Ilvaite: A Study of Temperature Dependent Electron Delocalization by the Mössbauer Effect

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Abstract. The mixed valence iron silicate ilvaite, CaFe$_2^{2+}$Fe$_3^{3+}$Si$_2$O$_8$(OH), displays electron delocalization associated with Fe$^{2+}$ → Fe$^{3+}$ charge transfer as observed by Mössbauer spectroscopy. Previous studies report the observation of an 'electron hopping phenomenon' with resolution of discrete valence states below 320 K. Mössbauer spectra of a suite of naturally occurring ilvaites were recorded over a temperature range, 80 K to 575 K. Five quadrupole doublets were resolved by computer fitting and assigned to Fe$^{2+}$ (A), Fe$^{2+}$ (B), Fe$^{3+}$ (A), and Fe$^{2+}$ (A) → Fe$^{3+}$ (A) $\parallel c$ and $\perp c$. Contrary to prior work, doublets associated with electron delocalization are resolved at 80 K and preclude the use of a Verwey-type order-disorder model. We propose a thermal activation model and discuss its criteria from molecular orbital and mineralogical viewpoints.

Introduction

Intervalence charge transfer (ct) in minerals has generated much recent interest as an explanation for anomalous color, spectra, electrical properties, and magnetic properties, and anomalous temperature variations of these properties in lunar and terrestrial materials (Smith and Strens, 1976; Osborne et al., 1978). Ct optical transitions have been invoked to explain the spectra of biotite, kyanite, cordierite, andalusite, and various pyroxenes and amphiboles. Electron delocalization has been observed in the Mössbauer spectra of hematite-ilmenite solutions (Warner et al., 1972) and magnetic (Kündig and Hargrove, 1969). Magnetite has been the classic model for such electron delocalization, exhibiting 'averaged' valence on Fe(B) sites above 119 K. The magnetite structure (an inverse spinel) contains Fe$^{3+}$ in A (tetrahedral) sites and Fe$^{2+}$ and Fe$^{3+}$ separated by 2.97 Å in infinite chains of edge-shared B (octahedral) sites. An order-disorder transition was postulated by Verwey and Haayman (1941) to explain the 119 K transition with attendant crystallographic, nuclear magnetic, conductivity, and Mössbauer changes. Controversy has recently arisen concerning the number
of disorder parameters necessary (Cullen and Callen, 1971) and the validity
of the Verwey order-disorder model versus a band model or polaron model
(Verble, 1974; Evans 1975) suggesting that application of the Verwey model
to other phases should be made with caution.

The aim of our study is to examine the effects of temperature on electron
delocalization in ilvaite and to derive a model for delocalized ct phenomena
in mineral systems. Primary use was made of the technique of Mössbauer
spectroscopy (gamma ray resonance). Application of the Mössbauer effect to
delocalization studies is interesting in that the effect measures a nuclear transition
with a lifetime on the order of $10^{-7}$ s while electronic delocalization transitions
are more rapid ($<10^{-9}$ s). The excited nuclear state is shifted from zero energy
due to $d$-electron shielding effects on $s$-electron density and is split into a quadru-
pole doublet due to asymmetric electronic environments (electric field gradient).
The excited nucleus is split only by electronic states longer-lived than $10^{-7}$ s.
Short-lived states such as delocalization transitions are observed as an average
of their ground and excited states if they occur with sufficient frequency during
the nuclear transition. Averaged Mössbauer doublets are observed in hematite-
ilmenite solutions (Warner et al., 1972) and spinels (Lotgering and van Diepen,
1977) while average magnetic hyperfine sextets have been observed in magnetite
(Kündig and Hargrove, 1969; Sawatzky et al., 1969).

Background

The structure of ilvaite ($Pbnm-D_{4h}^{16}$, $a=8.82$ Å, $b=13.07$ Å, $c=5.86$ Å, $Z=4$CaFe$_2^{2+}$Fe$_3^{3+}$Si$_2$O$_8$(OH) was first correctly assigned by Belov and Mokeeva
(1954) as a sorosilicate. Recent refinement was done by Beran and Bittner
(1974) and a neutron diffraction study was performed by Haga and Takeuchi
(1976). The structure consists of a framework of infinite double chains of edge-
shared Fe(A) octahedra linked by isolated Si$_2$O$_7$ groups. Six-coordinate Fe(B)
sites and seven-coordinate Ca sites are coordinated with oxygens from this
framework. Fe(A) sites are nearly regular octahedra with an average metal-
oxxygen ($M$–$O$) distance of 2.081 Å (ranging from 2.006 Å to 2.172 Å). Fe(B)
sites are distorted with four long planar and two short apical $M$–$O$ distances
(2.266 Å to 2.039 Å) averaging 2.190 Å. O–Fe(B)–O angles deviate from 180°,
with O(2)–Fe (B)–O(4) as low as 162.9°. Figure 1 shows one unit of the double
chain and an associated Fe(B) site and gives metal-metal distances for Fe(A)–
Fe(A) and Fe(A)–Fe(B) edge-shared interactions.

Three models for occupation of Fe(A) (eight sites per unit cell) and Fe(B)
(four sites per unit cell) by Fe$^{2+}$ and Fe$^{3+}$ have been proposed: (1) Fe$^{2+}$
in Fe(A) and Fe$^{3+}$ in Fe(B) (Belov and Mokeeva, 1954); (2) Fe$^{2+}$ in Fe(B)
and statistical distribution of Fe$^{2+}$ and Fe$^{3+}$ over Fe(A) (Beran and Bittner,
1974); and (3) statistical distribution of Fe$^{2+}$ and Fe$^{3+}$ over both sites. Model
2 is supported by normal Fe$^{2+}$ preference over Fe$^{3+}$ for larger, more distorted
sites due to ionic radius and crystal field effects. Further confirmation comes
from comparison with average $M$–$O$ values for octahedral iron in silicates