Influence of Nonstoichiometry and the Presence of Maghemite on the Mössbauer Spectrum of Magnetite†

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Abstract: Several samples of large- and small-particle magnetite (Fe_3O_4), as well as its thermal decomposition products formed at different temperatures and atmospheres, have been studied extensively by Mössbauer spectroscopy (MS), both with and without an applied field of 6T. Synthetic mixtures of magnetite and poorly- or well-crystallized maghemite have also been studied. Large-particle magnetite (MCD > 200 nm), when heated in air for 12 hours at T < 400 ° C, transforms to a mixture of well-crystallized hematite and magnetite, the latter one remaining stoichiometric, according to the relative area-ratios obtained from MS. Thermal treatment at 1300 ° C in a controlled O_2 partial pressure, produced a mixture of stoichiometric and nonstoichiometric magnetite, but the latter component seems to be composed of particles with different degrees of nonstoichiometry. The Mössbauer spectra of the decomposition products at T < 200 ° C in air of small-particle magnetite (MCD ~ 80 nm) could be successfully interpreted as a mixture of magnetite and maghemite, rather than nonstoichiometric magnetite. This suggestion is further supported by the experiments with the synthetic mixtures. It is clearly demonstrated that is not possible, even by applying a strong external field, to separate the contribution of the A-site of magnetite from that of maghemite.

Key Words: Magnetite • Mössbauer effect • Nonstoichiometric magnetite

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