THE EFFECT OF LOCAL MAGNETIC INTERACTIONS ON THE CRYSTAL FIELD SPECTRA OF Fe$^{3+}$ IN MINERALS  
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An understanding of the factors affecting spectral band intensities in ferric oxides and silicates is necessary when attempting to extract mineralogical information from both laboratory and remote-sensed spectra of unknown materials. The purpose of this paper is to discuss the relation between chemical bonding, magnetism and spectra of Fe$^{3+}$ in minerals and to apply this formalism to the visible region spectrum of Mars [1].

The visible region spectra of ferric oxides and silicates consists of the $6A_1+4E, 4A_1$ crystal field transition and the low energy absorption edge of the oxygen to metal charge transfer (i.e. valence band to crystal field orbital) transitions. The $6A_1+4T_2$ band occurs at longer wavelengths (0.65 microns) yet is often masked by the more intense $6A_1+4E, 4A_1$ feature. The positions of both the oxygen to metal charge transfer [2] and the $6A_1+4E, 4A_1$ crystal field transition of Fe$^{3+}$ depend only on the covalency of the metal-ligand interaction and show little variation in the spectra of ferric oxides and silicates. In particular, the $6A_1+4E, 4A_1$ transition appears between 0.4 and 0.45 microns in the spectra of nearly all ferric oxides, silicates and sulphates [3,4,5,6,7,8]. The differences in color and visible region spectra among these minerals is due to changes in the relative intensity of the $6A_1+4E, 4A_1$ transition. In hematite (red), the $6A_1+4E, 4A_1$ absorption band is of sufficient intensity to give rise to band saturation in the diffuse reflectance spectra at wavelengths below 0.55 microns while for goethite and many ferric sulphates (yellow) the same spectral feature is of low enough intensity that its position can be measured in diffuse reflectance spectra.

In isolated complexes, the Fe$^{3+}$ crystal field transitions are spin-forbidden. Hence, band intensities in the spectra of these compounds are very weak. In dimer complexes and in minerals, however, the spin selection rule can be greatly relaxed when unpaired electrons on next-nearest neighbor Fe$^{3+}$ ions are allowed to couple magnetically [3,4,5,7,8,9,10]. For the case of a simple dimer complex, the magnetic interaction may be qualitatively described by the spin Hamiltonian $H = -J \cdot S_A S_B$ where $J$ is the exchange integral and $S_A, S_B$ are the net spins of the two ions A and B. Application of the spin Hamiltonian as a perturbation yields the new states shown schematically in Figure 1. In the new states transitions between the hextet and quartet spectroscopic states take on a spin-allowed character.

This "cooperative intensification" mechanism is responsible for the intense red color of iron oxides such as hematite ($\alpha$-Fe$_2$O$_3$) and maghemite ($\gamma$-Fe$_2$O$_3$). In the structures of the iron oxides and clay minerals, FeO$_6$ octahedra share edges (also faces and corners) to form chain and sheet units.
Adjacent Fe$^{3+}$ ions are coupled antiferromagnetically by superexchange via the bridging $O^{2-}$ ligand. The extent of the superexchange interaction, however, is dependent on the charge-density at the bridging ligand. If, as in some structures, the bridging ligand is bonded to an electron withdrawing center (i.e., a highly polarizing cation such as $H^+$, $Si^{4+}$, $Al^{3+}$) the superexchange interaction will diminish and the Fe$^{3+}$ crystal field transitions will regain their spin-forbidden character and be lowered in intensity. This is observed in the case of the ferric oxyhydroxides where Fe(O,OH)$_6$ octahedra are linked, in part, by OH$^-$ ions; because of the decreased superexchange interaction these phases take on a pale yellow to orange color.

In the visible region spectra of the bright regions of Mars the intensity of the $^6A_1$-$^4E$, $^4A_1$ band is much less than that found in the spectra of mixtures containing iron oxides, oxyhydroxides and (to a lesser extent) nontronite [11,12]. As argued by [12], the spectrum of Mars at wavelengths below 0.7 microns is essentially that of the Fe$^{3+}$ bearing mineralogy since both dilution effects and the presence of other minerals have little effect on the Fe$^{3+}$ spectrum in this wavelength region. The low intensities of the crystal field bands (in particular, the $^6A_1$-$^4E$, $^4A_1$ feature) indicate that the degree of magnetic interaction between second-nearest neighbor Fe$^{3+}$ ions in the structure of the Martian Fe$^{3+}$ mineral(s) is lower than that found in the Fe$_2$O$_3$ and FeOOH phases. In a recent paper [12], we pointed out this feature and tentatively invoked a disordered or amorphous structure to account for the decreased magnetic coupling. Recent investigations [13,14], however, have demonstrated that in several Mars-like spectra analogue materials (palagonite and hydrated Fe(OH)$_3$ gel) iron does not occur as isolated paramagnetic Fe$^{3+}$ ions. This is evidenced by low temperature magnetic ordering and by broad X-ray diffraction lines at 1.4 and 2.5A. In these samples, there appear to be Fe(O,OH,OH$_2$)$_6$ octahedra in edge-sharing arrangements forming chain and sheet structures; if the magnetic interaction between next-nearest neighbor Fe$^{3+}$ ions did not depend on the bridging ligand, one might expect strong local magnetic coupling and consequent spectral band intensification. The effect of hydroxyl bridging on the superexchange interaction, however, explains how such structures can exist in these materials without giving rise to 'undesirable' spectral behavior in the visible region.

In summary, a model for the local structure of the Martian Fe$^{3+}$ mineralogy is suggested. Fe(O,OH,OH$_2$)$_6$ octahedra may be in edge or corner-sharing arrangements, yet the Fe centers are linked by hydroxyl groups. A large degree of hydroxylation—indicated by the spectral band intensities—would prevent long-range structural order (cf. amorphous Fe(OH)$_3$,x H$_2$O gel) and, as such, Mars spectral analogue materials and presumably the Martian soil are X-ray amorphous.

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