Structural Fe^{3+} in Natural Kaolinites: New Insights from Electron Paramagnetic Resonance Spectra Fitting at X and Q-Band Frequencies

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Abstract: Structural Fe^{3+} in kaolinites and dickites covering a broad range of disorder was investigated using electron paramagnetic resonance (EPR) spectroscopy at both the X and Q-band frequencies. A procedure based on a numerical diagonalization of the spin Hamiltonian was used to accurately determine the second and fourth-order fine-structure parameters. A *least-squares* fitting method was also developed to model the EPR spectra of Fe^{3+} ions in disordered local environments, including multimodal site-to-site distributions. Satisfactory fits between calculated and observed X and Q-band spectra were obtained regardless of the stacking order of the samples.

In well-ordered kaolinite, Fe^{3+} ions are equally substituted in sites of axial symmetry ($Fe_{(II)}$sites, namely $Fe_{(II)a}$ and $Fe_{(II)b}$) which were determined to be the two non-equivalent Al1 and Al2 sites of the kaolinite structure. In dickite, Fe^{3+} ions were also found to be equally substituted for Al^{3+} in the two non-equivalent Al sites of the dickite structure. In poorly ordered kaolinites, the distribution of the fine-structure parameters indicates that Fe^{3+} ions are distributed between $Fe_{(II)}$ sites and other sites with the symmetry of the dickite sites.

Hence, when stacking disorder prevails over local perturbations of the structure, the near isotropic resonance owing to Fe^{3+} ions in rhombically distorted sites ($Fe_{(I)}$ sites) is a diagnostic feature for the occurrence of C-layers in the kaolinite structure, where C refers to a specific distribution of vacant octahedral sites in successive layers.

Key Words: Dickite • Disorder • EPR • Fe^{3+} • Kaolinite

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