MÖSSBAUER EFFECT STUDIES OF IRON IN KAOLIN.
I. STRUCTURAL IRON

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Abstract—^{57}Fe Mössbauer spectra of a cleaned Weipa, Australia, kaolin showed that a considerable fraction of the structural iron exhibits paramagnetic relaxation between 4°K and 300°K, the first time that this has been observed for ferric ions in a mineral. The sample also contained a very fine particle ferric oxide/oxyhydroxide phase, probably of secondary origin.

Key Words—Iron, Kaolinite, Mössbauer effect, Paramagnetism, Structural substitution.

INTRODUCTION

Mössbauer spectroscopy has been widely employed in the study of the iron associated with clay minerals (see Coey, 1975; Ericsson *et al.,* 1977). During a study of the iron mineralogy of the Weipa bauxite (Cape York Peninsula, Australia) and the clays underlying it, various natural and cleaned kaolins have been examined using this technique. The identification of iron sites in a cleaned kaolin specimen is herein reported; the following paper (Fysh *et al.,* 1983) extends the investigation to include the effects of various beneficiation processes. Because of its ability to distinguish between Fe in the form of poorly crystallized iron oxides and structural Fe in clays, Mössbauer spectroscopy is a useful technique for monitoring the results of iron-removal processes employed to increase clay brightness.

One interesting result of the present work is the observation of a magnetically split Mössbauer spectrum arising from paramagnetic structural iron in the Weipa and other commercial kaolins. We believe this to be the first observation of a zero-field paramagnetic hyperfine split (HFS) Mössbauer spectrum for any mineral.

THE NATURE OF THE IRON ASSOCIATED WITH KAOLIN

The partial substitution of Al in kaolinite by Fe has been the subject of numerous studies. Malden and Meads (1967) used Mössbauer spectroscopy to establish the presence of octahedrally co-ordinated Fe^{3+} within the kaolinite structure. They also indicated the possibility of Fe^{2+} substitution, which was subsequently confirmed by Jefferson *et al.* (1975). Cuttler (1980) showed that Fe^{2+} substitutes trioctahedrally in the gibbsite-like sheet of the kaolinite, with three Fe^{2+} ions replacing two Al^{3+} ions to maintain charge neutrality. Since the initial observations of Malden and Meads (1967), the substitution of iron in kaolinite has been confirmed by electron

microprobe (e.g., Jepson and Rowse, 1975), chemical (e.g., Rengasamy *et al.,* 1975), electron spin resonance (ESR) (e.g., Meads and Malden, 1975), and infrared (Mendelovici *et al.,* 1979) studies. The considerable number of studies employing ESR techniques have recently been reviewed by Hall (1980).

Hogg *et al.* (1975) noted the importance of distinguishing between Fe present within the kaolinite structure and Fe located in the impurities such as mica and iron oxides/oxyhydroxides which are common in kaolin ores. Both they and Janot *et al.* (1973) identified fine particles of hematite and goethite in kaolin samples. Jefferson *et al.* (1975) found that the non-structural Fe of iron-stained kaolins was present as either a noncrystalline gel, coating the surface of the kaolinite flakes, or as a fine coating of goethite. They noted that kaolins with significant iron coating may be cleaned by acid, but that chemical attack has no effect on the structural iron, ferrous or ferric. Angel and Vincent (1978), using ESR, identified a lepidocrocite-like phase as a surface coating in English kaolins, and a hematite- or goethite-like phase associated with American kaolins. The latter was resistant to chemical removal.

Whereas Mössbauer spectroscopy can usually resolve the spectral contributions of structural and impurity Fe in clays, very fine iron oxide particles contribute a Mössbauer spectrum which is not very different to that arising from Fe in some structural sites. Such fine particles show relaxation effects at room temperature (see Fysh and Clark (1982a, 1982b) for further discussion). Several workers (e.g., Janot *et al.,* 1973; Jefferson *et al.,* 1975) have used low temperatures to slow the magnetic relaxation of fine oxide particles present, resulting in a greater proportion of spectral area in magnetically split subspectra. When considering the possible existence of an Fe-rich phase associated with montmorillonites, Goodman (1978) concluded that extremely small particles of iron oxide or oxyhydroxide were present in some low-Fe montmorillonites. These particles showed no magnetic ordering even at 5°K, and Goodman suggested an upper limit on volume of $\ll 10^4$ Å^3.

EXPERIMENTAL

All of the raw and beneficiated kaolin samples used in this work were provided by Comalco. The kaolin for this study was cyclone-separated to remove coarse particles (predominantly quartz), dried, and subjected to a centrifugal size separation and magnetic separation, with the non-magnetic fraction comprising the

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sample studied here. Further details of the processes are given in the following paper. The present sample is designated as specimen K3.

Mössbauer absorbers for this work were made by placing ~250 mg/cm² of sample (~3–6 mg Fe/cm²) into Perspex piston-type holders, larger quantities having been found to result in unacceptably high γ-ray absorption. Because all samples were in the form of fine powders (typically ~10 μm in diameter), no grinding was necessary, and spectral broadening from large iron mineral particles was unlikely. Mössbauer spectra were acquired in the constant acceleration mode into 512 channels (folded) with, typically, 2×10^6 counts/channel. The same drive and ^{57}Co(Rh) source were used for both room-temperature and low-temperature experiments, the latter being made with the specimen placed in a liquid nitrogen/helium cryostat. The least-squares fitting assumed Lorentzian line-shapes, with doublets and corresponding line pairs in magnetically split spectra constrained to have equal width and intensity.

RESULTS

Figure 1 shows the Mössbauer spectra of the sample at three different temperatures. The room temperature spectrum (Figure 1a) is principally a quadrupole split doublet, but the curved baseline indicates a considerable contribution from a relaxed subspectrum. The behavior cannot be due to a range of iron environments in the kaolin as a range of environments would result in a more Gaussian shape which would fall away in the wings even more rapidly than a Lorentzian line-shape. The least squares fit to Figure 1a comprises a doublet plus a relaxed subspectrum calculated using the relaxational model of Blume and Tjon (1968). The fitted parameters are given in Table 1. The isomer shifts show that both subspectra are due to Fe^{3+}, with the parameters of the doublet agreeing well with those of Malden and Meads (1967) and later workers for octahedrally coordinated Fe^{3+} in the kaolinite structure.

The relaxed subspectrum may result from either fine, superparamagnetic (SPM) iron oxide particles on the clay surface, or from paramagnetic relaxational broadening of the Mössbauer line. If the relaxation is SPM in origin, the relaxed component should disappear as the temperature is lowered and be replaced by the magnetically split spectrum of the compound responsible. Paramagnetic relaxation spectra should also sharpen with decreasing temperature, although the extent of the decrease and the shape of the observed spectrum will depend strongly on the particular relaxation mechanism.

The 77°K and 4.2°K spectra, Figures 1b and 1c, are also significantly relaxed. Each was fitted with two magnetically split subspectra, a relaxed subspectrum, and the central doublet. The parameters are given in Table
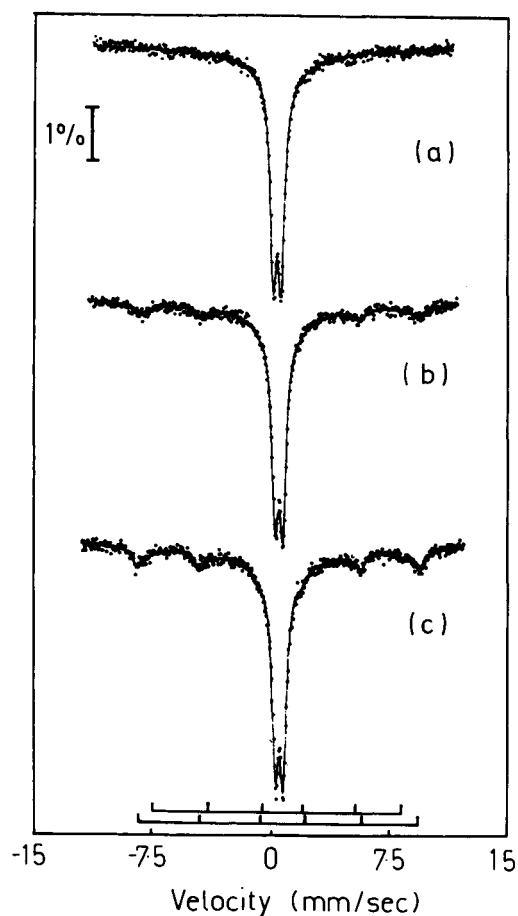

Figure 1. Mössbauer spectra of cleaned Weipa kaolinite taken at (a) room temperature, (b) 77°K and (c) 4.2°K. The bar diagrams indicate the line positions for the two magnetically split subspectra in the 4.2°K spectrum.

1. As at 300°K, the relaxed component contributes about 20% of the total spectral area in each (although the relaxation rate must decrease with temperature), while the areas associated with the two magnetically split subspectra increase as the temperature decreases.

The magnitude of the splitting for the outer magnetically split subspectrum is too large to arise from any known magnetically ordered impurity in the kaolin, and is in fact characteristic of the paramagnetic hyperfine split spectrum of high-spin Fe^{3+} in the S = 5/2 state. The smaller magnetically split subspectrum may also be paramagnetic in origin, or it may be due to some magnetically ordered iron mineral impurity, as is considered below.

Expected paramagnetic HFS Mössbauer spectra

The conditions for the observation of paramagnetic HFS were given by Wickman *et al.* (1966) and Wickman and Wertheim (1968), together with details of the spectra expected under different crystal field splittings.

Table 1. Mössbauer parameters for the least square fits to the spectra in Figure 1.[1]

Temperature (°K)	Subspectrum	Isomer shift (mm/sec)	Quadrupole splitting (mm/sec)	Hyperfine field (kOe)	Area (%)
300	doublet	+0.35(2)	0.52(2)	0	80
	relaxed	+0.35(2)	—	—	20
77	doublet	+0.47(2)	0.52(2)	0	62
	relaxed	+0.47(2)	—	—	20
	magnetic(1)	+0.47(2)	−0.19	495(3)	3
	magnetic(2)	+0.47(2)	−0.09	549(3)	15
4.2	doublet	+0.47(2)	0.52(2)	0	55
	relaxed	+0.47(2)	—	—	20
	magnetic(1)	+0.47(2)	−0.19	495(3)	4
	magnetic(2)	+0.47(2)	−0.09	555(3)	21

[1] The number in parentheses indicates the error in the last figure. Values marked with a dash could not be determined from the fits but are not zero, while those for which no uncertainty is given could only be determined approximately because of the low intensity of the spectral lines concerned. Isomer shifts are given with respect to α-iron at room temperature and the quadrupole splitting is $\frac{1}{2}e^2qQ$ for the doublet and $\frac{1}{2}e^2qQ \cdot \left(\frac{3 \cos^2\theta - 1}{2} \right)$ for the magnetically split subspectra.

A suitable crystal field Hamiltonian for Fe^{3+} in kaolin is (e.g., Meads and Malden, 1975)

$$H_{CF} = D[S_z^2 - \frac{1}{3}S(S + 1)] + E[S_x^2 - S_y^2],$$

where S is the ionic spin quantum number, and the first and second terms represent the axial and rhombic components of the crystal field respectively. These terms split the six-fold degenerate electronic ground state into three Kramer's doublets.

ESR measurements on both natural and synthetic kaolinites have identified three distinct iron sites within the kaolinite structure, although some disagreement exists as to the actual parameters describing each (Hall, 1980). Meads and Malden (1975) gave the following average values for natural kaolins (where $\lambda = E/D$): center I $\lambda = 1/3$, D = 1.2 cm^{-1}; center IIA $\lambda = 0.234$, D = 0.585 cm^{-1}; center IIB $\lambda = 0.207$, D = 0.322 cm^{-1}. Center I becomes more populated as crystallinity decreases, indicating that it is associated with Fe^{3+} ions adjacent to stacking disorders (Mestdagh et al., 1980). Centers IIA and IIB are associated with Fe^{3+} in regions of high crystallinity and regular stacking, and the difference between the two has been attributed to the existence of two distinct orientations of surface OH groups (Hall, 1980). Although these three sites are not resolved in the room temperature Mössbauer spectrum of kaolinite, Komusinski et al. (1981), in an ESR-Mössbauer study of a variety of kaolins, noted a correlation between the Mössbauer linewidth and the number of Fe^{3+} sites detected by the ESR measurements. The paramagnetic HFS spectra arising from each of the three sites are expected to be somewhat
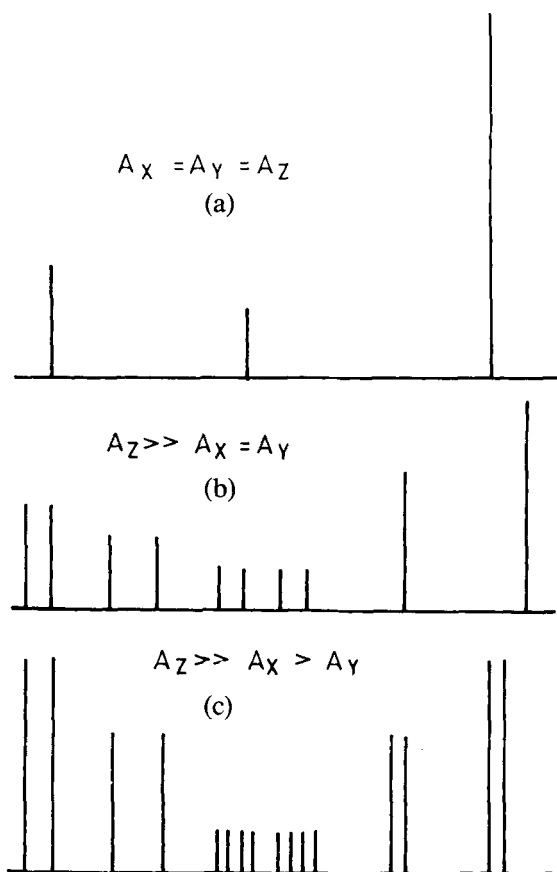

Figure 2. Predicted Mössbauer line positions corresponding to three different crystal field splittings.

different, depending on the value of λ. (In the following the levels are denoted by the pure S_z values which they have at $\lambda = 0$).

Under the conditions for paramagnetic HFS, the very slow electronic relaxation rate results in each of the three Kramer's doublets giving rise to independent contributions to the Mössbauer spectrum through the magnetic hyperfine interaction whose Hamiltonian is

$$H_{MHF} = A_z S_z I_z + A_x S_x I_x + A_y S_y I_y.$$

The values of A_x, A_y, A_z, the hyperfine interaction constants determining the coupling between the total electronic and nuclear angular momenta S and I, respectively, depend on the symmetry of the crystal field splitting, and Wickman et al. (1966) have calculated their variation as a function of λ. The resulting Mössbauer spectra for the three sets of conditions on A_x, A_y, A_z which are of interest here are given by the bar diagrams in Figure 2. These diagrams have been scaled to the same A_z value but the maximum value of A_z will be different for each of the Kramer's doublets. Figure 2 may now be used in conjunction with Figure
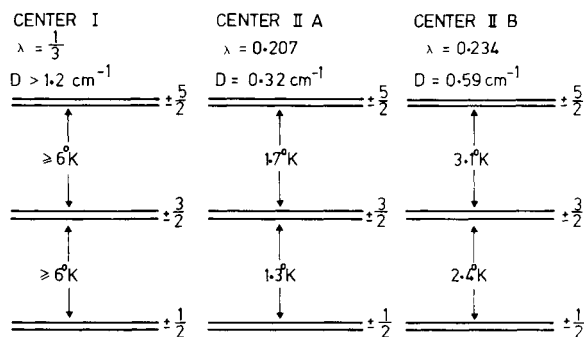
Figure 3. Energy level diagram for the three iron sites in kaolin.

Figure 4. Room temperature ESR spectrum of cleaned Weipa kaolinite.

7 from Wickman *et al.* (1966) to predict the Mössbauer spectra for each of the iron sites in kaolin.

Consider first the 5/2 Kramer's doublet; for site I, $\lambda = 1/3$ which makes $A_z \gg A_x > A_y$, so that a spectrum somewhat similar to that in Figure 2c is expected. The overall splitting of the spectrum will be $5/2 \times 220$ kOe (the hyperfine splitting associated with one unit of spin angular momentum in Fe^{3+}) = 550 kOe. For sites IIA and IIB the values of A_x and A_y decrease further with respect to A_z and become more nearly equal, as in Figure 2b. For the 3/2 Kramer's doublet; the values of A_x, A_y, and A_z are equal for site I, and the three line spectrum expected for an isotropic hyperfine interaction (Figure 2a) should be observed. For sites IIA and IIB, $A_z > A_x > A_y$, and a spectrum somewhat similar to that in Figure 2b is expected, with a total splitting of ~330 kOe.

For the 1/2 Kramer's doublet for all three sites, $A_y \gg A_x > A_z$. Although this situation would give a complicated spectrum with a maximum splitting of 110 kOe it is anticipated that only a quadrupole split doublet will be observed because of the fast relaxation paths available, as is explained below. In the absence of other interactions to mix the three degenerate electronic levels, the spectra arising from each will superimpose in the experimentally observed spectrum.

Site populations

Before the magnetically split subspectra observed can be identified with those predicted above, the relative occupancies of the various electronic states must be considered. The splittings of the levels for the three iron sites in kaolin are shown in Figure 3 based on the data of Meads and Malden (1975). The room temperature ESR spectrum of the specimen is shown in Figure 4, with the peaks corresponding to the various iron centers indicated. The central peak (center I) contributes ~45% of the total area, indicating the fairly low crystallinity of the Weipa kaolin. Thus, approximately 45% of the iron nuclei are expected to have a site symmetry for which, according to Figure 3, the 5/2
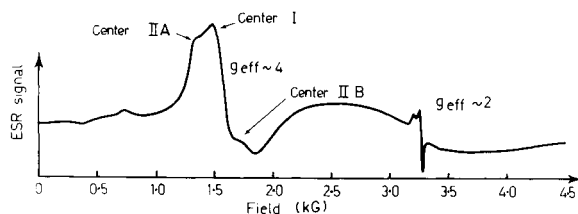
level is almost totally thermally depopulated at 4.2°K. Therefore the only 5/2 level Mössbauer subspectrum expected arises from centers IIA and IIB (principally the former).

Using the solutions to the total Hamiltonian given by Wickman *et al.* (1966) the expected splittings of the outer Mössbauer absorption peaks for type I and type II iron sites (the IIA and IIB λ values are too similar to give any appreciable difference in the 5/2 spectra expected from each) are:

	LH peak	RH peak
center I	31 kOe	3 kOe
center II	10 kOe	0 kOe

Although the experimental resolution of the outer magnetically split subspectral peaks is very poor, there appears to be no tendency for those at the low velocity end of the spectrum to be any better resolved. Further, the separation of the pairs of peaks at both ends is ~30 kOe, and inasmuch as the center I site 5/2 level is the only one capable of contributing a splitting of this size, but is thermally depopulated at 4.2°K, the inner magnetically split sub-spectrum must be due to a magnetically ordered impurity mineral.

Relaxation and magnetic effects

Although the expected hyperfine split spectrum of the 5/2 level for the type II sites can be identified, that predicted for the 3/2 level is absent in the experimental spectrum; instead only a relaxed subspectrum can be seen. This situation is not unexpected, as the relaxation rate will be faster for the 3/2 level (see e.g., Wickman *et al.,* 1966) and hence average the observed magnetic hyperfine splitting to zero. For the 1/2 level, the relaxation rate will be faster again because the $J_z = 1/2 \leftrightarrow J_z = -1/2$ transitions are allowed, and magnetic hyperfine splitting should not be observed here either.

The relaxation mechanisms in a paramagnet are generally of two kinds; spin-spin relaxation and spin-lattice relaxation (see Wickman and Wertheim, 1968). Spin-spin relaxation, which in its simplest form consists of mutual spin flips of neighboring ions, is essentially temperature independent. However, decreased Fe concentration (increased Fe–Fe separation) increases the spin-spin relaxation time (e.g., Wignall,
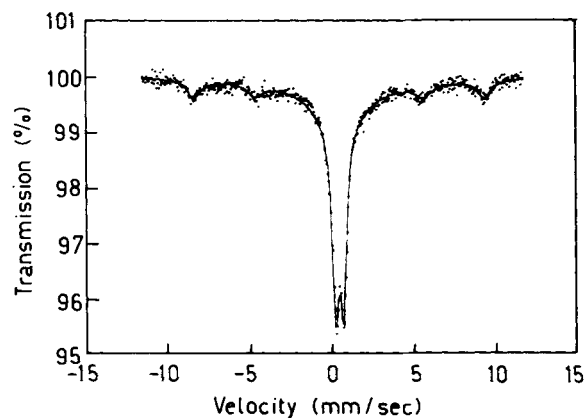
Figure 5.   Mössbauer spectrum of handpicked clay specimen taken at 4.2°K.

1966), and the observation of paramagnetic hyperfine structure in the Mössbauer spectrum of kaolinite is thus related to the low Fe substitution of the structure.

Chemical analysis of the Weipa kaolins studied indicated about 3 mole % replacement of Al by Fe, giving an average Fe–Fe separation of ~3.2 lattice spacings or ~10 Å in the basal plane. This distance is about the same as that in several other Fe^{3+} compounds which exhibit paramagnetically split Mössbauer spectra at low temperatures, although it should be noted that the spin-spin relaxation time depends to some extent on the type and configuration of the intervening non-magnetic atoms. An additional factor favoring long spin-spin relaxation times in sheet silicate minerals is the large basal spacing, considerably increasing the Fe–Fe distances in one dimension. Changes in this spacing with hydration may also affect the observation of paramagnetic hyperfine structure.

Spin-lattice relaxation processes occur via the coupling of the ionic spins to the structural phonon modes, and the energy change of a spin flip results in the creation or annihilation of a phonon. Clearly such processes are temperature dependent through the phonon population, and it is because of the increase in spin-lattice relaxation rate that no hyperfine splitting of the Mössbauer spectrum of kaolin is seen at 300°K. The relaxed component of the 300°K spectrum must be predominantly due to nuclei in the 5/2 state for which the spin-lattice relaxation time is still not short enough to completely average out the paramagnetic hyperfine splitting. There is a small reduction in the fitted value of the larger hyperfine field in going from 4.2°K to 77°K, reflecting the beginning of its inward collapse due to the increasing spin-lattice relaxation rate. No change in splitting was observed for the inner magnetically split subspectrum, consistent with the behavior expected for a material with a high ($\gg 77$°K) ordering temperature.

The iron which contributes the smaller hyperfine split subspectrum at 4.2°K is most probably similar to that described by earlier workers (see previous references) as various poorly crystalline oxide phases coating the kaolinite surface. It has been suggested (e.g., Veith and Jackson, 1974; Jefferson et al., 1975) that such oxide coatings arise when structural Fe^{2+} oxidizes to Fe^{3+} and migrates to the clay surface during weathering, forming a noncrystalline gel coating. Such gel coatings are usually only observed on clays having little or no structural Fe^{2+}. At 77°K such a gel may not be magnetically ordered. As reviewed by Bowen (1979), many ferric gels have been observed to order only below this temperature. On the basis of the present results it is not possible to distinguish whether the Fe on the surface of the kaolinite is in the form of a noncrystalline gel, or a very finely divided, aluminous goethite. The physical extent of the iron coating may well be such that it is not particularly meaningful to try and classify it as one of the known crystalline oxyhydroxide iron minerals. From the variety of particle sizes and ordering temperatures reported in the literature for so-called "amorphous" or noncrystalline iron gel phases it seems likely that a whole range of structures (and compositions, if Al is incorporated) exist for such compounds.

The kaolin used in the present investigation was taken from the pallid zone beneath the mottled clays underlying the ironstone and bauxite at Weipa (Loughnan and Bayliss, 1961). The iron oxides/oxyhydroxides associated with the kaolin in the pallid zone have likely resulted from a secondary precipitation of descendant iron in solution, originating in the weathering zone (Fysh and Clark, unpublished results). The iron oxide in the pallid zone is generally in localized areas extending for several centimeters, suggesting that after initial nucleation, precipitation occurred preferentially in these mottled regions. Thus, rather than having resulted from weathering of structural Fe^{2+}, the iron oxide coating on the Weipa kaolin is probably secondary in origin.

Figure 5 shows the 4.2°K Mössbauer spectrum of a sample of clay handpicked from a region of the clay profile which appeared to be free from secondary iron oxide staining. The spectrum contains almost none of the smaller magnetically split subspectrum, and is well fitted by only one magnetically split subspectrum, a relaxed subspectrum and a central doublet, with all parameters being in excellent agreement with those of the corresponding subspectra from Figure 1. Figure 5 confirms that the smaller magnetically split subspectrum is due to surface iron, and that any splitting of the individual lines of the 550 kOe subspectrum of Weipa kaolin is not resolved at 4.2°K.

It is worth noting that the quadrupole splitting associated with the 5/2 magnetically split subspectrum is somewhat less than half that of the doublet, consis-

tent with the proposed interpretation for structural iron paramagnetic HFS. The principal axes of the EFG are most probably arranged with one axis perpendicular or nearly perpendicular to the basal plane and the other two axes approximately in the plane. The direction of the dominant magnetic interaction will be towards the nearest impurity iron atom (which will most commonly be in the basal plane because of the shorter cation–cation distances). Its direction, however, may make many different angles with the EFG direction, reducing the measured quadrupole splitting, but not to zero because the angle between the two interactions is not statistically random.

Figure 6 shows the spectrum of the original sample taken at 4.2°K in an external field of 60 kG applied parallel to the gamma-ray direction, which should reduce the intensities of lines 2 and 5 to zero. Application of a large external field such as this can simplify spectra by predominating over the effects of the crystal field. The magnetic splitting measured from the outer lines (495 ± 5 kOe) is 60 kOe less than the zero field splitting of the 5/2 level. This spectrum indicates that the majority of the iron ions now lie in the −5/2 state, as would be expected from the induced splitting in the electronic energy levels.

The quadrupole splitting of the spectrum is zero to within experimental accuracy. Wickman *et al.* (1966) observed a substantial decrease in the quadrupole splitting of the hyperfine split spectrum of paramagnetic iron in a metalloprotein for large applied magnetic fields. Such a decrease results because the principal quantization direction is no longer determined by the distribution of Fe^{3+} within the structure, but rather by the direction of the external magnetic field. In a powder absorber the principal axis of the quadrupole interaction is randomly oriented with respect to the new direction of quantization, and the net quadrupole splitting decreases accordingly.

The effect of the external magnetic field on the surface Fe associated with the kaolin will depend on the type of magnetic ordering it exhibits. Ross and Longworth (1980) measured the spectrum at 4.2°K and in a 45 kG longitudinally applied magnetic field of a noncrystalline ferric hydroxide phase precipitated on a sandy clay. The spectral contribution of the gel was not well resolved from that of other Fe species present, but it appeared to be quite broadened, with a splitting of about 490 kOe. Thus, it is likely that the small amount of Fe on the surface of the kaolinite contributes to the inner shoulders of the spectrum in Figure 6. The total area of the asymmetric contribution is greater than that which would be due only to the impurity mineral, indicating that not all of the Fe is in the −5/2 state. Mørup *et al.* (1978) obtained similar spectra for frozen ferric nitrate solutions in externally applied fields, although in that study fields of 50 kG resulted in symmetric lineshapes.
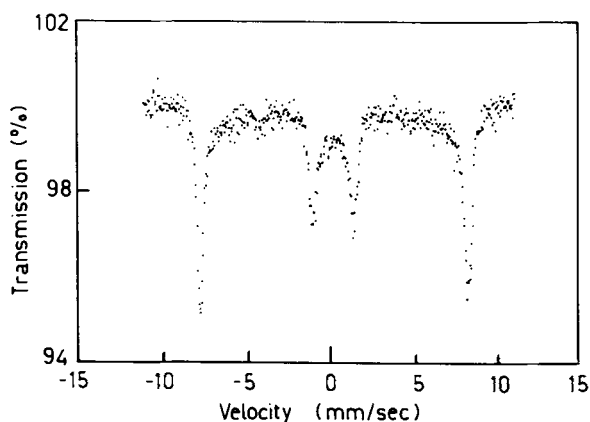

Figure 6. Mössbauer spectrum of cleaned Weipa kaolinite at 4.2°K and in an external field of 60 kG applied parallel to the gamma-ray direction.

The intensities of lines 2 and 5 did not entirely disappear as expected, indicating incomplete alignment for at least one component of the spectrum. The most probable cause is the existence of surface domains in a very fine grained (~30–100 Å), magnetically ordered material such as has been seen in synthetic γ-Fe_2O_3 (Coey, 1971; Morrish and Clark, 1974) and precipitator fly-ash (Aikin and Cashion, 1983). The best estimate for the positions of lines 2 and 5 in Figure 6 indicate a total splitting intermediate between those of the main and shoulder components of the outer lines. Thus, it is due to either the surface iron described above or another magnetic impurity (probably an oxide/oxyhydroxide) which consists of particles sufficiently small to give a doublet spectrum at 4.2°K in the absence of an applied magnetic field.

CONCLUSIONS

The kaolin sample studied here contains structural iron which exhibits paramagnetic relaxation, as well as iron in surface material comprising at least one magnetically ordered phase consisting of very fine particles. One question which needs consideration is why low temperature paramagnetic hyperfine splitting of kaolin structural iron has not been observed previously. The room temperature spectra of various kaolins in the literature suggest relaxed behavior in several samples (e.g., Jefferson *et al.*, 1975; Komusinski *et al.*, 1981), although it appears to have been overlooked. One possible reason is that the spectra in question may have been obtained with an experimental configuration that resulted in baseline curvature even for non-relaxed spectra. In this situation such curvature is usually included as a fitting parameter; such a method of fitting would have obscured the behavior observed here.

Investigations of kaolin at temperatures of about 85°K have also been reported (Janot *et al.*, 1973; Jefferson *et al.*, 1975; Cuttler, 1980) without the observation of

paramagnetically split spectra. In the first two of these studies some sort of magnetically ordered impurity mineral accompanied the kaolin, and in sufficient quantities the more intense spectral lines of the resultant magnetically split subspectrum would have obscured those of the kaolin. A further explanation is that for some of the kaolins in these studies the structural Fe content was high enough to increase the spin-spin relaxation rate of the $\pm 5/2$ states significantly. This seems unlikely, however, as the Fe contents reported are generally lower than the 1.7 wt. % Fe_2O_3 of the Weipa sample. The kaolin studied at low temperatures by Cuttler (1980) was synthetic, and the Fe present was almost entirely Fe^{2+}. The spin-spin relaxation rate of Fe^{2+} is much greater than that exhibited by Fe^{3+} because the coupling of the lattice modes to the total angular momentum is via the orbital contribution. Further measurements, possibly on $^{57}Fe^{3+}$-enriched kaolins, in small applied magnetic fields should be capable of revealing considerable information regarding the local Fe site symmetry in kaolinite, and the relationship between Fe concentration and crystallinity. In the following paper the iron site identifications made here are used to interpret the effects of cleaning on the Fe associated with kaolinite.

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Резюме—Мессбауеровские спектры [57]Fe чистого каолинита Вайпа из Австралии показали, что значительная фракция структурного железа проявляет парамагнитную релаксацию между 4° и 300°К. Это наблюдалось первый раз для железных ионов в минерале. Образец содержал также очень мелкую фазу окиси/оксигидрата железа, вероятно, вторичного происхождения. [E.G.]

Resümee—[57]Eisen-Mössbauerspektren eines gereinigten Kaolin von Weipa, Australien, zeigte, daß ein beachtlicher Teil des in der Struktur eingebauten Eisens paramagnetische Relaxation zwischen 4°K und 300°K zeigt. Dies wurde zum ersten Mal bei einem Fe^{3+}-Ion in einem Mineral beobachtet. Die Probe entheilt außerdem eine sehr feinteilige Fe^{3+}-Oxid/Oxihydroxid-Phase, die wahrscheinlich sekundär entstanden ist. [U.W.]

Résumé—Des spectres de Mössbauer [57]Fe d'un kaolin nettoyé de Weipa, Australie ont montré qu'une fraction considérable du fer structural exhibait une relaxation paramagnétique entre 4°K et 300°K, la première fois que ceci a été observé pour des ions ferriques dans un minéral. L'échantillon contenait aussi une phase de particule ferrique oxide/oxyhydroxide très fine, probablement d'origine secondaire. [D.J.]