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MAGNETIC ORDERING IN A MONTMORILLONITE OBSERVED BY ^{57}Fe MÖSSBAUER SPECTROSCOPY AT 1.3 K

Key Words—Iron, Magnetic ordering, Montmorillonite, Mössbauer spectroscopy.

Recently Cardile *et al.* (1985) reported the low-temperature ^{57}Fe Mössbauer spectroscopy of a series of nontronites with different iron contents and interlayer cations. The Mössbauer spectra of all the samples investigated showed clear evidence for magnetic ordering of the Fe^{3+} ions in the composite sheets of the nontronite structure. Magnetic ordering was observed in the spectra at about 4.2°K and below, depending on the particular sample, but neither this temperature nor the details of the magnetic ordering seemed to be directly correlated with the iron content.

It is therefore of interest to investigate the possible effects of the iron content on the magnetic ordering properties of a phyllosilicate with much lower iron content. Montmorillonites have a similar structure to nontronites, although Fe^{3+} can occupy both cis- and trans-octahedral sites in the non-centrosymmetric structure (see, e.g., Rozenson and Heller-Kallai, 1977). In addition, montmorillonites have a considerably lower iron content than nontronites. The present note reports the low-temperature ^{57}Fe Mössbauer spectroscopy of a Mg-saturated montmorillonite.

EXPERIMENTAL

The sample studied was a montmorillonite with an iron content of 7.41% from Drayton, Queensland, Australia. The analysis of a Ca-saturated sample gave the composition $Ca_{0.27}(Si_{3.49}Al_{0.51})(Al_{0.94}Fe_{0.49}Mg_{0.82}Ti_{0.01})O_{10}(OH)_2$ when calculated in the conventional manner. The iron content is substantially lower than the 20 to 35% of the nontronites studied by Cardile *et al.* (1985).

The ^{57}Fe Mössbauer spectra were obtained using a conventional constant acceleration spectrometer, with the sample in a pumped liquid-helium-bath cryostat to give the low temperatures. The velocity scale was calibrated with reference to natural iron, with the midpoint of the iron hyperfine spectrum defining zero velocity. The spectra were computer-fitted to a number of Lorentzian peak lineshapes using a non-linear regression χ^2 minimization procedure.

RESULTS

The 4.2°K and 1.3°K Mössbauer spectra of the Drayton montmorillonite are shown in Figure 1, together with the computer fits to these spectra. The 4.2°K spectrum showed no evidence of magnetic effects and consisted of a quadrupole-split doublet with broad lines, indicative of the presence of several overlapping components. This spectrum is similar to that reported for other montmorillonites at higher temperatures (e.g., Goodman, 1978; Rozenson and Heller-Kallai, 1977). The 1.3°K spectrum, however, showed two distinct subspectra: a central doublet similar to that observed in the 4.2°K spectrum, representing a spectral component essentially unaffected by any magnetic hyperfine interactions, and a sextet indicative of magnetic ordering. Some additional broadening was also observed in the central region of the spectrum and primarily affected the envelope of the doublet feature. The broadening could have been a third very broad component arising from unresolved magnetic hyperfine splitting.

The 4.2°K spectrum was computer fitted to a single doublet component, whereas the 1.3°K spectrum was fitted to one doublet and one sextet component. This relatively simple approach to the computer analysis provided good fits to the experimental data; the resulting Mössbauer parameters are given in Table 1. These fits should not be taken to imply that only one iron environment corresponds to each of the fitted components. On the contrary, for the sextet component the data are inadequate to resolve closely overlapping components, as observed in the magnetically split nontronite spectra reported by Cardile *et al.* (1985).

DISCUSSION

The 1.3°K spectrum indicates that two distinct types of iron atom were present in the sample and gave rise to different types of hyperfine behavior at this temperature. Such a situation could have arisen in several ways. One possibility is that the iron was not evenly distributed throughout the structure and that iron-rich domains or clusters existed which were thus "nontronite-like" and exhibited magnetic ordering at low temperatures. Another possibility is that small particles of iron oxides or oxyhydroxides were present which, because of their particle size, only showed magnetic ordering in the Mössbauer spectra at this very low temperature, a phenomenon described by Mørup *et al.* (1981) as superparamagnetism. A third possibility is that the montmorillonite consisted of a uniform material, but with a range of particle sizes giving super-

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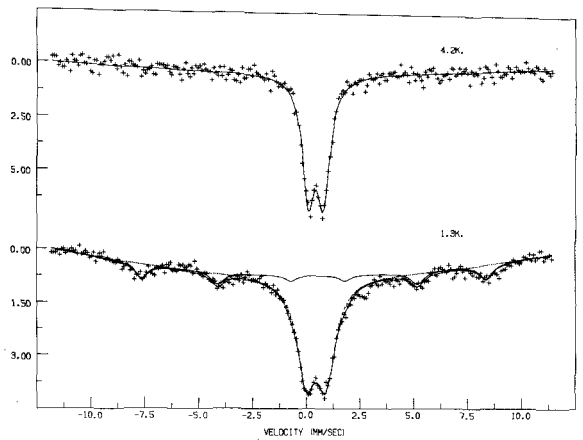

Figure 1. Low-temperature ^{57}Fe Mössbauer spectra of Mg-saturated montmorillonite from Drayton, Queensland, Australia.

paramagnetic behavior such that at a given temperature only iron atoms in particles larger than a critical diameter exhibited a magnetically split Mössbauer spectrum (Mørup *et al.*, 1981). This third possibility requires a large number of extremely small particles or domains within the sample. It is also possible that the magnetically split component arose from a slowly relaxing paramagnetic ion, as has been reported for kaolinite (Fysh *et al.*, 1983); however, this possibility appears to be improbable, as the spectrum obtained in zero applied field is unlikely to be a simple sextet, as was noted in the present spectrum.

The Mössbauer parameters of the doublet of the low-temperature montmorillonite spectra were typical for Fe^{3+} and are consistent with those reported previously from higher temperature measurements (e.g., Goodman, 1978; Rozenson and Heller-Kallai, 1977). The magnetic hyperfine field value for the sextet component of the 1.3°K spectrum was close to that observed in the low-temperature spectra of nontronites (Cardile *et al.*, 1985), but is also consistent with what might be expected for iron oxides or oxyhydroxides.

Goodman (1978) presented evidence from higher temperature Mössbauer spectra and electron paramagnetic resonance spectroscopy, that suggests that some of the iron in montmorillonite samples may be in a separate iron-rich phase. The present results provide support for this idea and confirm the usefulness of obtaining Mössbauer spectra at very low temperatures in order to distinguish the various iron components by their magnetic behavior.

Further Mössbauer measurements over a wider range of temperatures are needed to gain a more complete understanding of the nature of the magnetic behavior of such materials. It would also be useful to investigate a range of montmorillonite samples to determine the extent to which their magnetic behavior is dependent on composition both before and after treating them to remove possible contaminant iron oxides or oxyhydroxides.

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Table 1. Mössbauer parameters of Mg-saturated montmorillonite from Drayton, Queensland, Australia.

Temperature (°K)	Doublet component			Sextet component			
	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Area (%)	Hyperfine field (tesla)	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Area (%)
4.2	0.55 ± 0.01	0.70 ± 0.02	100	—	—	—	—
1.3	0.56 ± 0.01	0.92 ± 0.02	81 ± 1	49.6 ± 0.5	0.56 ± 0.01	0.17 ± 0.02	19 ± 1