^{57}Fe Mössbauer Effect Study of Al-Substituted Lepidocrocites†

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Abstract: Seven Al-containing lepidocrocite samples, γ-$Fe_{1-x}Al_XOOH$, prepared from $FeCl_2/Al(NO_3)_3$ solutions with initial Al/(Al + Fe) mole ratios C_i of 0.0025, 0.01, 0.025, 0.05, 0.075, 0.10 and 0.15 mol/mol, were examined by means of Mössbauer spectroscopy at room temperature (RT) and at various temperatures in the range of 8 to 80 K. The spectra at RT and 80 ° K consist of broadened quadrupole doublets and were analyzed in terms of a single doublet and of a model-independent quadrupole-splitting distribution, the latter yielding the best fit. The observed variations of the quadrupole-splitting parameters with increasing C_i are inconclusive as to whether the Al cations are substituting into the structure. The temperature at which the onset of magnetic ordering is reflected in the spectra, was measured by the thermoscan method with zero source velocity. A gradual shift from 50 K for C_i = 0.0025 mol/mol to 44 K for C_i = 0.10 mol/mol was observed for that temperature. As compared to earlier studies of Al-free γ-FeOOH samples with similar morphological characteristics, the fractional doublet area in the mixed sextet-doublet spectra at 35 K is significantly higher for the present lepidocrocites. This observation is ascribed to the substitution of Al cations into the lepidocrocite structure. A similar conclusion is inferred from the variation with C_i of the maximum-probability hyperfine field derived from the spectra recorded at 8 K and fitted with a model-independent hyperfine-field distribution. The magnetic results suggest that for the sample corresponding to C_i = 0.15 mol/mol, not all of the initially present Al has been incorporated into the structure.

Key Words: Al Substitution • Lepidocrocite • Mössbauer Spectra

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