Electronic Supporting Information

for

Spectroscopic characterization of Fe-doped synthetic chrysotile by EPR, DRS and magnetic susceptibility measurements

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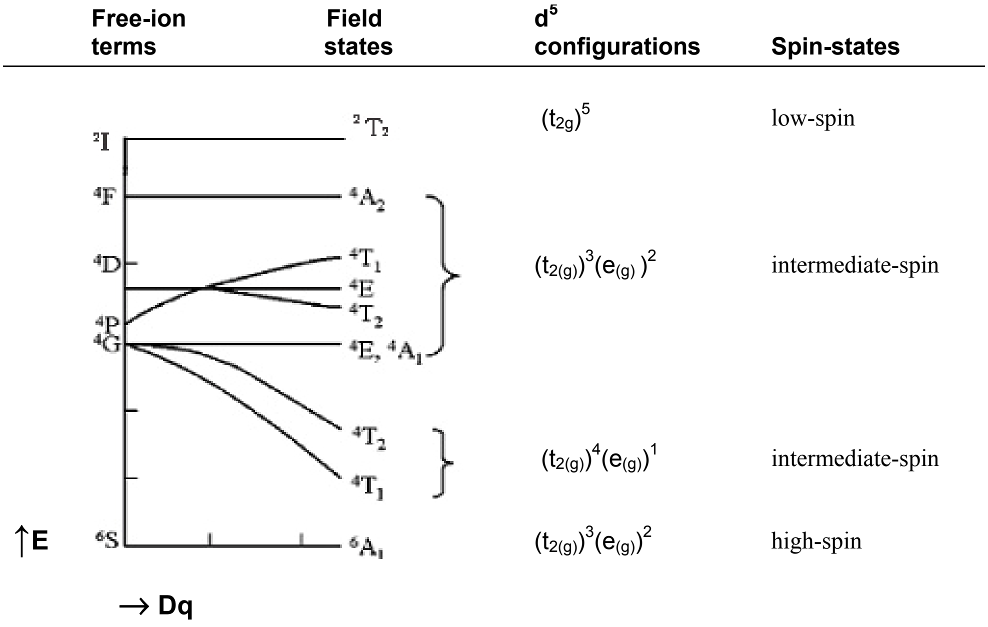
Metal-Ligand bonding theoretical aspects

The electrostatic crystal field theory

The spin S of a 3d^5 Fe(III) free ion, as involved in a ligand field, can have three possible values: high-spin state (S=$^5/_2$, ^{6}S as free ion term), low-spin state (S=$^1/_2$, ^{2}I as free ion term), intermediate-spin state (S=$^3/_2$, ^{4}G as free ion term). For a Fe^{3+} cation in octahedral (O$_h$) and tetrahedral (T$_d$) coordination the energies of the crystal field states can be schematically described by the same energy level diagram, E *vs* Dq, where E is the energy, and Dq represents the strength of the crystal field.



Scheme 1. The free-ion terms, the field states, the associated configurations and the spin states for the ground and the two excited states for the d^5 configuration in regular O$_h$ and T$_d$ symmetries. For the O$_h$ field states add the g subscripts, and for T$_d$ symmetry drop the g subscripts and reverse the order of t$_2$ and e orbitals.

The effective ground state of a d^5 Fe^{3+} configuration is: in O$_h$ symmetry-high-spin (S=$^5/_2$, ^{6}A$_{1g}$(^{6}S), t$_{2g}$^{3}e$_g$^{2}) or low-spin (S=$^1/_2$, ^{2}T$_{2g}$(^{2}I), t$_{2g}$^{5}) depending on the strength of the ligand-field, whereas in T$_d$ symmetry the orbitally no-degenerate (^{6}A$_1$(^{6}S), e^{2}t$_2$^{3}), As direct consequence of the ligand-field theory, regular O_h and T_d centres cannot possess a ground state of intermediate spin ($S={}^3/_2$, ${}^4T_{1(g)}({}^4G)$, $t_{2(g)}{}^4e_{(g)}{}^1$). However, when the molecular symmetry becomes lower than the octahedral and tetrahedral ones (*i.e.* in a distorted cubic environment), iron(III) centres might have a ground state of intermediate spin.

The only one sextet ${}^6A_{1(g)}({}^6S)$ ground state arises from the ground state $(t_{2(g)})^3(e_{(g)})^2$ configuration. All the excited states are a quartet ligand field states. The first excited state configuration is $(t_{2(g)})^4(e_{(g)})^1$ that gives the ${}^4T_{1(g)}({}^4G)$ state (with the $({}^\alpha t_{2(g)})^3({}^\beta t_{2(g)})^1({}^\alpha e_{(g)})^1$ configuration) and the ${}^4T_{2(g)}({}^4G)$ state (with the $({}^\alpha t_{2(g)})^3({}^\beta t_{2(g)})^1({}^\beta e_{(g)})^1$ configuration). The second excited state configuration $(t_{2(g)})^3(e_{(g)})^2$ with the two possible "spin-flip" excited configurations $({}^\alpha t_{2(g)})^2({}^\beta t_{2(g)})^1({}^\alpha e_{(g)})^2$ and $({}^\alpha t_{2(g)})^3({}^\alpha e_{(g)})^1({}^\beta e_{(g)})^1$ give the other excited quartet states. The doublet ${}^2T_{2g}$ $({}^2I)$ ground state arises from the ground state $(t_{2g})^5$ low-spin configuration (O_h symmetry only).

Several factors determine which of the possible spin configurations a Fe(III) ion will assume, and they may influence an equilibrium between the spin states, so that a crossover situation is to be expected. In the crossover region ground and excited states are very close in energy. The ligand field theory predicts that the ${}^4T_{1(g)}$ state of intermediate spin is never the lowest, and typically the ${}^2T_{2(g)}$ low-spin state is slightly lower in energy than the ${}^6A_{1(g)}$ high-spin state. The external influence of the temperature can produce discontinuities in the magnetic behaviour modifying the relative positions of the term levels and inducing a phase change, so that upon cooling the sample from ambient temperature a conversion from different spin-state might occur.

Molecular orbital theory

The molecular orbital diagrams with σ–π character for octahedral ML_6 and tetrahedral ML_4 complexes show the possible ligand–to-metal charge transfer (LMCT) transitions. The irreducible components of the reducible representations Γ_σ and Γ_π are: in O_h symmetry $\Gamma_\sigma = a_{1g} + t_{1u} + e_g$ and $\Gamma_\pi = t_{1g} + t_{2g} + t_{1u} + t_{2u}$, whereas in T_d symmetry $\Gamma_\sigma = a_1 + t_2$ and $\Gamma_\pi = e + t_1 + t_2$. For an O_h complex of Fe^{3+}two distinct LMCT transition can be present: $L(t_{1g}) \rightarrow M(t_2^*)$; $L(t_{1g}) \rightarrow M(e_g^*)$. For a T_d complex there are four possible LMCT transitions: $L(t_1) \rightarrow M(e)$; $L(t_1) \rightarrow M(t_2^*)$; $L(t_2) \rightarrow M(e)$; $L(t_2) \rightarrow M(t_2^*)$, which can or cannot be observed. For a d^5 system in T_d symmetry high-spin configurations $e^2t_2^3$ are always favoured and preferred respect to the $e^4t_2^1$, and ligand-to-metal transitions $L(t_1) \rightarrow M(t_2^*)$ and $L(t_1) \rightarrow M(e)$ are, typically, observed.

EPR Spectroscopy

The number and position of EPR transitions for isolated Fe^{3+} ions in a site of well defined symmetry observable in a powder spectrum depends sensitively on the local ligand-field symmetry of the sites (reflected by the magnitude of the zero-field splitting (zfs) parameters *D* and *E*) and possible magnetic interactions between them.

The spin-Hamiltonian operator *H*, at the second-order approximation, is

$$\boldsymbol{H} = \mu_B \mathbf{B}\cdot \mathbf{g} \cdot \mathbf{S} + D\{S^2_z - {}^1/_3(S(S+1))\} + E(S^2_x - S^2_y)$$

where μ_B is the Bohr magneton, and **B** the external magnetic field vector, **S** is the spin vector, of components S_x , S_y , and S_z , and $S = {}^5/_2$ is the spin of the Fe^{3+} ions. *D* is the axial zfs parameter, E characterizes the rhombic distortion, making all three axes distinct from each other. The non zero value for *E* activates the S_x and S_y operators in the zfs Hamiltonian. *E/D* shows the degree of rhombic distortion in the electronic environment and has a limited range, which in this case is 0–

$^1/_3$.The zfs is quantified as a correction to the energies of the individual spin states from spin-orbit coupling. A purely axial distortion (E/D = 0) leads to a differential stability of the three pair of spin configuration (ms = ± 5/2, ± 3/2, ± ½) proportionally to S^2_z in unity of the zfs D parameter.

When D = 0 there is no zfs and a single EPR line is expected at g = 2.0, being the orbital angular momentum of high-spin Fe(III) L = 0. When 0 < D < hν the three pair of levels are split in zero field, but the separation is smaller than hν and the typical EPR spectrum is broad and unresolved. In the case D >> hν the individual pair of ms levels are separated and transitions between the pair levels occur, but for the usual selection rule ($\Delta m_s = \pm 1$) only within the ms ± ½ levels of the ground doublet.

In the presence of a rhombic distortion of the ligand-field the g values of the three doublets of the S = $^5/_2$ system change as a function of *E/D*, and depending of its value it becomes possible to observe ESR signal arising from the ± $^3/_2$ and. ± $^5/_2$ doublet of the excited states. Assuming that *E* and *D* are small (*E/D* < 0.1, usual approximation for Fe^{3+}) **g** becomes isotropic.

UV/Visible Diffuse Reflectance Spectroscopy

For a d^5 ion all the transitions from the ground $^6A_1(^6S)$ state to the excited quartet ligand field states are, in principle, forbidden for both spin and Laporte selection rules. When in Fe-doped synthetic chrysotile iron occupies Mg site and/or in the Si site, these no-spin-allowed transitions can occur with a definite transition probability becoming allowed or assisted through the magnetic coupling of electronic spins of next-nearest neighbour Fe^{3+} cation. In the presence of magnetic coupling, it becomes necessary to consider the spectroscopic selection rules for the Fe^{3+}-Fe^{3+}pairs.

The Heisenberg Hamiltonian operator H, accounting for the coupling between the two ferric centres, is

$$\mathbf{H} = J S_a \cdot S_b$$

where J is the Heisenberg exchange integral and S_a and S_b are the electronic spin of the two Fe^{3+} cations. Assuming that this Hamiltonian perturbs the ligand field states of the uncoupled ferric cations, the energies of the states for the Fe^{3+}-Fe^{3+} pair are given by

$$E = (J/2)[S(S+1) - S_a(S_a+1) - S_b(S_b+1)]$$

where *S* is the net spin of the pair with values $|S_a+S_b|$, $|S_a+S_b-1|$, ..., $|S_a-S_b|$.

The single excitation processes

Qualitatively, a pair $Fe_a^{3+}(^6A_1)$-$Fe_b^{3+}(^6A_1)$, in ground state with $S_a = S_b = {}^5/_2$, will have the resulting pair-states with S = 5, 4, 3, 2, 1, 0. If one of the two Fe^{3+} cations in the pair is excited to a quartet ligand field state, $S_a = {}^5/_2$, $S_b = {}^3/_2$, the resulting spin of the $Fe_a^{3+}(^6A_1)$-$Fe_b^{3+}(^4T_1)$ pair will be S = 4, 3, 2, 1. Transitions among S = 1,2,3,4 states in the pair $Fe_a^{3+}(^6A_1)$-$Fe_b^{3+}(^6A_1)$ and in the pair $Fe_a^{3+}(^6A_1)$-$Fe_b^{3+}(^4T_1)$ can occur with $\Delta S = 0$ and be spin allowed, but Laporte-forbidden. In doped chrysotile, as in doped silica materials and in iron oxides, the Laporte selection rule can be relaxed by covalent bonding with oxygen trough the 3d orbitals of the magnetically coupled Fe pair and O 2p orbitals.

The double excitation processes

The two adjacent Fe^{3+} cations in $Fe_a^{3+}(^6A_1)$-$Fe_b^{3+}(^6A_1)$ pairs magnetically coupled can be simultaneously excited to a quartet ligand field state. If both Fe^{3+} cations have an excited quartet state, $S_a = S_b = {}^3/_2$, for the $Fe_a^{3+}(^4T_1)$-$Fe_b^{3+}(^4T_1)$

double excited pair the resulting pair-states will have S = 3,2,1,0. From the S = 0,1,2,3 states in the $Fe_a^{3+}(^6A_1)$-$Fe_b^{3+}(^6A_1)$ ground state transitions to the same states in the $Fe_a^{3+}(^4T_1)$-$Fe_b^{3+}(^4T_1)$ double excited quartet state can occur with $\Delta S = 0$. The double excitation processes occur at energies that are approximately the sum of two single-ion Fe^{3+} ligand field transitions.

Deconvolution of DRS spectra

The whole region from 200 to 750 nm of UV-Visible-DRS spectra for the Fe-doped chrysotile samples is shown.

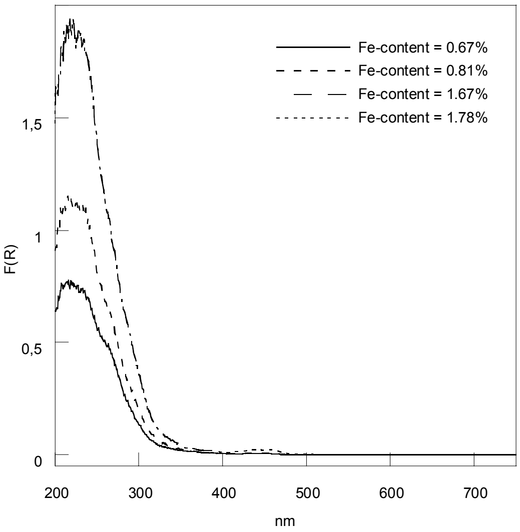


Figure 1. Experimental DRS spectra of Fe-doped chrysotile samples in region 200-750 nm

Conforming to literature data it can be considered correct to deconvolve the experimental DRS spectra of iron-doped chrysotile samples considering the four regions as reported in Table 1.

Table 1. Regions and their theoretical bands expected in DRS spectra of Fe(III) doped materials

Region 200-400 nm	**Region 400-600 nm**
Mainly LMCT transitions $t_{2(g)}(\pi^*) \leftarrow t_{1(g)}(\pi)$ $e_{(g)}(\sigma^*) \leftarrow t_{1(g)}(\pi)$ Partially d-d transitions $^4T_1\,(^4P) \leftarrow {}^6A_1(^6S)$ at 290-310 nm $^4E\,(^4D)$ and $^4T_2\,(^4D) \leftarrow {}^6A_1(^6S)$ at 360-380 nm	Contributions possibly overlapped of d-d transitions $^4E, A_1(^4G) \leftarrow {}^6A_1(^6S)$ at ~ 430 nm, Pair excitation processes resulting from the Fe^{3+}-Fe^{3+} pairs $^4T_1(^4G) + {}^4T_1(^4G) \leftarrow {}^6A_1(^6S) + {}^6A_1(^6S)$ Charge-transfer band tail
Region 600-750 nm	**Region 750-900 nm** [a]
d-d transition $^4T_2(^4G) \leftarrow {}^6A_1(^6S)$ at ~ 640 nm	d-d transition $^4T_1(^4G) \leftarrow {}^6A_1(^6S)$ at ~ 900 nm

[a] Fe-doped chrysotile samples do not show bands in this region

Magnetic susceptibility

Being Fe-doped chrysotile a polynuclear material with tetrahedral and octahedral layers, where in the minimal

$Mg_3Si_2O_5(OH)_4$ trioctahedral unit five paramagnetic iron centres in exchange coupling are expected, the Heisenberg, Dirac, and Van Vleck (HDVV) Hamiltonian must be considered.

The following equation describes the HDVV Hamiltonian

$$H = \sum_{i<j} J_{ij}(S_i \cdot S_j)$$

where the J_{ij} indicates the exchange coupling parameter between two neighbouring ions and has the dimension of energy.

The interactions between the electronic spin of each Fe(III) ion creates several energy levels that are usually accessible at normal temperatures and can give rise to a non-Curie behaviour for the magnetic properties of the doped-chrysotile samples. When the resulting ground state of the exchanged coupled Fe-system has S = 0 (diamagnetic singlet state), the material it is said to be antiferromagnetically coupled (EPR silent). On the contrary a paramagnetic state ($S \neq 0$) indicates ferromagnetic coupling (EPR detectable).

A further complication to the understanding of the magnetic aspects of iron-doped chrysotile could arise from the presence of a ferrimagnetic sub lattice in mixed octahedral-tetrahedral layers with uncompensated magnetic spins (*i.e.* in presence of an antiparallel coupling the number of moments, or size of the moments, or both, can be not equal). The simplest comparable example is the magnetite, Fe_3O_4, an inverse spinel $[(Fe^{3+})_{Td}\,(Fe^{2+}Fe^{3+})_{Oh}\,O_4]$ with two chemical and structural similar centres of iron (III) ions in T_d and O_h coordination to oxygen. Ferrimagnetism is found in the magnetite, as in general is found when the crystal structure of a compound is complicated. Considering that a ferrimagnetic transition presents usually a weak moment, this could explain the discontinuities observed at high iron loading.

Curie behaviour can be represented as a line parallel to the T axis in a $\chi_M T$ *versus* T plot, where the ordinate gives the Curie constant C, or as a straight line passing through the origin in a χ_M^{-1} *versus* T plot whose slope gives C^{-1}.

The Curie constant and the effective magnetic moment, μ_{eff} in Bohr magneton (μ_B), are defined for a molecule with no orbital angular momentum as follows:

$$C = \chi_M T = Ng^2\beta^2/3k \cdot [S(S+1)] = 0.125g^2 \cdot [S(S+1)] \text{ emu mol}^{-1}\text{ K}$$

$$\mu_{eff} = (3k/N\beta^2)^{1/2}\,(\chi T)^{1/2} = 2.828\,(\chi T)^{1/2}\,\mu_B$$

where N is Avogadro's number, *k* is Boltzmann's constant, β is the Bohr magneton of the electron, g is the electron Landè g factor can be used to characterize the magnetic properties of the system, are depending on the value of electronic spin S.

For a Fe^{3+} ion in ground state $^6A_1$, with $S={}^5/_2$, L=0, $J={}^5/_2$, where g =2.0023, the value expected is C = 4.377 emu mol^{-1} K calculates both with the spin-only formula, and with the spin-orbit coupling formula for a free Fe^{3+} ion, $3d^5$, $^6S_{5/2}$ term. The values of the Curie constant become with g = 2.0 C = 0.375 emu mol^{-1} K, when $S = {}^1/_2$, and C = 1.876 emu mol^{-1} K, when $S = {}^3/_2$.

For a Fe^{3+} ion in high-spin ground state the expected value is $\mu_{eff} = 5.916\ \mu_B$ calculated with both the spin-only and the spin-orbit coupling formula. The values of μ_{eff}, with g = 2.0, become 1.732 μ_B when $S = {}^1/_2$, and 3.873 μ_B when $S = {}^3/_2$. Being the chrysotile a poly-nuclear material, for the presence of five not-interacting Fe(III), distributed in both sites of the minimal $Mg_3Si_2O_5(OH)_4$ trioctahedral unit of chrysotile, a theoretical value of the magnetic moment larger than μ x 5 is expected.

General References

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