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Electron Delocalization in Ilvaite, a Reinterpretation of Its ^{57}Fe Mössbauer Spectrum

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Abstract. The Mössbauer spectra of ilvaite $CaFe_2^{2+}Fe^{3+}[Si_2O_7/O/OH]$ and their temperature dependence between 298 K and 455 K can be satisfactorily least-squares fitted by a superposition of the resonances for $Fe^{2+}(8d)$, $Fe^{3+}(8d)$ and $Fe^{2+}(4c)$. The relative areas under the three resonances are nearly equal and vary only weakly with temperature. No additional resonances or line broadenings have to be introduced, if we assume that the hyperfine interactions of $Fe^{2+}(8d)$ and $Fe^{3+}(8d)$ fluctuate between their values due to electron hopping between the iron ions at the $8d$ sites. Hopping can be assumed to occur homogeneously among nearly equivalent sites. The fluctuation rate is described by an Arrhenius law with a pre-exponent of about $9 \times 10^8\,s^{-1}$ and an activation energy of 0.11 eV indicating non-adiabatic hopping. In addition to the intersite hopping process, the strong decrease of the quadrupole splitting and the isomer shift of $Fe^{2+}(8d)$ between 298 K and 360 K suggests the occurrence of intrinsic charge delocalization from $Fe^{2+}(8d)$ which does not involve the neighbouring $Fe^{3+}(8d)$ ions.

Introduction

The mineral ilvaite, is a sorosilicate with the orthorhombic space group *Pbnm* (Belov and Mokeeva 1954; Beran and Bittner 1974; Haga and Takeuchi 1976). The Ca^{2+} ions occupy the positions $4c$ of that space group and are coordinated by six O^{2-} and one $(OH)^-$. Iron occupies two distinct crystallographic positions, (i) the fourfold position $4c$ with symmetry m and (ii) the eightfold position $8d$ with the symmetry 1. Both sites are nearly octahedrally coordinated: $4c$ by six O^{2-} and $8d$ by five O^{2-} and one $(OH)^-$. According to the chemical formula the Fe^{2+}:Fe^{3+} ratio is equal to 2:1. The existence of two Fe^{2+}- and one Fe^{3+}-quadrupole interaction patterns of nearly equal intensity in the room temperature Mössbauer spectra shows that (i) the $4c$-position is completely occupied by Fe^{2+}, and (ii) the $8d$-position is randomly filled by Fe^{2+} and Fe^{3+} (Herzenberg and Riley 1969). Recent high accuracy X-ray diffraction studies by Finger et al. (1982) infer rather a monoclinic structure for many ilvaites. These slight deviations from orthorhombic symmetry will, however, be of no relevance for the following discussion.

The crystal structure of ilvaite can be described as a framework of infinite edge-sharing double chains of $Fe(8d)O_5OH$-octahedra connected by Si_2O_7-groups and running parallel to the **c**-axis. The sixfold coordinated interstices of the framework are occupied by $Fe^{2+}(4c)$ and the sevenfold coordinated interstices by Ca. A portion of the crystal structure of ilvaite is shown in Figure 1.

Similarly as in magnetite, Fe_3O_4, where extended electron delocalization is known to occur above ~120 K (Bauminger et al. 1961), in ilvaite Fe^{2+} and Fe^{3+} are found to occupy the same crystallographic position in more or less random distribution. In addition, the $Fe^{2+}-Fe^{3+}$-distances in the double chain are relatively short, i.e. 283, 301, and 303 pm (Beran and Bittner 1974) and therefore electron delocalization like the one observed in magnetite is expected. Indeed evidence for a mixed valence state of iron due to electron delocalization was reported in several studies, which all agree on an averaged hyperfine interaction of the Fe-atoms at the $8d$-sites above ~400 K. However, there are some discrepancies between the different investigations concerning the formation of this mixed valent state of iron at the $8d$ sites, which result from a different evaluation and interpretation of the Mössbauer spectra taken at temperatures up to 400 K. According to Gerard and Grandjean (1971), Grandjean and Gerard (1975) and Heilmann et al. (1977) there is an unusual strong decrease of the quadrupole splitting and the isomer shift of Fe^{2+} at the $8d$ sites with temperature whereas the parameters of Fe^{3+} at the $8d$ sites remain constant or even seem to increase between 350 K and 400 K, leading to a collapse of both subpatterns above 400 K. In contrast to these papers Nolet and Burns (1978, 1979) report two doublets with quadrupole splittings and isomer shifts intermediate to those of Fe^{2+} and Fe^{3+} in $8d$ to occur in addition to the doublets of $Fe^{2+}(4c)$, $Fe^{2+}(8d)$ and $Fe^{3+}(8d)$ even in the liquid nitrogen spectra of ilvaite, which they assign to $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer parallel and perpendicular to the double octahedron chain, respectively. The intensities of these "intermediate", in part asymmetric, doublets are found to increase with temperature at the cost of the intensities of the doublets of Fe^{2+} and Fe^{3+} in $8d$ and no anomalous shifts of the peaks are observed. This is interpreted as a depopulation with temperature of certain electronic levels associated with

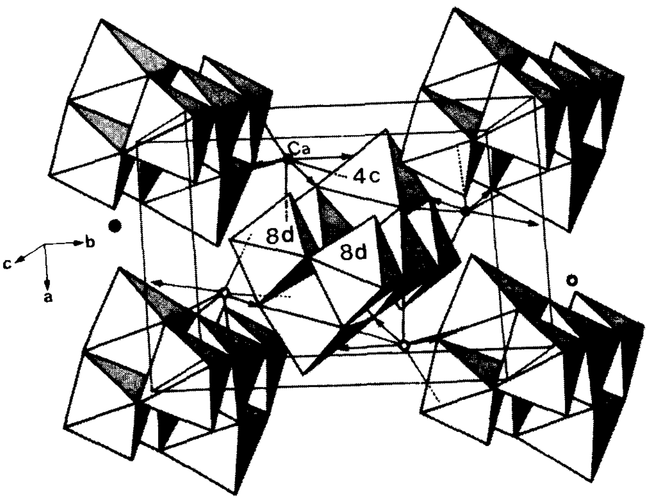

Fig. 1. Portion of the crystal structure of ilvaite modified from Belov and Mokeeva (1954), showing edge-sharing ribbons of 8*d*-sites running parallel to **c**

"quenched" valences accompanied by a simultaneous population of new delocalized levels associated with "intermediate" valences. Amthauer and Evans (1978) and Evans and Amthauer (1980) also report the occurrence of an additional broad resonant absorption pattern in the room and high temperature Mössbauer spectra of ilvaite up to 400 K which they assign to electron transfer between localized Fe^{2+} and Fe^{3+} centers. However, the intensity of this subpattern does not increase with temperature and the formation of only one 8*d*-doublet with averaged hyperfine interaction above 400 K is refered to a similar collapse of the Fe^{2+}- and Fe^{3+}-subpatterns as reported by Gerard and Grandjean (1971) and Heilmann et al. (1977). A Mössbauer study by Yamanaka and Takeuchi (1979) on different ilvaites performed between 300 and 4 K does not report any spectral features due to electron delocalization at all.

In all these studies the spectra were evaluated assuming Lorentzian line shape of the resonant absorption patterns. This may be justified if the electron exchange is much faster than nuclear Larmor precession or much slower than the mean life time of the excited ^{57}Fe nuclear level. It cannot be adequate for exchange rates ranging from the order of magnitude of the inverse mean life time ($\sim 10^7\,s^{-1}$) of the excited ^{57}Fe nucleus up to frequencies corresponding to the involved hyperfine interactions (10^8-$10^{10}\,s^{-1}$). Therefore strong relaxation effects such as line broadening, deviations from Lorentzian shape, and line shifts have to be expected. No attempt was reported to fit the data using a relaxation model appropriate for relaxation rates comparable to hyperfine splitting. Thus the discrepancies between the different papers on the Mössbauer spectra of ilvaite may be caused by the simplified fitting procedures, used to evaluate the data in the former investigations.

Therefore, the aim of the present paper is (i) an analysis of the temperature dependent Mössbauer spectra of ilvaite in the transition region using a relaxation model and (ii) a critical discussion of the former results. Ilvaite is a suitable sample to test such a fitting model because of the relatively good resolution of the spectra and because only one crystallographic site is involved in the electron exchange. For this purpose a new data set was collected between 295 and 500 K.

Experimental Methods

The Mössbauer spectra were recorded with a 1024 multichannel analyzer using a constant acceleration electromechanical drive system with a symmetric triangular wave form. Two mirror symmetric spectra, each 512 channels, were recorded simultaneously. For all the experiments a ^{57}Co/Rh source was used, which was kept at room temperature. The absorber thickness was 4 mg Fe/cm^2. The absorber was heated in a vacuum furnace evacuated to pressures less than 10^{-5} torr. The temperature was kept constant within ± 1 degree. More details of our standard Mössbauer technique are reported in Amthauer et al. (1976). The sample is from Seriphos, Greece. Its chemical formula as determined by electron microprobe analysis can be given as

$$Ca_{0.98}Mn_{0.023}Fe^{2+}_{1.94}Fe^{3+}_{1.03}Al^{3+}_{0.05}[Si_{2.02}O_7/O(OH)].$$

Relaxation Model and Results

The experimental spectra recorded between 298 K and 455 K are shown in Figures 2a and 2b. Their principle features are the same as described previously (e.g. Evans and Amthauer 1980). The room temperature spectra can be described by three quadrupole doublet patterns of nearly equal intensities for $Fe^{2+}(8d)$, $Fe^{3+}(8d)$ and $Fe^{2+}(4c)$. Above about 400 K the $Fe^{2+}(8d)$ and $Fe^{3+}(8d)$ patterns are collapsed to a single doublet. In the intermediate temperature range line shifting and broadening is especially visible in the Doppler velocity interval between +1.0 and +2.0 mm/s. Just this feature gave reason to introduce additional resonances in previous fitting attempts. In the following treatment we shall demonstrate that this is unnecessary if fluctuations of the hyperfine interactions are taken into account.

We now give a brief description of the relaxation model used and also derive the analytical solution since some erroneous formulae were reported in the literature (Gerard and Grandjean 1975). We assume that the electronic state of any iron ion located in a 8*d* site fluctuates stochastically between that of Fe^{3+} and Fe^{2+} due to electron hopping. Thus both isomer shift and quadrupole interaction fluctuate simultaneously between the characteristic values for Fe^{3+} and Fe^{2+}. The fluctuations shall occur independently of each other. The time elapsing between successive jumps shall be long compared to the characteristic period of lattice vibrations. Following the concepts given e.g. by Blume (1968) for the description of Mössbauer spectra in the presence of stochastic hyperfine fluctuation, we can give a simple solution for the present problem.

Neglecting some constant prefactors, the resonance absorption cross section ϕ for unpolarized gamma radiation with frequency ω in a polycrystalline absorber is given by

$$\phi(\omega) \sim -\mathrm{Im} \sum_{\substack{m_e n \\ m_e' n'}} p_n d_{m_e m_e'} [\mathbf{G}]_{\substack{m_e n \\ m_e' n'}} . \tag{1}$$

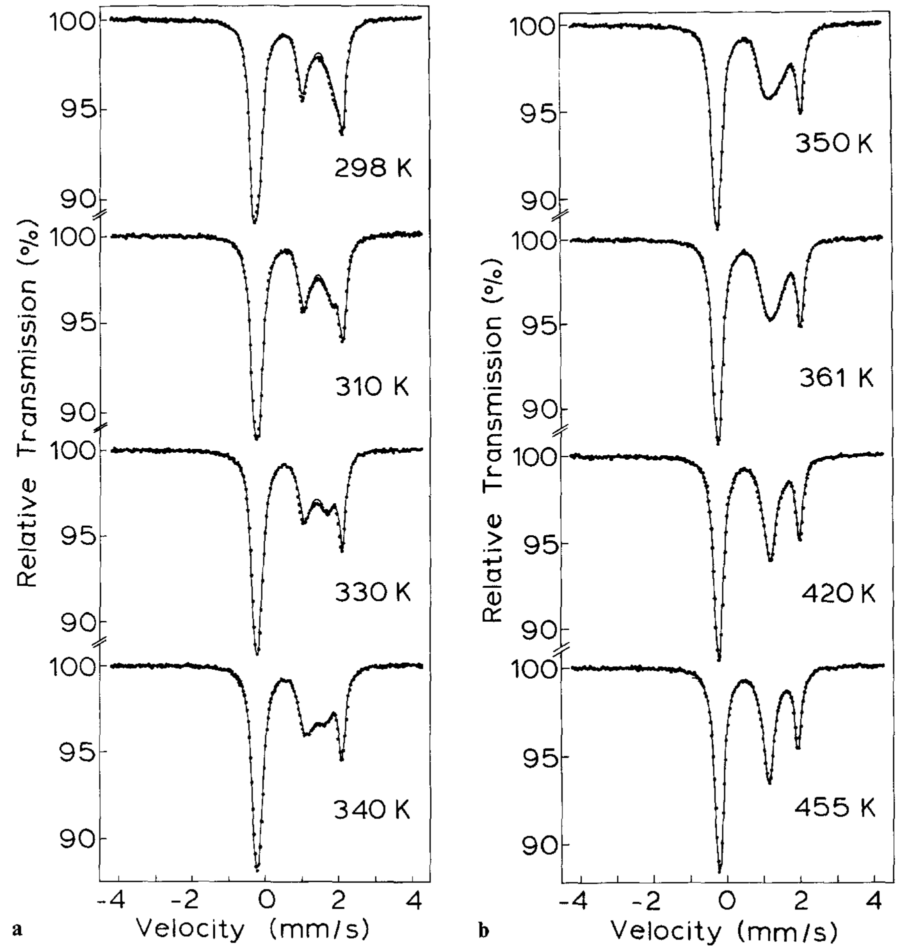

Fig. 2a and b. Mössbauer spectra of ^{57}Fe in ilvaite taken at temperatures between 298 K and 455 K. The solid line represents a least squares fit to the experimental data assuming three doublets for $Fe^{2+}(4c)$, $Fe^{2+}(8d)$ and $Fe^{3+}(8d)$, respectively, and considering charge fluctuation between Fe^{2+} and Fe^{3+} in $8d$ by an appropriate relaxation model

The matrix elements of the Green's function superoperator $\hat{\mathbf{G}}$ are given by

$$[\mathbf{G}^{-1}]_{\substack{m_e n \\ m'_e n'}} = \{(\omega + i\Gamma/2)\,\delta_{m_e m'_e}\delta_{nn'} - [\mathbf{H}(n)]_{m_e m'_e}\delta_{nn'} - i\lambda(1-p_n)\,\delta_{m_e m'_e}(1-2\delta_{nn'})\} \tag{2}$$

m_e, m_g denote excited and ground state nuclear angular momentum quantum numbers, n labels the atomic states (here: $n=1 \leftrightarrow Fe^{2+}(8d)$, $n=2 \leftrightarrow Fe^{3+}(8d)$), Γ the minimum experimental linewidth, λ is the transition probability per s between atomic states n, the relative populations of which are given by p_n, $\delta_{\nu\nu'}$, is the Kronecker symbol, i the imaginary unity.

$\mathbf{H}(n)$ is the hyperfine Hamiltonian for the nucleus of an atom in state n:

$$\mathbf{H}(n) = \tfrac{1}{4}\mathrm{e}^2 q_n Q[\mathbf{I}_z^2 - \tfrac{1}{3}\mathbf{I}^2] + S_n \tag{3}$$

(e is electronic charge, Q is the nuclear quadrupole moment, $\mathbf{I}_z$ and $\mathbf{I}$ are nuclear angular momentum operators, q_n is the zz-component of an axially assumed electric field gradient, S_n is the isomer shift). With $\mathbf{H}(n)$ being diagonal in nuclear variables (as in equation (3)) one obtains $m_e = m'_e$ in equations (1) and (2). The intensities of the spectral components are given by the matrix elements of the nuclear current operator $\mathbf{j}$:

$$d_{m_e m'_e} = \sum_{m_g} \langle m_e | j^+ | m_g \rangle \langle m_g | j | m'_e \rangle . \tag{4}$$

Expression (2) can be easily inverted and we yield an analytical solution for (1):

$$\phi(\omega) \sim \frac{(\Gamma/2+\lambda)\,A - (\omega - p_1\varepsilon_2 - p_2\varepsilon_1)B}{A^2+B^2} + \frac{(\Gamma/2+\lambda)\,A' - (\omega - p_1\varepsilon'_2 - p_2\varepsilon'_1)\,B'}{A'^2+B'^2} \tag{5}$$

with

$$\begin{aligned}
A &= (\omega-\varepsilon_1)(\omega-\varepsilon_2) - \Gamma/2(\Gamma/2+\lambda),\\
A' &= (\omega-\varepsilon'_1)(\omega-\varepsilon'_2) - \Gamma/2(\Gamma/2+\lambda),\\
B &= (\Gamma/2+\lambda)\,\omega - \Gamma/2(\varepsilon_1+\varepsilon_2) - \lambda(p_1\varepsilon_1 + p_2\varepsilon_2),\\
B' &= (\Gamma/2+\lambda)\,\omega - \Gamma/2(\varepsilon'_1+\varepsilon'_2) - \lambda(p_1\varepsilon'_1 + p_2\varepsilon'_2),\\
\varepsilon_1 &= S_1 + 1/4e^2 q_1 Q,\\
\varepsilon'_1 &= S_1 - 1/4e^2 q_1 Q,\\
\varepsilon_2 &= S_2 + 1/4e^2 q_2 Q,\\
\varepsilon'_2 &= S_2 - 1/4e^2 q_2 Q.
\end{aligned}$$

Indeed expression (5) may also be easily obtained by appropriately adopting the well-known expressions given by Wickmann (1966) for a flipping of the magnetic hyperfine interaction.

For zero relaxation rate λ we get two quadrupole doublets with Lorentzian lines of width Γ, relative intensities p_1 and p_2, isomer shifts S_1 and S_2, and quadrupole splittings $1/2e^2q_1Q$ and $1/2e^2q_2Q$, respectively.

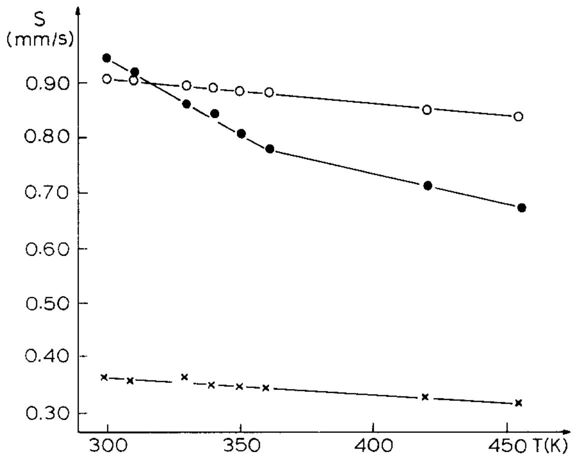

Fig. 3. Isomer shifts relative to a ^{57}Co/Rh-source (add 0,114 mm/s for α iron standard) of Fe^{2+} in 4*c* (open circles), Fe^{2+} in 8*d* (solid circles), and Fe^{3+} (crosses) in ilvaite as function of temperature assuming electronic relaxation between Fe^{2+} and Fe^{3+} in 8*d*

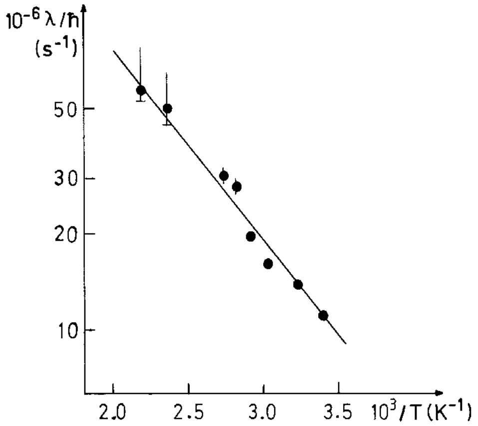

Fig. 5. Relaxation rate λ as function of inverse temperature in ilvaite

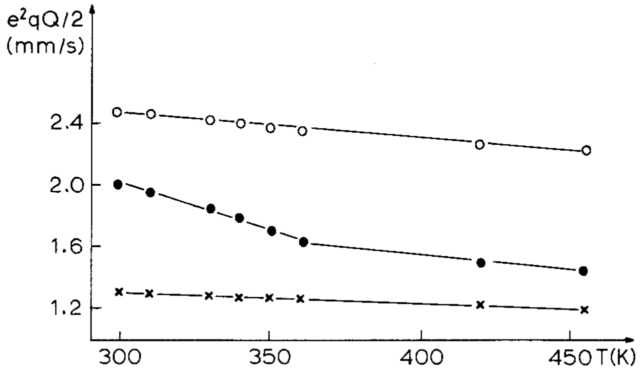

Fig. 4. Quadrupole splittings of Fe^{2+} in 4*c* (open circles), Fe^{2+} in 8*d* (solid circles), and Fe^{3+} in 8*d* (crosses) in ilvaite as function of temperature assuming electronic relaxation between Fe^{2+} and Fe^{3+} in 8*d*

For increasing λ one obtains broadened lines with shifted positions. Finally for $\lambda \gg |\varepsilon_1 - \varepsilon_2|$, $|\varepsilon_1' - \varepsilon_2'|$ one sharp doublet with line positions $p_1\varepsilon_1 + p_2\varepsilon_2$ and $p_1\varepsilon_1' + p_2\varepsilon_2'$ is retained.

For the least-squares fit of the experimental data we used expression (5) for the spectral contribution of Fe^{2+}(8*d*) and Fe^{3+}(8*d*). For Fe^{2+}(4*c*) which was assumed not to be involved in the relaxation process an independent doublet was added. The minimum experimental linewidth Γ was constrained for all the doublets to 0.22 mm/s. (This width was found in the limit of slow relaxation for all doublets.)

The solid lines in Figures 2a and 2b represent the fits thus obtained. Reasonable fits can only be achieved if one assumes that q_1 and q_2, i.e. the electric field gradients for Fe^{2+}(8*d*) and Fe^{3+}(8*d*) have equal sign.

The relative areas of the spectral contributions for Fe^{2+}(8*d*), Fe^{3+}(8*d*) and Fe^{2+}(4*c*) are 0.35, 0.38 (i.e. $p_1 \sim p_2 \sim 0.5$) and 0.27 at 298 K. They change smoothly to 0.34, 0.36 and 0.30 at 455 K. In view of possible (but neglected) slight differences in the recoilfree-absorbed fraction of resonant radiation for the different sites the thus obtained Fe^{2+}/Fe^{3+} ratio is consistent with the result of the microprobe analysis. The variations of the isomer shifts S and quadrupole splittings $1/2e^2qQ$ for the three iron sites with temperature are shown in Figures 3 and 4. In Figure 5 we have plotted the fitted relaxation rate λ logarithmically against inverse temperature. A straight line can be fitted to these data, i.e.

$$\lambda = \lambda_0 e^{-E/k_B T} \qquad (6)$$

giving an activation energy $E = 0.11 \pm 0.01$ eV for the hyperfine fluctuations due to hopping. The pre-exponent λ_0 is $(9.0 \pm 0.5) \times 10^8 s^{-1}$.

Discussion

Three sets of hyperfine interactions, for Fe^{2+}(8*d*), Fe^{3+}(8*d*) and Fe^{2+}(4*c*), turned out to be sufficient in our evaluations, if the hyperfine interactions for Fe^{2+}(8*d*) and Fe^{3+}(8*d*) are allowed to fluctuate between their values as it should be expected for electron hopping occuring between these sites. The relative intensities of the resonances for the three electronic configurations are only weakly temperature dependent which can be explained by a slightly different temperature dependence of the recoilfree fractions. In contrast to the fits reported by Nolet and Burns (1979) using five doublets with apparent severe differences in the areas of the high velocity and low velocity lines of each doublet, we kept the corresponding areas equal. No additional resonances with temperature dependent intensities and hyperfine parameters and also no line broadenings except those which are caused by relaxation had to be introduced to yield satisfactory fits ($\chi^2 \lesssim 3$) to the data (typical number of counts ca. 3×10^6/channel). Although a narrow distribution of relaxation rates could improve fit quality near room temperature (see central part of spectra near ca. +1.5 mm/s) we restricted our analysis to a single relaxation rate. In contrast, the qualitative description of the spectra of FeZnTi spinels with electron exchange between octahedral Fe^{2+} and Fe^{3+} required wide distributions of relaxation rates of the order of magnitude of the hyperfine splitting yielding "continuous" absorptions to account for the broad ill-defined lines (Lotgering and van Diepen 1977). In these spinels a strong perturbation of the electron delocalization due to varying next nearest cation neighbours, chemical inhomogeneities, defects of the crystal structure, etc. has to be expected.

The question concerning a distribution of relaxation rates may be related to the stoichiometry and the impurity content of the natural ilvaite crystals thus causing differences in the spectra of different specimens. Microprobe analysis showed the contents of ions such as Mn^{2+}, Mg^{2+}, Al^{3+} substituting for Fe^{2+} and Fe^{3+} to be relatively small in our sample and therefore the acceptance of one distinct relaxation rate is justified especially with regard to the fact that electron exchange takes place between Fe^{2+} and Fe^{3+} ions in one crystallographic site of the ilvaite structure.

The isomer shifts $S(Fe^{3+}, 8d)$ and $S(Fe^{2+}, 4c)$ (see Fig. 3) show a weak decrease with increasing temperature as expected from the variation of the second-order Doppler shift. Also the slight decrease with increasing temperature of the quadrupole splittings (Fig. 4) for these sites is typical of a valence contribution dominated electric field gradient with a temperature dependence determined by the Boltzmann population of the orbital states split by the crystal field. The relatively high values of quadrupole splitting and isomer shift for $Fe^{3+}(8d)$ are both indicative that the actual d-electron configuration is not $3d^5$ but rather $3d^{5+x}$ yielding an increased s-electron shielding by the $3d$ electrons. The sign of quadrupole interaction for $Fe^{3+}(8d)$ and $Fe^{2+}(8d)$ had to be assumed to be the same. This may occur if also for $Fe^{3+}(8d)$ the valence contribution to the electric field gradient is considerably larger than the ligand contribution. This again supports a higher d occupancy than $3d^5$ for $Fe^{3+}(8d)$. Note that previous evaluation attempts neglecting relaxation (Heilmann et al. 1977, Evans and Amthauer 1980) had the inevitable result that both isomer shift and quadrupole splitting for $Fe^{3+}(8d)$ were slightly increasing on approaching 400 K from below. Our data show that $Fe^{3+}(8d)$ is involved in the electron hopping with $Fe^{2+}(8d)$, but that no additional change of electron configuration of $Fe^{3+}(8d)$ occurs with temperature.

In contrast both isomer shift and quadrupole splitting for $Fe^{2+}(8d)$ reveal a relatively strong decrease between room temperature and ca. 360 K. At still higher temperatures the variation of these quantities is again flat and their values indicate an intermediate electronic configuration between divalent and trivalent. We interpret this behaviour with an intrinsic delocalization of d electron density from $Fe^{2+}(8d)$. This delocalization occurs in addition to the intersite electron hopping between $Fe^{2+}(8d)$ and $Fe^{3+}(8d)$. The charge delocalized from $Fe^{2+}(8d)$ does not occupy another localized state and rather can be thought to be transfered to band-like states, a view, which is also supported by previous pressure data (Evans and Amthauer 1980). $Fe^{2+}(8d)$ becomes more trivalent in character by this process, whereas $Fe^{3+}(8d)$ remains unchanged.

The anomalous variation for the quadrupole interaction of $Fe^{2+}(8d)$ has been previously described qualitatively by Grandjean and Gerard (1975) assuming a fast fluctuation ($\sim 10^{12}\,s^{-1}$) of the $Fe^{2+}(8d)$ hyperfine interactions with those of a "trivalent" state. This "trivalent" state is generated at the former $Fe^{2+}(8d)$ site due to charge delocalization. The thereby delocalized charge of $Fe^{2+}(8d)$ is not transfered to $Fe^{3+}(8d)$ neighbours which stay unaffected by this fluctuation process. This model is in principle identical to our view of the intrinsic delocalization. It should, however, not be confused with the intersite electron hopping which was neglected by those authors.

The hyperfine fluctuation due to intersite electron hopping occurs at a far slower time scale (10^7–$10^8\,s^{-1}$, see Fig. 5) and thus makes necessary the data evaluation using the explicit relaxational line shape given in Equation 5. Nota bene, the analysis showed that all $Fe^{2+}(8d)$ and $Fe^{3+}(8d)$ ions are involved in the relaxation process with nearly constant occupation. This gives strong evidence that the hopping occurs homogeneously among nearly equivalent sites along the $8d$ chains. The fitted activation energy $E = 0.11$ eV of the Arrhenius law describing the temperature dependence of the fluctuation of the hyperfine interactions is markedly smaller than one quarter of the optical absorption energy maximum $\frac{1}{4}E_0 = 0.38$ eV assigned to $Fe^{2+} \rightarrow Fe^{3+}$ charge transfer recorded on ilvaite (Amthauer and Rossman 1984). $\frac{1}{4}E_0$, would be the maximum possible value for the activation of hopping due to the small polaron mechanism, if charge transfer occurs between neighbouring parabolic potential wells (Austin and Mott 1969). The comparatively low activation energy evaluated from the Mössbauer spectra may arise from deviations of parabolic potential shape and overlap effects.

The reported activation energy from the conductivity on similar ilvaite samples are 0.24 eV and 0.15 eV (Gerard and Grandjean 1975; Heilman et al. 1977) and thus are higher than the activation energy of 0.11 eV from our Mössbauer data. This may be caused by compositional differences and also by the fact that these *dc* data are not based on measurements on single crystalline material. Preliminary data from a single crystal of the presently studied ilvaite show a strongly anisotropic conductivity behaviour with highest conductivity along the c-axis parallel to the $8d$ double chains. Careful measurements of the temperature dependence are under progress.

The pre-exponent of the Arrhenius law in Equation 6, $\lambda_0 = 9 \times 10^8\,s^{-1}$ indicates that the electron hopping occurs "non-adiabatically". This means that the chance for an electron hop is small during a typical optical phonon fluctuation period (a pre-condition we had already introduced for the relaxation treatment). λ_0 is basically determined by the square of an overlap integral $I = I_0 e^{-\alpha R}$ between neighbouring iron ions, $R \sim 3$ Å being the nearest neighbours distance of these ions and α^{-1} a typical fall-off distance of the wave function. According to Austin and Mott (1969) λ_0 is slightly temperature dependent:

$$\lambda_0 = \frac{\sqrt{\pi}}{\hbar} \frac{I^2}{\sqrt{E \cdot k_B T}}. \qquad (7)$$

From our data one thus estimates I to be only about 0.15 meV which is mainly caused by the smallness of the involved exponential.

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