<td>0.865</td>
</tr>
<tr>
<td>( 6 \text{ Fe}^{3+} )</td>
<td>1.225</td>
<td>1.252</td>
<td>-0.0002</td>
<td>0.877</td>
</tr>
<tr>
<td>( 7 \text{ Fe}^{2+} + \text{Fe}^{3+} )</td>
<td>1.617</td>
<td>1.713</td>
<td>-0.0008</td>
<td>0.896</td>
</tr>
<tr>
<td>( 8 \text{ Fe}^{2+} + \text{Fe}^{3+} )</td>
<td>2.155</td>
<td>2.287</td>
<td>-0.0018</td>
<td>0.990</td>
</tr>
<tr>
<td>( 9 \text{ Fe}^{2+} \Delta )</td>
<td>2.336</td>
<td>2.489</td>
<td>-0.0018</td>
<td>0.985</td>
</tr>
<tr>
<td>( 10 \text{ Fe}^{2+} \Delta )</td>
<td>2.45</td>
<td>2.507</td>
<td>-0.0010</td>
<td>0.988</td>
</tr>
</tbody>
</table>

Figure 19 - \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) fit to \( y = a_1 x + a_0 \), \( \text{Fe}^{2+} + \text{Fe}^{3+} \) charge transfer fit to \( y = a e^{b x} \) where \( y = 1/\Gamma \) and \( x = 1000/K \)

<table>
<thead>
<tr>
<th>Peak</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>Correlation Coefficient ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{2+} \Delta )</td>
<td>0.2115</td>
<td>0.0002</td>
<td>0.959</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} )</td>
<td>0.2214</td>
<td>0.0006</td>
<td>0.961</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>( a )</th>
<th>( b )</th>
<th>Correlation Coefficient ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Fe}^{2+} + \text{Fe}^{3+} )</td>
<td>5.198</td>
<td>-0.072</td>
<td>0.958</td>
</tr>
</tbody>
</table>

Note: Plot of regression fit for \( 1/\Gamma \propto e^{-E/kT} \) model of \( \text{Fe}^{2+} + \text{Fe}^{3+} \) charge transfer widths (after Sawatzky et al., 1969). Model yields an activation energy of 0.0062 eV for ilvaite thermal transfer. (cf. page 57)
(Sawatzky et al., 1969). Such variation can be seen in Figure 19 with ferrous and ferric widths of Il 3 spectra increasing approximately linearly and widths of intermediate species decreasing with increasing temperature. Sawatzky et al. (1969) model the change in peak width, $\Delta \Gamma$, as an activated process with activation energy $\varepsilon$ and $1/\Delta \Gamma = e^{-\varepsilon/kT}$.

Figure 20 illustrates the cause of the enormous temperature variation of the spectra and observed differences from sample to sample. The intensity of the outermost ferrous doublet showed little variation with temperature within the counting statistics of the spectra. Hence, the axis labelled normalized intensity in Figure 20 represents the ratio of intensity of the peak, $x$, to the intensity of the highest velocity ferrous peak. Normalization is required to eliminate variations due to counting times, source activity, and sample thickness. For the sake of clarity, and due to the constraints necessarily imposed on the tightly overlapped low velocity region, only high velocity intensities are included in Figure 20.

It is immediately apparent that, compared to the "normal" Fe$^{2+}$ species, the intensities of the other ferrous peak at high velocity and the ferric peak decrease
Figure 20. Normalized intensities of the peaks of the IL 3 temperature profile versus temperature. Peaks normalized to Fe$^{2+}$(B). Only high velocity intensities are shown due to constraints on low velocity intensities.
with increasing temperature. Contemporaneous with the intensity decrease of the Fe\(^{3+}\) and Fe\(^{2+}\) peaks, the additional peaks increase with temperature, one with a gentle slope and the second with a sharp rise between 320 and 370°K. The interpretations of Gerard and Grandjean (1971), who cited movement of one ferrous peak to lower velocity "undergoing a change which gives it a ferric character," are thus rejected by the above data. The "electron-hopping process" in ilvaite is now interpreted as population of intervalence molecular orbitals centered no longer on a single Fe\(^{2+}\) or Fe\(^{3+}\) cation but spread instead over an Fe\(^{2+}\)-Fe\(^{3+}\) couple. Such an interpretation explains the coordinated decrease of intensity of Fe\(^{2+}\) and Fe\(^{3+}\) peaks with increase of the additional peaks now assigned to Fe\(^{2+}\)+Fe\(^{3+}\) intervalence charge transfer. These "trapped" and "pure" valence levels decrease as electrons acquire the thermal energy necessary to occupy the intervalence charge transfer levels.

The task remains to assign the Mössbauer peaks to crystallographic positions in the ilvaite structure. The one ferric doublet is easily assigned to Fe\(^{3+}(A)\) because almost all Fe\(^{3+}\) is located at the A site.
according to Haga and Takeuchi (1976) and Beran and Bittner (1974). Such an assignment is supported crystal-chemically because the A site is the smaller of the two iron sites and Fe$^{3+}$ shows a preference for smaller sites (compared to Fe$^{2+}$ and Mn). No evidence was found for a second doublet with parameters to be expected for ferric iron on the B site. The outermost ferrous doublet was assigned to Fe$^{2+}$(B) on the basis of arguments advanced in Section 1.3. Since Fe$^{2+}$(A)+Fe$^{3+}$(A) is expected to predominate over Fe$^{2+}$(B)+Fe$^{3+}$(A) due to shorter metal-metal distances (Loeffler et al., 1976) and similar symmetries (Day, 1976; Hush, 1967), the Fe$^{2+}$(B) doublet should be invariant with temperature and increased charge transfer. Similarly, the innermost ferrous doublet, showing dramatic decrease in intensity with increasing temperature, was assigned to Fe$^{2+}$(A). This doublet varies in intensity from approximately equal to Fe$^{2+}$(B) at 80K (as expected from stoichiometry and from Haga and Takeuchi's site occupancy study) to below the resolution of our spectrometer at 390K.

The two intervalence charge transfer peaks were assigned as follows. As noted above, Fe(B)$\rightarrow$Fe(A) charge transfer is expected to contribute weakly, if at all,
to observed electron delocalization. Furthermore, the Fe(A)\textsuperscript{2+}-Fe(A)\textsuperscript{2+} interaction in the c-direction (i.e. along the Fe(A) octahedral chains) occurs with the shortest metal-metal distance and has the possibility of extended delocalization along the chain. Day (1976) discussed such metal chain compounds and showed that extended chain delocalization may be important in increasing intervalence charge transfer probability (e.g. Pt\textsubscript{en}Br\textsubscript{3}, a Class II compound showing some intervalence charge transfer, yet with a very large Pt-Pt distance of 5.60Å). Considering this long-range delocalization effect and the fact that a chain delocalization would be more dependent on a thermal activation mechanism than a pair delocalization, the innermost charge transfer doublet which shows the largest temperature increase was assigned to Fe\textsuperscript{2+}(A)\textsuperscript{-}Fe\textsuperscript{3+}(A)\textsuperscript{+} parallel to c (in the z-direction). The second charge transfer doublet was, therefore, assigned to Fe\textsuperscript{2+}(A)\textsuperscript{-}Fe\textsuperscript{3+}(A)\textsuperscript{+} c (in the xy-plane), also correlating with a short Fe-Fe distance, but not showing dramatic temperature increase due to the restriction to pair delocalization. These assignments are summarized in Figure 21. Intensity plots in Figure 20 have been labelled appropriately.
Figure 21. Summary of assignments of Mössbauer doublets in ilvaite.
No correlation has been found with Mn content and extent of charge transfer in room temperature spectra. This is to be expected as Mn prefers the Fe(B) sites (Haga and Takeuchi, 1976) and would be expected to have no affect on $\text{Fe}^{2+}(\text{A}) \rightarrow \text{Fe}^{3+}(\text{A})$ intervalence charge transfer. The observed variations of room temperature spectra can, however, be directly correlated to the amount of intervalence charge transfer occurring and relative intensity of charge transfer peaks compared to trapped valence absorption. This effect should be explainable in terms of other sample-to-sample differences such as formation conditions affecting the extent of ordering of Fe$^{2+}$ and Fe$^{3+}$ on Fe(A) sites and the ferrous/ferric ratios.

3.2 Site Occupancies

The site occupancy data of Beran and Bittner (1974) and Haga and Takeuchi (1976) is further supported by the Mössbauer results of this research. Evidence shows that at $80^\circ\text{K}$, approximately equal amounts of iron are present as $\text{Fe}^{2+}(\text{A})$, $\text{Fe}^{3+}(\text{A})$, and $\text{Fe}^{2+}(\text{B})$ with small contributions from intervalence charge transfer species to the A site occupancies. These iron species account for 31.30, 40.03,
and 28.67 percent, respectively, of the total iron when corrected for Fe$^{2+}$(A) and Fe$^{3+}$(A) present as intervalence charge transfer peaks.

Little can be said about the site preferences of Fe$^{2+}$ and Fe$^{3+}$ for A or B from the Mössbauer data as site preferences from neutron diffraction and x-ray experiments were employed to argue assignments. Two points concerning site occupancies can be made, however. There is a negative correlation between the relative intensity of the Fe$^{2+}$(B) doublet and Mn content by electron microprobe. This indicates that Mn does substitute primarily for Fe$^{2+}$ in the B site as expected from crystal-chemical arguments. It is, however, difficult to quantify this correlation as normalization of intensities to A site doublets is impossible due to varying amounts of intervalence charge transfer. Herzenberg and Riley (1969) argued for a distorted environment (i.e. B site) for ferric iron in ilvaite in order to produce the large quadrupole splitting analogous to epidote (Bancroft et al., 1967). However, in this study, Fe$^{3+}$ is assigned to the A site, the more regular octahedron, on the basis of site preference data and normal Fe$^{3+}$ preference for a small site (with Fe$^{2+}$ preference for a distorted site). It remains necessary
to explain the large quadrupole splitting of Fe$^{3+}(A)$.
The probable answer lies in the effects on "trapped" ferric valence sites of chain delocalized electrons which exist even at 80°K. Such electrons may cause distortion of the electronic environments throughout the chain and account for the large Fe$^{3+}(A)$ quadrupole splitting and the small Fe$^{2+}(A)$ quadrupole splitting (relative to Fe$^{2+}(B)$, the more distorted site).

3.3 **Electron Hopping - A Model**

Hush (1967) and Day (1976) have discussed some qualitative theoretical aspects of intervalence charge transfer as have Loeffler et al. (1976) and others. In general, intervalence charge transfer is invoked fairly frequently in the geochemical and spectrochemical literature with little regard for the theory behind such mechanisms. Similarly, in solid state physics and materials literature much has been said about theory and this or that model with little reference to physical systems which support the model. In this work, I have attempted to demonstrate the existence of intervalence charge transfer in ilvaite and turn attention now to constraints upon and implications for models of "electron-hopping."
The foundations for any such model must lie in a molecular orbital treatment of the Fe$^{2+}$-Fe$^{3+}$ couple. To review briefly, a molecular orbital picture of an Fe-coordination sphere describes a "mixing" of Fe atomic orbitals (s, p, d) and ligand orbitals (in ilvaite and most minerals, oxygen orbitals). These ligand orbitals are combined in symmetry-adapted linear combinations (SALC's) which transform similarly under symmetry operations. The Fe atomic orbitals and oxygen SALC's are then combined under symmetry constraints to form molecular wave functions and corresponding molecular energy levels. To a good approximation, these molecular energy levels, when filled, correspond to our traditional picture of a metal cation with its valence electrons surrounded by anions. The molecular wave functions take the form:

\[ \psi(a_{1g}) = c_1(4s) + c_2 \frac{1}{2\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \] (bonding)

\[ \psi^*(a_{1g}) = c_1(4s) - c_2 \frac{1}{2\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \] (antibonding)

The constants, \( c_1 \) and \( c_2 \), describe the amount of metal or ligand "character" to the molecular wave function; \( c_1 = 1, c_2 = 0 \) would be equivalent to a non-bonded Fe(4s) atomic
orbital and $c_1 = 0$, $c_2 = 1$ would similarly be localized on the oxygens. $c_1$ and $c_2$ are further constrained by requiring the wave functions to be normalized or

$$c_1^2 + c_2^2 + c_1c_2G = 1$$

where $G$ is the group overlap integral given explicitly as

$$\int \psi_M \phi_L \, d\tau$$

and measuring the amount of interaction between metal atomic wave functions and ligand SALC wave functions. The amount of "mixing" is, therefore, dependent on the degree of overlap between atomic orbitals and SALC's and on the ratio $c_1/c_2$. The energies of the molecular orbitals may be calculated from the secular equation

$$|H_{ij} - WG_{ij}| = 0$$

(Sample calculations for MnO$_4^-$ and CrF$_6^{3-}$ are given in Ballhausen and Gray, 1964, Chapter 8).

In order to apply such a molecular orbital treatment to an intervalence charge transfer couple, it is necessary to form Fe SALC's and then to mix these with ligand SALC's of appropriate symmetry. Even for the highest symmetry (each Fe in pure octahedral $O_h$), however, the symmetry reduction on going to an Fe-Fe couple is great. An edge-shared octahedral pair can have, at most, $D_{2h}$ symmetry
and complex computer calculations are required to generate energy levels which are, at best, oversimplified models for real, less symmetric mineral systems.

This method provides an analytic solution for the molecular wave functions and energy levels but is extremely difficult to solve. An alternate way of picturing the interaction is as a small distortion of a normal octahedral FeO$_6$ system employing perturbation calculations. Mayoh and Day (1974) describe the wave function for the Fe$^{2+}$ d$^6$ electron as

$$\psi_0 = \psi_A^{2+} \psi_B^{3+}$$

and for the electron transfer as

$$\psi_1 = \psi_A^{3+} \psi_B^{2+}$$

These wave functions transform with the same symmetry, and the ground and excited states are, therefore, represented by the normalized linear combinations,

$$\psi_g = (1 - \alpha)^{1/2} \psi_0 + \alpha \psi_1$$

$$\psi_{ex} = (1 - \beta)^{1/2} \psi_1 + \beta \psi_0$$

The constant $\alpha$ is the delocalization coefficient of the
system. If $\alpha$ is very small, $\psi_g \approx \psi_0$ and the best description of the system is as discrete $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ octahedral sites. If $\alpha$ is large ($\alpha \approx 0.7071$), $\psi_g \approx \alpha \psi_0 + \alpha \psi_1$ and the electron is shared equally by both sites, i.e. delocalized over the entire system. If $\alpha$ is small but finite, $\psi_g \approx x \psi_0 + y \psi_1$ and $x \gg y$. The valence states are essentially trapped but there exists a small, finite probability of exchange. In any system with $10^{23}$ or more atoms, even assuming a certain statistical disorder to the necessary $\text{Fe}^{2+}$-$\text{Fe}^{3+}$ pairs as in ilvaite, such a finite probability should affect mineral properties.

In the case of $\alpha$ small but finite, the probability of transfer can be increased by addition of energy to increase the stability of $\psi_1$ relative to $\psi_0$. Such energy effects can be seen in the Mössbauer spectrum of ilvaite. Thermal vibrational energy of the electrons increasing with temperature increases the number of $^{57}\text{Fe}$ nuclei which see, over the lifetime of the Mössbauer transition ($10^{-7}$ sec), a statistically averaged electronic environment due to rapid intervalence charge transfer. Similarly, other materials may require larger energy inputs to show charge transfer, an example of which would be semiconductor materials requiring electric activation over a "band gap."
A qualitative method of picturing the energy requirements is supplied by Day (1976). Day pictures the energy levels of the $\text{Fe}^{2+}d^6$ electron as a potential well with vertical energy scale and horizontal vibrational scale centered at $r_0$, the equilibrium radius of the atomic orbital. Such a well would be similar to a Hartree-Fock potential modified to consider only distance greater than $r_0$ from the Fe nucleus and, therefore, symmetric about $r_0$. Within such a well exist discrete vibrational energy levels with a ground state dependent on the configuration of the system. Day proposed "mixing" two such potential surfaces analogous to "mixing" two $\text{FeO}_6$ molecular orbital function sets. Figure 22 illustrates such an interaction. Two identical potential wells representing the configurations $\text{Fe}^{2+}_A\text{Fe}^{3+}_B$ and $\text{Fe}^{3+}_A\text{Fe}^{2+}_B$ or $\psi_0$ and $\psi_1$ have been drawn.

Energies corresponding to optical transitions from the ground state $\text{Fe}^{2+}_A\text{Fe}^{3+}_B$ to the excited state $\text{Fe}^{3+}_A\text{Fe}^{2+}_B$ ($E_{OP}$) and thermal transitions from the ground state $\text{Fe}^{2+}_A\text{Fe}^{3+}_B$ to the delocalized state ($\text{Fe}^{2+}_A\text{Fe}^{3+}_B+\text{Fe}^{3+}_A\text{Fe}^{2+}_B$) ($E_{TH}$) are labelled appropriately. At the crossing point of the two configurations, there occurs a resonance interaction similar to the symmetry-constrained interaction which combines $\psi_0$ and $\psi_1$ to generate $\psi_g$ and $\psi_{ex}$. Two new
surfaces are then formed, corresponding to \( \psi \) and \( \psi_{\text{ex}} \), separated by the energy, \( H_{\text{res}} \), and given explicitly by,

\[
E_g = \int \psi_A^{2+} \psi_B^{3+} H \psi_A^{2+} \psi_B^{3+} d\tau + \int \psi_A^{3+} \psi_B^{2+} H \psi_A^{3+} \psi_B^{2+} d\tau
- \int \psi_A^{2+} \psi_B^{3+} H \psi_A^{3+} \psi_B^{2+} d\tau
\]

\[
E_{\text{ex}} = H\psi_0 + H\psi_1 - H_{\text{res}}
\]

The magnitude of \( H_{\text{res}} \) determines the extent of electron delocalization in the ground state in an energy field just as \( \alpha \) determines the extent of delocalization in the ground state in a wave function field. For \( H_{\text{res}} \) large, the electron is completely delocalized and the material is a Class III compound (dashed lines in Figure 22). For \( H_{\text{res}} \) small, the electron is trapped in a localized ground state and has some probability with appropriate thermal excitation of undergoing transfer. This Class II system is illustrated by the dotted lines in Figure 22.

This potential energy surface picture is applied to the ilvaite system in Figure 23. The top diagram illustrates the \( Fe^{2+}(A) \rightarrow Fe^{3+}(A) \) transition with the inter-
Figure 22. Potential surfaces for the configurations $\psi_A^{2+}\psi_B^{3+}$ and $\psi_A^{3+}\psi_B^{2+}$ (after Day, 1976). Interactions shown for $H_{res}$ large giving delocalized ground state electrons and a Class III system (dashed lines) and $H_{res}$ small giving trapped valence ground states and a Class II system.
Figure 23. Potential surface pictures for ilvaite intervalence charge transfer interactions. Top diagram shows the pair interaction $Fe^{2+}(A) \rightarrow Fe^{3+}(A) \perp c$ and the lower diagram illustrates the chain interaction $Fe^{2+}(A) \rightarrow Fe^{3+}(A) \parallel c$. 
action of two potential surfaces of small $H_{res}$. Valences are trapped and thermal activation provides a small number of electrons with the necessary energy to overcome the transfer barrier. Increasing temperature should increase this electron population of the transfer level concurrent with depopulation of the trapped valence ground states. This picture is supported by experimental results showing decreased Fe$^{2+}$ (A) and Fe$^{3+}$ (A) Mössbauer absorption with increasing temperature simultaneous with increased Fe$^{2+}$ (A)$\rightarrow$Fe$^{3+}$ (A) intervalence charge transfer absorption. The lower diagram shows the potential surface interactions for Fe$^{2+}$ (A)$\rightarrow$Fe$^{3+}$ (A) $\parallel c$. Because the octahedral chains run parallel to $c$, delocalization is possible over more than two sites. Potential surface representing

$\Psi_A^{2+} \Psi_B^{3+} \Psi_C^{2+} \Psi_D^{3+}$ $\Psi_A^{2+} \Psi_B^{3+} \Psi_C^{2+} \Psi_D^{3+} \Psi_A^{2+} \Psi_B^{3+} \Psi_C^{2+} \Psi_D^{3+} \Psi_A^{2+} \Psi_B^{3+} \Psi_C^{2+} \Psi_D^{3+} \Psi_A^{2+} \Psi_B^{3+} \Psi_C^{2+} \Psi_D^{3+}$, have been allowed to interact with the requirement that $H_{res}^{ij} = H_{res}^{jk}$. Valences remain trapped in the ground state but thermal activation now puts the delocalized electron into a chain-wide molecular energy level. The opportunity for this long range delocalization should increase the stability of this energy level relative to a pair delocalization and hence $H_{res}^{|| c}$ has been drawn as greater than
The long range delocalization effects on the stability of \( \text{Fe}^{2+}(A) \rightarrow \text{Fe}^{3+}(A) \) should be reflected in experiment, as has been reported above. \( \text{Fe}^{2+}(A) \rightarrow \text{Fe}^{3+}(A) \) increases dramatically over the temperature range 320-370°K as thermal activation facilitates population of the intervalence charge transfer molecular energy levels.

In light of the molecular orbital model of intervalence charge transfer just described, it is necessary to examine the variables important in physical systems. The intervalence charge transfer probability depends on the magnitude of \( H_{\text{res}} \) compared to \( H_{\psi_0} \) and \( H_{\psi_1} \). \( H_{\text{res}} \), given explicitly as

\[
H_{\text{res}} = \int \psi_A^{2+} \psi_B^{3+} H_{\psi_A^{3+} \psi_B^{2+}} d\tau,
\]

is just the exchange integral \( H_{01} \), which Ballhausen and Gray (1964) approximate as

\[
H_{ij} = -2G_{ij} (H_{ii} \times H_{jj})^{1/2}
\]

The \( H_{ii} \) terms are just the energies of each configuration and \( G_{ij} \) is the group overlap integral for the two metal coordination spheres. The presence of \( G_{ij} \) suggests that \( H_{\text{res}} \) will be a function of polyhedral connection with face-shared > edge-shared >> corner-shared. Given any of the above connections, \( G_{ij} \) (and hence \( H_{\text{res}} \)) will
increase with decreasing metal-metal distance, as coordination sphere orbitals increase overlap. $H_{\text{res}}$ should also depend on geometries of polyhedral orientations with special regard to the relative orientations of orbitals in the metal coordination sphere.

$H_{\text{res}}$ will also be maximized when energy differences between configurations are minimized, as occurs for all interaction integrals of the form $H_{ij}$. Intervalence charge transfer will, therefore, be favored for systems where $E^0_\psi - E^1_\psi$ is small. Since the ionization potential of Fe$^{2+}$ is equal and opposite to the electron affinity of Fe$^{3+}$, energy differences in such a homogeneous couple can only arise from differences in ligand fields. This is not the case for heterogeneous couples where ionization potential and electron affinity contribute to the energies $E^0_\psi$ and $E^1_\psi$. Energy differences in ligand fields are those due to coordination number, site symmetry, and mean M-O distance (or bond strength). The primary requirement is that the energies of the levels involved in the perturbation calculation, $\psi_{A}^{2+} \psi_{B}^{3+}$ and $\psi_{A}^{3+} \psi_{B}^{2+}$, be similar. Therefore, octahedral-octahedral, tetrahedral-tetrahedral, or cubic-cubic systems will be preferred over mixed systems. Likewise, transitions between
octahedral sites of similar symmetry are preferred over transitions between regular and distorted octahedra. In ilvaite (and in magnetite) these requirements are met by intervalence charge transfer between crystallographically equivalent sites. For mixed cubic-octahedral, cubic-tetrahedral, and octahedral-tetrahedral systems, the preference would be cubic-tetrahedral $>>$ octahedral-tetrahedral $>$ cubic-octahedral due to the inversion of the $t_{2g}$ and $e_g$ levels from octahedral to cubic or tetrahedral symmetries. Such mixed systems would require crystal field splittings of appropriate magnitude to bring $t_2$ and $e$ energy levels into correspondence.

Experimental results from ilvaite Mössbauer studies require intervalence charge transfer models to show increasing transfer with increasing temperature. The above model satisfies this requirement. (This model also explains the inverse temperature dependence of intensity of optical transitions for other Fe$^{2+}$-$\rightarrow$Fe$^{3+}$ mineral systems. In such transitions, the ground state is depopulated with increasing temperature and optical transition from the ground state to an excited transfer state decrease in intensity.) Results also require models to explain
decreased peak width with increasing temperature. Sawatzky et al. (1969) employed a mathematical model with an activation energy $\epsilon$ and $\frac{1}{\Delta \Gamma} = e^{-\epsilon/kT}$. This activation energy is simply $E_{TH}$ in Figure 22, the thermal energy required to transfer the electron from a ground state to a delocalized energy level. Other requirements of polyhedral connection, coordination number, symmetry, and mean metal-metal distance have been discussed above and are supported by this research.
BIBLIOGRAPHY


Ruby, S.L., 1973, Why MISPIT when you already have $\chi^2$?
In: Mössbauer Effect Methodology 8, (J. Gruverman, ed.), Plenum Press, N.Y.

Sawatzky, G.A., J.M.D. Coey, and A.N. Morrish, 1969,
Mössbauer study of electron hopping in the octahedral sites of $\text{Fe}_3\text{O}_4$.

Schmitt, H., 1939, The central mining district, New Mexico.

Shannon, E.V., 1918, On the occurrence of ilvaite in the South Mt. mining district, Owyhee Co., Idaho.
Am. J. Sci. 4th Ser., 45, 118-125.


Takeuchi, Y., 1948, The structure of lievrite $\text{HCaFe}_3^3\text{Fe}_2^2\text{Si}_2\text{O}_9$ x-rays.
Osaka Univ., 5, 8-14.