The Center Shift in Mössbauer Spectra of Maghemite and Aluminum Maghemites

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Abstract: Synthetic, relatively well-crystallized aluminum-substituted maghemite samples, $\gamma - (Al_y \cdot Fe_{1-y})_2O_3$, with y = 0, 0.032, 0.058, 0.084, 0.106 and 0.151 have been studied by X-ray diffraction and zero-field Mössbauer spectroscopy in the range 8 K to 475 K, and also with an external field of 60 kOe at 4.2 K and 275 K. It was found that there are two different converging models for fitting the zero-field spectra of the maghemites with a superposition of two Lorentzian-shaped sextets, both resulting in inconsistent values for the hyperfine fields (H_{hf}) and/or the center shifts (δ) of the tetrahedral (A) and octahedral (B) ferric ions. From the applied-field measurements it is concluded that there is a constant difference of 0.12 ± 0.01 mm/s between δ_B and δ_A , regardless of the Al content. For the Al-free sample the center shifts are found as: $\delta_A = 0.370$ mm/s and $\delta_B = 0.491$ mm/s at 4.2 K and $\delta_A = 0.233$ mm/s and $\delta_B = 0.357$ mm/s at 275 K (relative to metallic iron), with an estimated error of 0.005 mm/s. Both δ_A and δ_B are observed to decrease with increasing Al concentration. The effective hyperfine fields for the non-substituted maghemite sample are: $H_{eff,A} = 575$ kOe and $H_{eff,B} = 471$ kOe at 4.2 K and $H_{eff,A} = 562$ kOe and $H_{eff,B} = 449$ kOe at 275 K, with an error of 1 kOe. The B-site hyperfine field remains approximately constant with Al substitution, while for the A site a slight decrease with increasing Al content was observed.

Key Words: Al-Maghemite • Center shift • Maghemite • Mössbauer effect.

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