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COMMENT

Superparamagnetism and the Mössbauer spectrum of goethite: a comment on a recent proposal by Coey *et al*

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Abstract. The distinctive Mössbauer spectra of goethite cannot be explained on the basis of superparamagnetism. Consideration of superparamagnetic fluctuations in only the transverse components of the sublattice magnetization ('mode superparamagnetism', proposed by Coey *et al*), or of possible interactions between superparamagnetic particles, does not alter this conclusion.

Fine particles of goethite (α-FeOOH) exhibit a distinctive collapsed Mössbauer spectrum, resulting from a temperature-dependent, asymmetric magnetic hyperfine field distribution [1, 2]. This phenomenon has long been attributed to superparamagnetism [3, 4]. However, measurements of the anisotropy field [2, 5] show that the anisotropy energy density in goethite is too large to admit this explanation, at least on the basis of established theories of superparamagnetism. Recently Coey *et al* [6] have measured a spin flop field of 20 T in goethite, and confirmed that the anisotropy energy density in goethite is too large to result in superparamagnetism for the particle sizes which show a collapsed Mössbauer spectrum. They suggest that the broadening and collapse of the Mössbauer spectrum may result from superparamagnetic fluctuations in the transverse components of the sublattice magnetization only, an idea which they term 'mode superparamagnetism'. This idea stems from the observation of two different ordering modes for the transverse components in neutron diffraction patterns of different samples of goethite, and the suggestion that the anisotropy barrier between them may be much smaller than the dominant uniaxial anisotropy.

This phenomenon of 'mode superparamagnetism' might well occur in goethite, but it is shown here that it cannot explain the shape of the Mössbauer spectrum, or its temperature and sample dependence. If the longitudinal component of the sublattice magnetization remains stable, fluctuations in the transverse components can only reduce the observed magnetic hyperfine field by a small amount, proportional to the size of the transverse components. The magnetic sublattices are found to be inclined at an angle of 13° to the *b* axis [6]. If the transverse components fluctuate rapidly compared with the measurement time for Mössbauer spectroscopy, the observed magnetic hyperfine field will be proportional to the longitudinal component of the magnetization, which is just 3% smaller than the total sublattice magnetization. If the fluctuations are slow compared with the measurement time for Mössbauer spectroscopy, the spectral lines will be broadened, but the broadening will be limited to 3% of the magnetic hyperfine splitting. One of the distinctive features of the fine-particle goethite Mössbauer spectrum is that it frequently has significant contributions from

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a spread of hyperfine fields ranging from zero all the way up to a maximum field slightly smaller than that seen in pure, well crystallized goethite at the same temperature. This kind of spectrum clearly cannot be explained by fluctuations in the transverse components of the magnetization alone. Collective magnetic excitations, that is, rapid fluctuations of the magnetization about an easy direction in small particles, have previously been discounted as an explanation of the goethite Mössbauer spectrum for similar reasons [1]. These fluctuations produce at most a 15% reduction in the magnetic hyperfine field [7].

Previous work has shown that the magnetic hyperfine field distribution in goethite can be fitted very accurately by a Boltzmann distribution for the longitudinal component of the sublattice magnetization [2]. The energy barrier derived from these fits can be directly related to the Néel temperature of the sample in question. The lower the sample Néel temperature, the lower the energy barrier at a given temperature and the more collapsed the spectrum. Well crystallized goethites, with Néel temperatures approaching 400 K, have a sharp six-line spectrum at all temperatures up to within a few degrees of the Néel point. This relationship between the sample Néel temperature and the collapse of the Mössbauer spectrum suggests that the fluctuations are of the nature of critical fluctuations, directly related to the magnetic ordering process, and only indirectly related to the particle size, in that the smallest particles tend to have the lowest Néel temperatures [2, 8]. The reduced Néel temperatures found in fine-particle goethites are likely to be due to a high concentration of iron vacancies. A study of several goethite samples of varying crystallinity using positron annihilation lifetime spectroscopy has detected vacancy defects in goethite with a concentration proportional to the reduction in Néel temperature [9].

Exchange interactions between superparamagnetic particles have been proposed as an explanation of the reduced magnetic ordering temperatures and accompanying relaxation effects in the Mössbauer spectrum of fine-particle goethites [1]. This explanation requires rapid superparamagnetic relaxation above the transition temperature measured by Mössbauer spectroscopy, rather than the onset of paramagnetism and the accompanying disappearance of the sublattice magnetization. The anisotropy energy density is too large to permit rapid superparamagnetic relaxation for the relevant particle sizes, and neutron diffraction shows that the sublattice magnetization vanishes at the same temperature as the magnetic hyperfine splitting disappears in the Mössbauer spectrum [10].

Temperature-dependent, asymmetric magnetic hyperfine field distributions similar to those occurring in goethite are seen in Mössbauer spectra of a diverse range of materials [2, and references therein], including fine particles of most iron oxides and oxyhydroxides, diamagnetically substituted iron oxides and oxyhydroxides, and manganese Invar alloys. It might be expected that a satisfactory explanation of the goethite Mössbauer spectrum would also apply to at least some of these other materials, some of which are ferrimagnets or competing exchange systems rather than antiferromagnets. Indeed, the method of fitting developed for fine particle goethite, a Boltzmann distribution for the longitudinal component of the magnetization, has been successfully applied to Mössbauer spectra of ferrihydrite [11] and aluminous haematite [12].

Coey *et al* [6] measured a spin flop field of 20 T for goethite and found that the anisotropy energy density derived from this measurement was too large for the distinctive Mössbauer spectra of goethite to be explained by superparamagnetic fluctuations in the axial component of the sublattice magnetization. They proposed instead that these spectra might be explained by superparamagnetic fluctuations in only the transverse components of the magnetization, an idea which they called ‘mode superparamagnetism’. It has been shown here that this proposal cannot explain the shape of the goethite Mössbauer spectrum, its temperature and sample dependence, or the occurrence of similar spectra for a diverse

range of other materials. It must be concluded that these spectra do not result from superparamagnetism of any kind.

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