ELECTRON SPIN RESONANCE MORPHOLOGY & RELATED PROPERTIES OF SELECTIVELY DOPED SYNTHETIC KAOLINITES

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E L E C T R O N S P I N R E S O N A N C E

M O R P H O L O G Y

A N D R E L A T E D P R O P E R T I E S O F

S E L E C T I V E L Y D O P E D

S Y N T H E T I C K A O L I N I T E S

A Thesis submitted to the Council for National Academic Awards for the degree of Doctor of Philosophy by K.S. Richards, B.Sc.

The work described in this thesis was carried out in the Department of Mathematical Sciences at Plymouth Polytechnic, Plymouth, Devon in the period between September 1973 and September 1976.

This is to certify that, unless stated otherwise, the results presented here were obtained by Mr. K.S. Richards under my supervision.

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ABSTRACT

This thesis is divided into six chapters. The first chapter is an introduction to the structure and properties of natural kaolinites. The second chapter describes the synthesis of kaolinite and a study of various reaction parameters and their effect on the morphology of synthetic kaolinites.

Chapters 3 and 4 are devoted to Electron Spin Resonance in natural and doped synthetic kaolinites. Chapter 5 is a study of Fe^{2+} and Fe^{3+} in kaolinite by Mössbauer spectroscopy. The final chapter consists of a short summary and discussion with some suggestions for future work.

Copies of papers accepted and submitted for publication are bound at the end of this thesis.

C O N T E N T S

I N T R O D U C T I O N.

0.17% of the earth's mass is attributable to clay[1] but as it occurs solely in the crust it is a major constituent of our planet's surface. Early civilized man manipulated clays for domestic purposes and relied on basic physical and chemical properties of the material which nowadays are exploited in many technical applications. For example clays are used extensively in the chemical industry as catalysts, they are a constituent of paints, wallpaper, dyes, cosmetics, medicines and plastics.

Probably the most extensive commercial use of china clay is the coating or filling of paper. In contrast to most other clay minerals kaolinite usually occurs as a relatively pure white powder and its application in the paper industry depends on two main properties. These are apparent whiteness and rheological behaviour. The degree of whiteness and the rheological properties of a kaolinite in part determines its commercial value and has played an important role in the financial support for research programmes both in industry and academic institutions.

Past studies have shown that impurities and defects associated with kaolinite most probably affect whiteness and rheology.[2] Also it is known that variations in particle size affect brightness and rheology of a clay.[2]

The rheology of a clay-water system would also be expected to depend on the morphology of the clay particles.

This thesis describes a project which is a continuation of the work previously done in the same laboratory by P.L. Hall (1973) Ph.D. Thesis London University and J.P.E. Jones (1975) Ph.D. Thesis London University. An attempt has been made to synthesise kaolinites selectively doped with known impurities or induced defects and to study their possible effects on morphology and brightness.

CHAPTER 1

1.1 Basic Structure and Composition of Clay Minerals.

The general term clay describes layer silicate minerals with particle size less than about two micrometers. The basic crystal structure of clay minerals[3] comprise two basic units which are often referred to as the octahedral and tetrahedral layers.

The octahedral layer consists of divalent or trivalent cations octahedrally co-ordinated (six-fold co-ordination) to oxygen atoms and hydroxyl groups. For divalent cations such as Mg^{2+} all available cation sites are occupied and the structure is termed trioctahedral. This particular configuration may be regarded as a derivative of brucite $Mg_3 (OH)_6$. For trivalent cations such as Al^{3+} only two of three available cation sites are occupied. The configuration is said to be di-octahedral and may be regarded as a derivative of gibbsite $Al_2 (OH)_6$.

A tetrahedral array of oxygen atoms with silicon atoms co-ordinated at the centre (SiO_4 units) make up the tetrahedral layer. These tetrahedra are linked together to form a repeated, hexagonal, two dimensional network.

The two basic layers can be chemically combined in a number of ways and has resulted in clay minerals being subdivided into two main groups[3]. These are classified as 2:1 or 1:1 layer minerals.

The ratio indicates the number of tetrahedral to octahedral layers. The majority of clay minerals are of the 2:1 type formed by a single octahedral layer sandwiched between two tetrahedral layers, the most important members of this group being the micas, montmorillonites, chlorites and vermiculites.

The most important members of the 1:1 group are known as the Kandites and include the minerals kaolinite, dickite, nacrite, and halloysite. Dickite and nacrite are polymorphs of kaolinite differing mainly in the stacking of the layers. Halloysite may differ from kaolinite not only in stacking but also in its water content. The morphology of halloysite is markedly different from kaolinite consisting of long thin walled tubes.

1.2 Atomic Structure of kaolinite.

Kaolinite is a 1:1 dioctahedral clay mineral. The Al^{3+} cation is octahedrally co-ordinated to two oxygens and four hydroxyl groups forming an octahedral alumina layer. This layer is bonded to a tetrahedral silica layer to form a basic kaolinite unit. Fig. 1.1 Successive kaolinite layers are hydrogen bonded[3.4] to form kaolinite crystals.

The crystal structure was first determined by Gruner[5] who suggested a monoclinic structure. More detailed work by Brindley[6.7] gave a triclinic unit cell of dimensions.

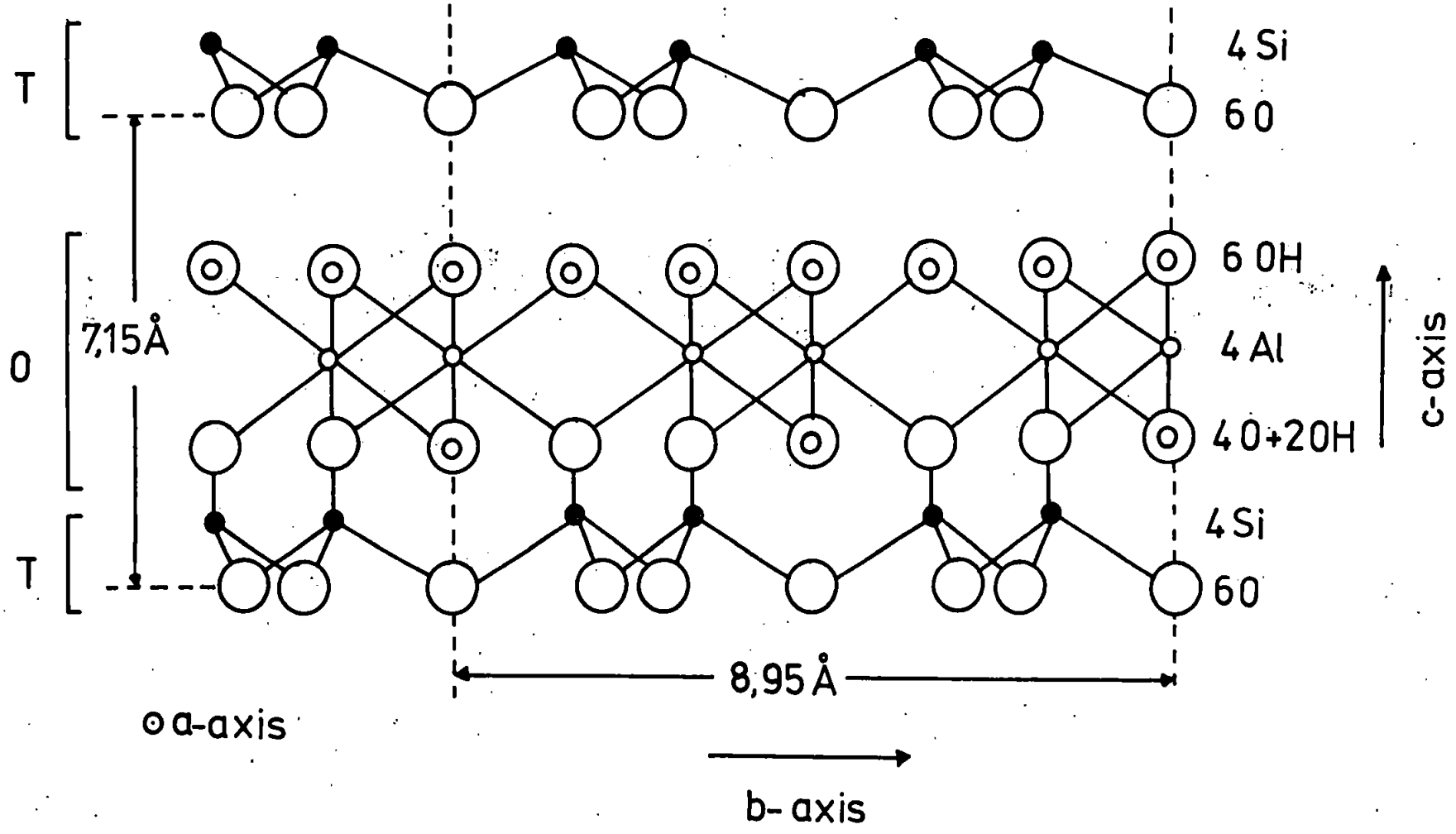


Fig 1.1 The structure of kaolinite $2[Al_2(OH)_4 \cdot Si_2O_5]$

$a = 5.15\text{Å}$ $b = 8.95\text{Å}$ $c = 7.39\text{Å}$

$\alpha = 91.8^\circ$ $\beta = 104.5^\circ$ $\gamma = 90^\circ$

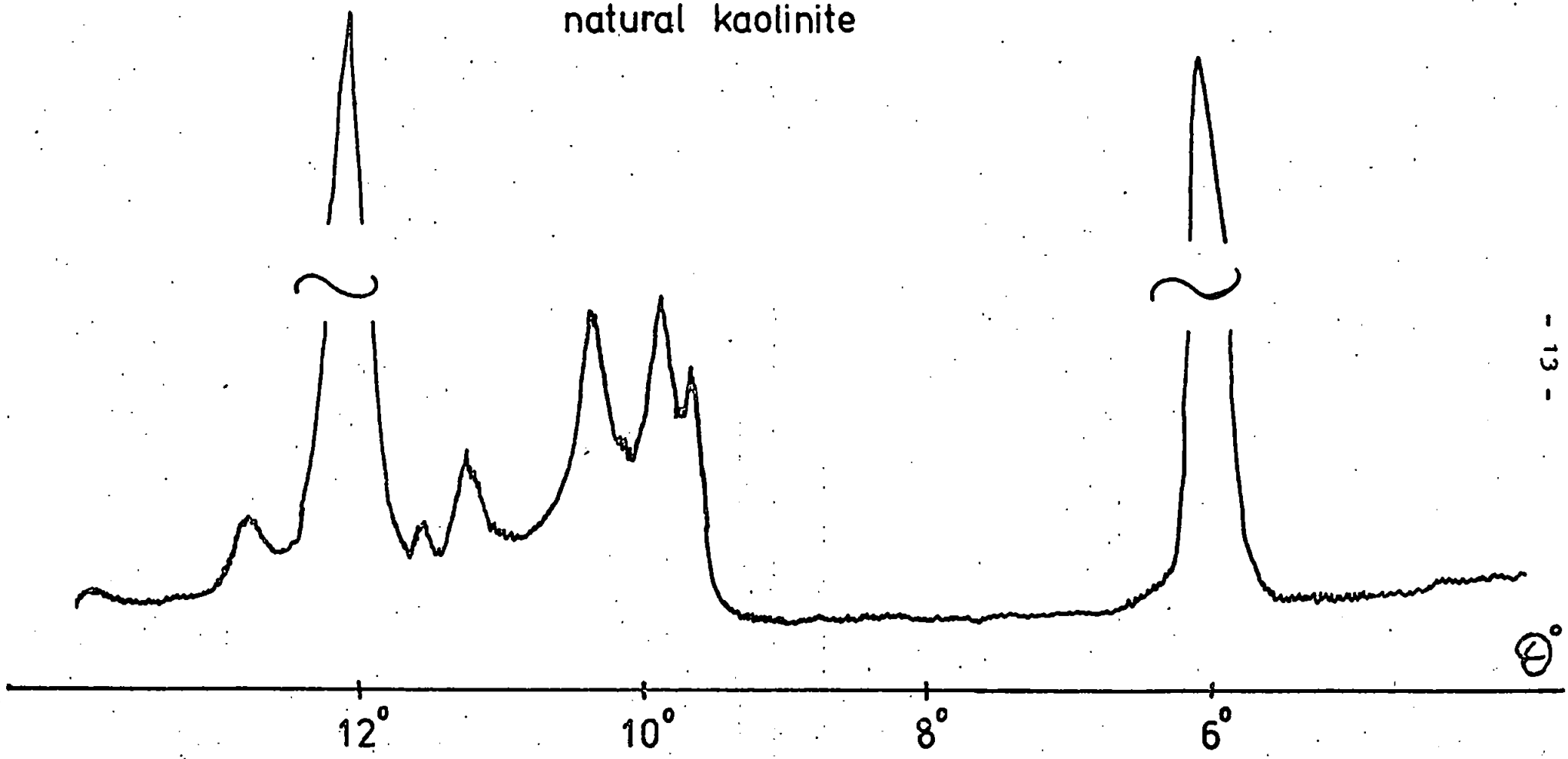
Repulsion between adjacent Al^{3+} ions produces lateral distortions in the octahedral layer with an increase in the crystal dimensions.

Since there is chemical bonding between the octahedral and tetrahedral layers the silicon tetrahedra rotate slightly both clockwide and anti-clockwise about an axis perpendicular to the layers thus destroying the ideal hexagonal symmetry of the tetrahedral layer. An X-ray diffraction spectra of a typical natural kaolinite is shown in Fig. 1.2.

1.3 Variations in crystallinity of kaolinite determined by X-ray diffraction.

Kaolinite usually consists of small hexagonal platelets with dimensions of the order of one micrometer e.s.d. The thickness of the platelets is typically 0.05 micrometers and hence the majority of crystals have large aspect ratios. Generally speaking the flat plate like nature of kaolinite crystals tends to make them sediment with their basal planes parallel to a substrate, thus preventing the preparation of completely random orientated samples. The effect of the preferred orientation is to produce an increase in the intensity of the basal reflections and prevents accurate quantitative analysis by X-ray diffraction. Various methods have been reported for reducing effects due to preferred orientation for quantitative analysis of kaolinite by X-ray diffraction.[8,9]

Fig 1.2 X-Ray Spectrum of a typical natural kaolinite



Quantitative analysis of natural kaolinites by X-ray diffraction is further complicated by the presence of additional mineral impurities which may have similar X-ray diffraction spectra. It is possible to distinguish some mineral impurities by treating the clay with certain polar liquids.[10] Kaolinite has no molecular water in its crystallisation and when treated with ethylene glycol does not show any observable differences in its X-ray diffraction pattern. However, minerals such as endellite (hydrated halloysite) and montmorillonite contain molecular water which can be displaced by ethylene glycol.[10] The displacement results in larger d-spacings and observable changes in X-ray diffraction spectra. The application of ethylene glycol provides a technique which is capable of detecting montmorillonite at concentrations as small as 1%.

For many natural samples of kaolinite some reflections which theoretically would be expected to occur are not resolved in the X-ray diffraction spectra. Explanations for their absence have been suggested by Brindley and Robinson.[4] It is proposed that the hydroxyl groups in an ideal kaolinite layer are arranged at regular intervals of $b/3$ along the b-axis. If the displacement however is random and not an integral multiple of $b/3$ then all reflections are eliminated except those with a k-Miller index of 0,3,6 etc.

Bailey[11] has also attributed crystallinity variations to the distribution of the vacant cation site. Newnham[12] and Radoslovich[13] reached similar conclusions.

In view of the intensity variations of basal reflections which may be caused by the degree of preferred orientation in various methods of sample preparation, Hinckley[14] has proposed a method of measuring crystallinity which permits a numerical parameter to be evaluated from the X-ray spectra with samples in a preferred orientation. The technique is illustrated in Fig. 1.3. Natural clays with high crystallinity typically have a Hinckley[14] crystallinity index of approximately 1.2 and poorly crystalline samples have an index less than 0.5.

1.4 Morphology of kaolinite.

The rheological properties of clay slips used for paper coating are determined to a very large extent by the morphology of the particles. The macroscopic shape of the particles however, does not appear to be directly correlated with internal structure or microcrystallinity. Although it is usual that kaolinites with high crystallinity show greater hexagonal form, identical Hinckley[14] crystallinity indices can be obtained from kaolinites with vastly different morphology. In the work reported here synthetic kaolinites have been produced with high crystallinity indices but with no detectable hexagonal form.

Diagram showing calculation of X-ray crystallinity index

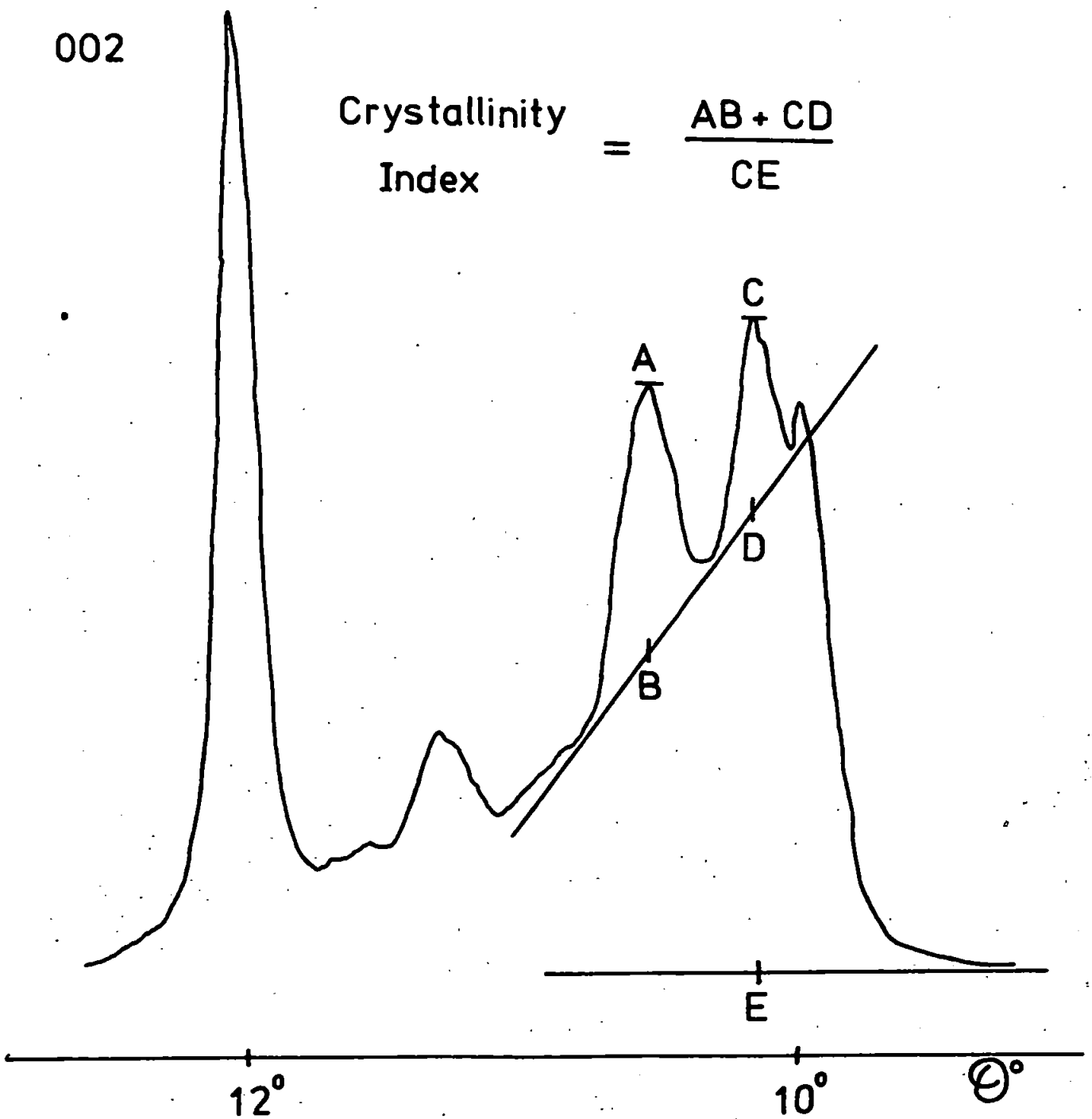


Fig 1.3

1.5 Impurities associated with kaolinite.

A chemical analysis of a typical natural kaolinite indicates the presence of iron, titanium, magnesium, calcium, potassium and sodium as impurities.[3] Also, most samples have either excess alumina or silica. Conventional wet chemical analysis can only determine elemental analysis by the production of oxides and therefore gives no indication whether the impurity is an additional mineral or not. The same criteria is true for analysis by X-ray fluorescence. Fig. 1.4 shows the X-ray fluorescence analysis of a typical natural kaolinite. However, by combining X-ray diffraction measurements with results obtained by chemical analysis it may be possible to determine both the elemental and mineralogical impurities associated with kaolinite. The mineral impurities quartz, anatase, rutile and montmorillonite are commonly found as well as micas. However, it is seldom possible to make analysis sufficiently quantitative to determine deviations from the ideal composition of kaolinite.

Natural kaolinites also may have a small organic component as an impurity.[15] Hall[15] has extensively studied the organic fraction associated with natural clays particularly ball clays which tend to be more heavily contaminated with organic matter than china clays.

Fig 1.4 X-ray flourescence analysis of a typical natural kaolinite

OXIDE	%	Theoretical composition
Al_2O_3	38·3	39·50
SiO_2	46·6	46·54
Fe_2O_3	0·49	—
TiO_2	0·05	—
MgO	0·20	—
CaO	0·20	—
K_2O	0·68	—
Na_2O	0·07	—
Ign loss	13·4	13·96

As well as surface contaminants and additional mineral impurities associated with kaolinite, it is known that certain impurities exist as substituents within the crystal structure.[15.16.17] For example titanium which is a common impurity in American clays may replace Si^{4+} ions with Ti^{4+} ions.[16] Vanadium is also a common impurity in American clays and is usually found with titanium. Work is at present being carried out in this laboratory to determine if vanadium is substituted within the kaolinite structure.

The viable exploitation of china clay deposits depend to a large extent on techniques which have been developed to increase whiteness and improve rheological behaviour. Both these parameters may depend on the presence of iron as an impurity. For example, magnetic separation of clay fractions to improve whiteness is used extensively in the clay industry. Also, although the reasons are not fully understood it is well known that removal or alteration of surface iron from china clays may improve the whiteness. The possible influence of substitutional iron on brightness has not been satisfactorily investigated mainly due to experimental difficulties, and the presence of surface iron.

The nature of iron impurities in kaolinites is of particular importance in this work. A more detailed discussion which includes the application of Electron Spin Resonance (E.S.R.) and Mössbauer

techniques to the study of iron in kaolinite is given in Chapters 3, 4 and 5.

Jones[17] has shown that, in addition to iron, magnesium as well as a number of identifiable defects can also substitute in kaolinite. These will be discussed in more detail in Chapter 4.

The impurities which co-exist with or substitute directly in natural kaolinite can easily lead to misinterpretation of experimental data. In his preliminary studies on natural kaolinites in this laboratory Hall[15] encountered considerable difficulties with the interpretation of his results due to the multiplicity of impurities. The situation was considerably improved by Jones[17] who first established methods of synthesis and doping kaolinites with known impurities. The techniques he developed allowed more accurate assignment of experimental results to specific impurities. The work to be reported here is a logical continuation of the work initiated by Hall[15] and Jones.[17]

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CHAPTER 2

SYNTHESIS OF KAOLINITE

2.1 Natural processes of synthesis.

Field studies by geologists combined with many laboratory studies of kaolinite have established that natural synthesis of kaolinites probably occurred either by hydrothermal alteration or weathering of rocks. Clays are frequently found surrounding metalliferous deposits.[1] For example kaolinite is often found surrounding a quartz vein deep beneath the ground where weathering could not have taken place. The formation of these clays is attributed to hydrothermal processes at temperatures between 250 and 405°C. Small amounts of silica and alumina are dissolved and combine with water to precipitate as kaolinite.

Acid conditions favour the growth of kaolinite whereas alkaline conditions favour the formation of smectites or micas.[1] It is thought that in the formation of kaolinite by the hydrothermal alteration of granite alkaline ions are initially removed thus creating the more favourable acid environment.

Weathering takes place at lower temperatures and pressures and it would appear that any aluminium-silicate parent rock or feldspar can produce kaolinite by weathering provided the K^+, Na^+, Ca^{2+} and Mg^{2+} ions are leached from the parent rocks.[2]

2.2 Methods of synthesis of kaolinite in the laboratory.

Three main methods of synthesis of kaolinite have been attempted in the laboratory.

2.2.1 Low temperature synthesis (less than 200°C)

The majority of successful methods of synthesis of kaolinites at low temperatures have been developed[1,3] by dissolving small amounts of alumina and silica from separate silica and alumina phases or from silica-alumina gels with the kaolinite precipitating from the weak solution. Such studies are particularly difficult due to the extremely slow reaction rates but are of particular interest to geologists and mineralogists in genisis studies.

2.2.2 Alteration of minerals at temperatures greater than 200°C.

In this technique kaolinite is produced by direct transformation through hydrothermal reaction of naturally occurring minerals such as feldspars.[1.3.] For this method of synthesis the purity of the kaolinite produced is limited by the trace impurity levels of the starting materials which is beyond the experimentors control. Pure minerals are comparatively rare and consequently the kaolinites formed are usually contaminated by unreacted materials as well as impurities associated with them. However, these methods are ideally suited for the production of phase stability diagrams for various mineral assemblies.

The two methods of synthesis just described have been extensively reviewed by Grim[1] and more recently by Jones.[3]

2.2.3 Hydrothermal synthesis of kaolinite at temperatures greater than 200°C.

Hydrothermal synthesis involves the dissolution of alumina and silica followed by recrystallisation to form kaolinite from aqueous solutions in sealed vessels at high temperatures and pressures. Early reports dating back to 1930 concentrated mainly on reactions of mixtures of alumina and silica or aluminium and silicon salts. The first extensive study of the $Al_2O_3/SiO_2/H_2O$ system following the development of X-ray diffraction identification of minerals was made by Noll.[4] Noll used a mixture of aluminium chloride and sodium silicate, hydrothermally reacting them to form a number of alumina-silicate minerals which included kaolinite.

Although the rate of hydrothermal reaction of silica alumina mixtures at temperatures of 200°C is very slow a number of successful synthesis of kaolinite using similar techniques to those employed by Noll[4] have been reported.[5.6.7]

Probably the most suitable starting materials for synthesis of kaolinites are co-precipitated alumina-silica gels in which the silica and alumina are much more intimately mixed. Many methods of gel preparation have been reported.[3.7.8.9.10]

In this work gels have been used exclusively and therefore a brief review will be given of relevant papers which describe gel production for kaolinite synthesis.

Ewell and Insley[8] prepared Al_2O_3- SiO_2 gels by co-precipitating a solution of aluminium sulphate and sodium silicate. The precipitate was filtered and washed with water. At this stage it was found that the gels contained sufficient Na_2O to produce three layer minerals such as montmorillonite. By electrodialysis for 2 to 3 days it was reported that the Na_2O content was reduced to less than 0.5%. The resulting gel was hydrothermally reacted at 310°C to produce kaolinite. The X-ray spectra shown were indicative of poorly crystallised kaolinite.

To avoid alkaline contamination Ray and Osborn[7] prepared gels from ethyl-ortho-silicate and aluminium nitrate by dissolving in ethyl alcohol and heating. Attempts were made to synthesise kaolinite, nacrite and dickite. The products were reported to be so finely grained that they yielded very diffuse X-ray diffraction spectra. The diffuse nature of the spectra prevented the identification of the different polymorphs.

Rayner[10] prepared silica-alumina gels by simultaneous hydrolysis of sodium aluminate and sodium silicate. In order to remove all the sodium ions the

precipitate was washed with ammonium nitrate and then repeatedly washed with water and centrifuged. The gel was then dried; the final sodium content being reported at less than 0.3%. The gel was hydrothermally reacted at different temperatures and for different reaction times. A sample exhibiting an X-ray diffraction spectra of well crystallised kaolinite was obtained by hydrothermal reaction of the gel at 300°C for 7 days.

2.3 The structure of alumina-silica gels.

Co-precipitated alumina-silica gels are amorphous and it is not possible to make conventional X-ray diffraction studies to elucidate their structure. Cloos[11] has proposed a structural model in which a central core of tetrahedral silica, with some aluminium substitution, is surrounded by hydroxy aluminium cations. The core carries a net negative charge which is balanced by the positive charge of the coating.

The established fact that in kaolinite the aluminium is in six-fold co-ordination has resulted in a number of studies of the co-ordination of aluminium in gels[12] prior to synthesis. Leonard et al[13] studied the variations of co-ordination of aluminium and silicon in an alumina-silicate gel as a function of alumina and silica concentrations. For a gel dried at 100°C the silicon had a co-ordination of four. The aluminium remained in four-fold co-ordination until the percentage of alumina reached about 33%.

The average co-ordination number of the aluminium then increased linearly with the percentage of alumina until at 100% alumina the gel consisted of only six co-ordinated aluminium. It has also been shown[12] that the co-ordination number of aluminium can be increased in a gel by lowering the pH of the reaction mixture.

2.4 Development of gels and methods of synthesis used in this work.

The first method of gel preparation attempted in this work was identical to that of De Kimpe[14] which involves the co-hydrolysis of aluminium iso-propoxide and tetra-ethyl silicate. Solid aluminium iso-propoxide and liquid tetra-ethyl silicate were slowly added to water with continuous stirring. The resulting mixture was then stirred vigorously for at least 24 hours to obtain complete hydrolysis. The gel was then recovered as a white powder by rotary evaporation of the solution. It was found, however, by X-ray fluorescence analysis that the silica alumina ratio in the final products varied greatly and consistent results were difficult to obtain. This effect was possibly due to incomplete hydrolysis of the tetra-ethyl silicate which hydrolisis more slowly than aluminium iso-propoxide, or alternatively due to evaporation of the tetra-ethyl silicate prior to hydrolysis. Indeed, results were improved slightly if all the tetra-ethyl

silicate was added to the water before any aluminium iso-propoxide giving the former a better chance to hydrolise. Aluminium iso-propoxide hydrolises relatively easily and in the majority of samples purchased it was apparent that some hydrolysis had already taken place. Thus when added with the tetra-ethyl silicate to water co-hydrolysis of the tetra-ethyl silicate and the already hydrolised aluminium iso-propoxide could not take place.

2.5 The liquid A Process

It was contemplated that consistent results might be obtained if a more intimate mix of silica and alumina could be formed by mixing the reactants as liquids prior to hydrolysis. However at room temperature aluminium iso-propoxide remains solid and melts at approximately 106°C. It was decided, therefore, that it might be possible to obtain an intimate mixture by adding an appropriate amount of tetra-ethyl silicate to hot liquid aluminium iso-propoxide immediately following its vacuum distillation. The proposed procedure was assisted by the fact that aluminium iso-propoxide behaves as a super cooled liquid and may take several hours to solidify even at room temperature. Also, it is known that metal alkoxides can exchange their alcohol groups[15] and for the process just described it was possible that such an exchange might occur. To assist the exchange the mixture was refluxed for

approximately 10 minutes. The results obtained were very encouraging. It was found that when the mixture cooled to room temperature it remained a clear liquid for periods up to five hours before any crystalline sediment became visible. Complete prevention of precipitation was finally achieved by the addition of 10% by volume of iso-propal alcohol to the mixture prior to refluxing. The resulting liquid remained clear for several weeks at room temperature. The liquid formed will be referred to as liquid A throughout the remainder of this text.

The gel was produced by hydrolising liquid A with excess water over a period of one week with occasional shaking. The most probable type of reactions during hydrolysis assuming no exchange of alcohol groups are of the form.

$$2\,Al(OPr^{i})_3 + 3H_2O \Rightarrow Al_2O_3 + 6PrOH$$

and $$Si(OEt)_4 + 2H_2O \Rightarrow SiO_2 + 4EtOH$$

X-ray fluorescence analysis of the final gel suggested the liquid A had undergone complete hydrolysis and consistent results were obtained for repeated trials.

The excess water was removed either by rotary evaporation or heating in a furnace at 110°C. At this stage it was noticed that the gel possessed an aroma characteristic of alcohols and it was suggested that the gel might still be contaminated with some organic matter.

Heating the gel at 1,000°C for 48 hours was considered to be sufficient to remove any remaining organic matter.

As far as the author is aware the method of gel production just described is unique and proved to be of great value in this work. Previous reports of gels prepared from sodium aluminate and sodium silicate or similar methods indicate that contamination with sodium ions always existed even after extensive washing and dialysis. For gels prepared from liquid A the only impurity likely to be present is organic in form and can easily be removed by heating at 1,000°C.

As well as providing a convenient source of intimately mixed alumina and silica, liquid A also provided a convenient means of controlled addition of dopants prior to hydrolysis. With all the required reactants initially in solution it was reasonable to expect that both doped and undoped gels produced from liquid A comprised homogeneous mixtures. To check the reproducibility and accuracy of the method gels with varying alumina-silica ratios were subjected to X-ray fluorescence analysis. The results showed close agreement between calculated and experimentally observed values.

2.6 Synthesis of kaolinite using liquid A., at pressures determined by the temperature of reaction.

Gels prepared from liquid A were reacted hydrothermally

in stainless steel pressure vessels similar to those designed by Tuttle.[16] Typically ½ gram of gel was placed with 1 cc of water in a P.T.F.E. tube plugged with P.T.F.E at both ends to produce a 70% filling factor. The P.T.F.E. tube was placed in the reaction vessel and water was introduced around the tube to balance the saturated vapour pressure of the reaction mixture. The bomb was sealed and heated to 280°C ∓ 5°C for 7 days in a furnace controlled by a Eurotherm P.D.1. controller. At the end of the reaction period the products were allowed to cool, poured from the P.T.F.E. tube and finally dried at 110°C.

2.7 The morphology of synthetic kaolinites.

Although there have been numerous reports of successful synthesis of kaolinite, in general the basis of identification of the products has been by X-ray diffraction and frequently the morphology of the products has not resembled that of natural kaolinites. In this work it has been found that the parameters which affect the synthesis and morphology of kaolinite include:-

1) The nature, composition and method of production of the starting material.
2) The temperature of reaction.
3) The pressure of reaction.
4) The time of reaction.
5) The pH of the reaction mixture.
6) The concentration and type of dopant.
7) Possible contamination from reaction vessels or from impurities in starting materials.
8) Cycles of cooling and reheating during synthesis.

Clearly, some of these parameters are inter-related. For example, cooling and reheating cycles cause pressure variations; dopants could affect pH. Assuming minimum inter-relation it is clear that a very large number of experiments would have to be performed to survey all the influences of variables 1 to 8. In this work at least 500 kaolinites have been synthesised under varying conditions in an attempt to determine the influence of factors 1 to 8 on morphology and properties of the synthetic kaolinites. Although it could be argued that this number is too small to provide reliable results, nevertheless a number of interesting and significant observations have been made.

The kaolinites formed have been studied by the techniques of X-ray diffraction and electron microscopy. X-ray diffraction spectra were obtained with an A.E.1 X-ray set. The crystallinity of the synthetic kaolinites were measured from the X-ray diffraction spectra using the method of Hinckley.[17] As mentioned previously in Chapter 1 the plate-like nature of kaolinite crystals tends to make them sediment with their basal planes parallel to the substrate, and enhances the intensity of the basal reflections. The degree of preferred orientation is determined by the degree of plate-like nature of the crystals, and hence the relative intensity of the 001 peak to non-basal reflections gives an indication of the morphology and relative plate thickness of the synthetic kaolinites.

Electron micrographs were obtained with a Phillips EM 300 electron microscope, to obtain an estimate of average particle size and to make comparisons of the shape of the kaolinite crystals. As there is no recognised quantitative method of describing the morphology of a kaolinite crystal, throughout this text synthetic kaolinites whose morphology is similar to that of natural kaolinites with clearly defined hexagonal form, will be referred to as having ideal morphology.

2.7.1 The affect on morphology of the composition and method of production of the gel.

Work by Jones[3] suggested that compared with other standard methods of gel preparations on average more crystalline kaolinite with reasonable morphology was obtained by using liquid A. Moreover it was also reported that results were not always reproducible and it was concluded that the repeated synthesis of kaolinite with ideal morphology was prevented by variations in conditions which were beyond experimental control. This being so, attempts were made in this work to identify the unknown parameters which previously had produced inconsistent results.

It was suggested that incomplete or partial hydrolysis of liquid A might have been responsible for Jones[3] results and therefore a number of different methods of hydrolysis were attempted.

Slow addition of water mixed with alcohol caused the liquid A to solidify and formed a compound which was identical in appearance to a clear glass. Although the clear glass-like material was amorphous to X-rays and it was not possible to identify the co-ordination numbers of the aluminium and silicon it was anticipated that due to its completely transparent appearance an ideal reaction had occurred for gel production. By heating the solid to remove any organic contaminants the structure broke up into a fine powder. The fracturing of the solid was probably caused by expansion through the release of alcohols trapped within the material. Following this treatment it was found that no marked change had occurred other than the reduction in particle size and clear glass like fragments were sufficiently large to be examined with an optical microscope.

Results obtained with this gel were disappointing. Hydrothermal treatment produced kaolinite with poor morphology and a low crystallinity index of 0.5.

Improved crystallinity and morphology was obtained from samples grown from liquid A which was added directly to excess water, followed by occasional shaking over a period of one week and then dried in a furnace at 105°C. The solid was fired at 1000°C to remove the organic contaminants. Up to this point the temperature for burning off the organic matter had been maintained at 500°C identical to the work of Jones.[3]

The possibility that the temperature of this firing stage might have affected the nature of the gel and hence the form of the kaolinite produced was investigated in more detail. It was eventually found that improved kaolinite was produced when the firing temperature of the gel was increased to 1,000°C. This is perhaps a surprising result. Leonard[13] has shown that the ratio of four-fold to six-fold co-ordinated aluminium increases with the firing temperature of the gel. Hence the use of lower temperatures were expected to produce a gel which would favour the synthesis of kaolinite. It is possible that either the higher temperature firings re-organised the gel structure in some way or alternatively more impurities were removed. Having established fairly consistent results by optimising the conditions of hydrolysis and treatment of the gel before hydrothermal reaction to form kaolinite it was now possible to study the affect of the alumina-silica ratio of the gel on the synthesis. A series of gels were prepared with various alumina-silica ratios. After 7 days of hydrothermal reaction it was found that all samples contained some detectable kaolinite except those which contained either 100% silica or 100% alumina.

Gels with an excess of alumina on hydrothermal reaction produced kaolinite and another crystalline phase which was identified as boehmite, whereas gels having an excess of silica produced only kaolinite. Gels consisting of 100% silica produced no crystalline phase.

Kaolinites with best morphology and X-ray crystallinity were formed from gels with an alumina-silica ratio close to the ideal ratio of 46%.

Having observed fairly minor variations in the morphology of the synthetic kaolinites by changing the method of gel production the parameters 2 to 8 were studied using alumina-silicate gels prepared by the method previously described and having a composition equal to the theoretical composition for the formation of kaolinite.

2.7.2 The variation in morphology of synthetic kaolinites at various pressures, temperatures and times of reaction.

Many authors have reported the effect of pressure, temperature and time of reaction on the synthesis of kaolinite.[8,10]

Rayner[10] studied synthesis rates and the kinetics of the formation of kaolinite and showed the reaction to be approximately of a first order type within the temperature range 180°C to 300°C. It has long been thought that different pressures and temperatures of reaction may be responsible for the formation of the polymorphs of kaolinite. Ewell and Insley[8] reported the synthesis of dickite at 340°C and 16 MPa. As far as the author is aware no successful synthesis of halloysite or nacrite has been reported. Recently Eberl and Hower[18] repeated Ewell and Insleys[8] work but were unable to grow any of the polymorphs of kaolinite. They reported that

natural halloysite was converted to kaolinite at 150°C which suggests that halloysite is a low temperature polymorph. Many experimentors have concentrated on synthesis at temperatures below 200°C but due to the extremely long reaction times involved it was not possible to carry out similar experiments in this work.

P.T.F.E. decomposes at about 320°C but is known to change its properties below this temperature. Experiments on synthesis so far described in this work were limited to temperatures not greater than 280°C. Attempts were made to synthesise kaolinites in P.T.F.E. tubes at temperatures in excess of 280°C but in all cases the resulting kaolinite was poorly crystalline and the P.T.F.E lost its plasticity. It was suspected that the breakdown of the P.T.F.E. was in some way affecting the synthesis as previous reports would suggest that kaolinite may be synthesised at temperatures up to 405°C.[1]

In order to estimate the total time necessary for complete reaction, a series of kaolinites were produced from a gel at 280°C which was reacted for periods ranging from 1 day to 3 weeks. The kaolinites produced were then studied by X-ray diffraction. Although kaolinite was detectable after only one day the X-ray diffraction pattern became more distinct following 6 days reaction. Thereafter, no significant change in the X-ray diffraction pattern was observed. On the basis of these results it was assumed that after one week no further reaction would occur. To check this assumption a number of samples

reacted for various times were subjected to thermogravimetric analysis (T.G.A.)

Pure kaolinite contains 13.5% water which it loses completely on dehydroxylation at 550°C. In this work T.G.A. has been used to estimate the amount of kaolinite in a sample by measuring the weight loss of the sample between 450°C and 600°C. It was assumed that the mixture after reaction contained only kaolinite and some unreacted gel so that all weight loss could be attributed to kaolinite in the sample. However it should be noted that the dehydroxylation temperature of boehmite is the same as that of kaolinite and may constitute an error in the results. At least 3% boehmite is required for detection by X-ray diffraction. The percentages of kaolinite quoted below assumes no boehmite or similar phase to be present in the sample. Samples reacted for 6 days contained between 85 and 92% kaolinite and this value could not be increased by further reaction.

All experiments on synthesis so far described were performed at pressures determined solely by the saturated vapour pressure of the reactants at the temperature of reaction. In order to study the effect of pressure on the reaction of kaolinite synthesis and also to study the effect of temperatures greater than 280°C it was decided to construct a system in which the pressure could be varied independantly of temperature. The design of the system required that the P.T.F.E. reaction tubes were replaced by platinum tubes.

A photograph of the experimental rig is shown in Fig. 2.1. Three tube furnaces were constructed using Nichrome 5 element wire wound round a hollow cylindrical alumina former. The heating elements were then thermally insulated using superplastic 85 and mounted in a cylindrical asbestos tube mounted vertically as shown. The furnaces were controlled by three E.C.C. temperature controllers using NiCr/NiAl thermocouples. Three Tuttle bombs were constructed with high pressure joints fitting in the caps (Fig.2.2). Up to 300 MPa were produced by a Stanstead A04 12 pump driven by compressed air and distributed to the Tuttle bombs by a system of high pressure valves and tubes (Autoclave Engineers 400 MPa). A safety blow out valve was fitted (Autoclave Engineers 300 MPa) and also a reservoir was attached (capacity 200cc) to prevent pressure fluctuations. The fluid for transmitting the pressure comprised a mixture of water and 10% soluble machine oil.

Platinum tubes 120mm long with 5mm o.d. and 0.2mm wall thickness were used as reaction liners. The tubes were sealed by flattening their ends and then welding. The technique for welding the tubes to produce a satisfactory seal required some development. Initially the arc was produced by direct shorting of a heavy duty car battery but did not produce satisfactory results. Attempts to smooth the discharge using a large capacitor and choke were unsuccessful and eventually a satisfactory controllable arc was obtained using a 12 amp variac across

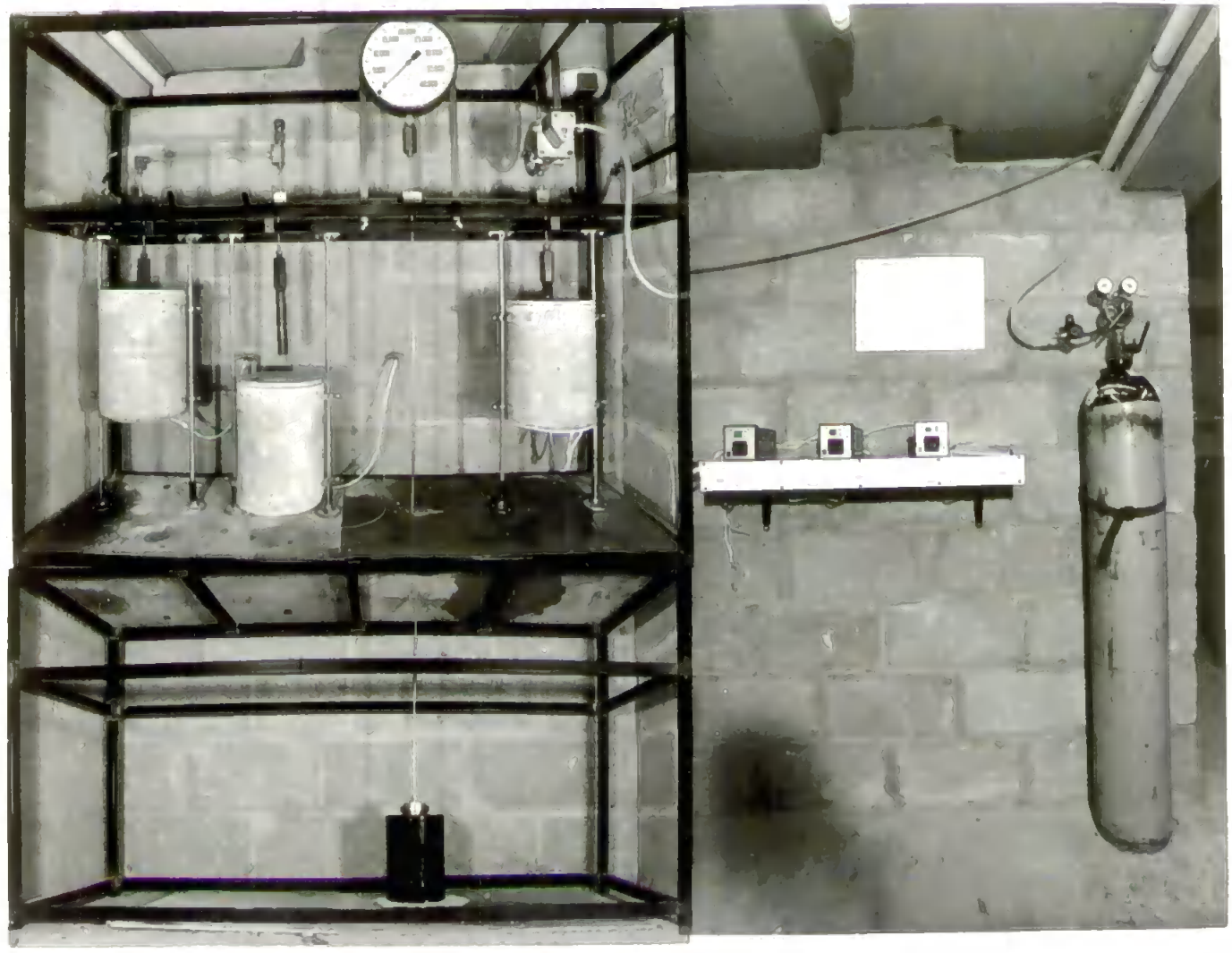


Fig. 2.1. Apparatus for synthesis at various pressures and temperatures.

High pressure joint

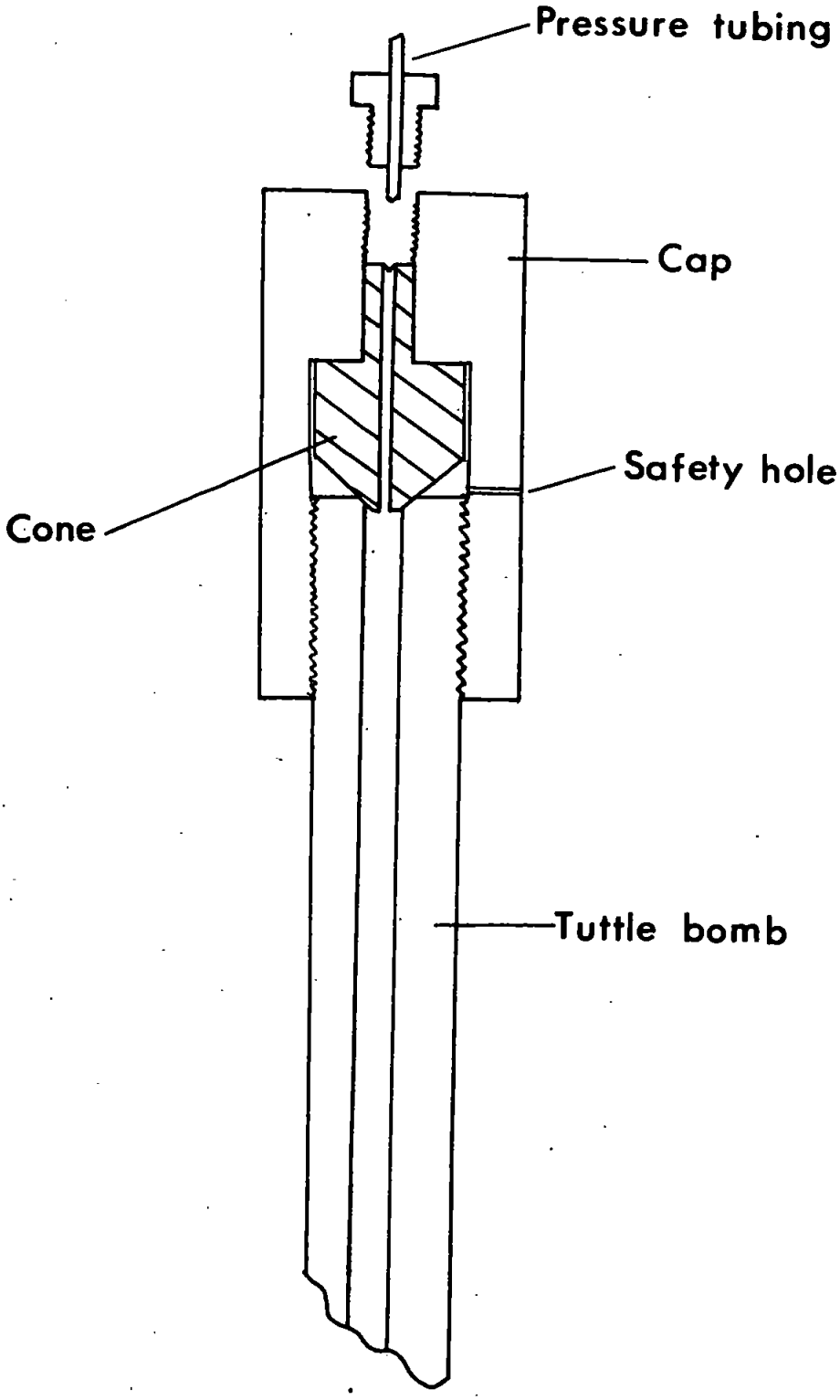
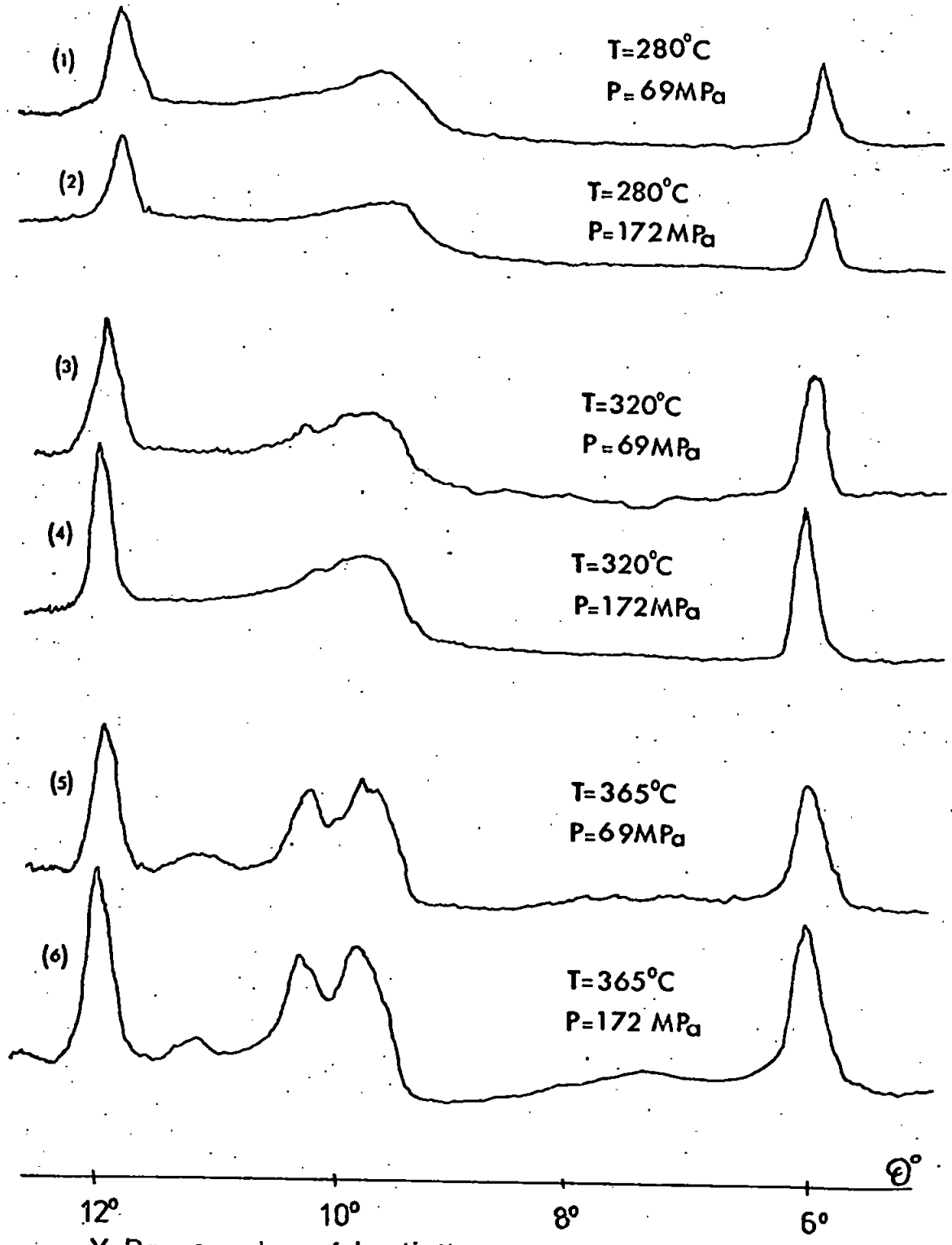


Fig 2.2

a 100 volts bridge rectifier with a 1.1 H choke. A voltage of approximately 80 volts was used for welding.

It should be pointed out that the number of experiments which could be carried out with the variable pressure apparatus was considerably limited by financial constraints due to the high cost of platinum. Also it was found from preliminary experiments that after being subjected to pressures in excess of 5,000 psi the reaction tubes had been compressed to such an extent that it was not possible to re-use them. For all the experiments at controlled pressures a single undoped gel was used. Typically 0.3gm of gel was placed with 0.8cc of water in a platinum tube welded at both ends. The tubes were then placed in the Tuttle bombs which were filled with the pressure transmitting fluid. After the bombs were connected to the pressure line pressures greater than the s.v.p. were applied. The furnaces were then raised to surround the Tuttle bombs and brought to the desired temperature.

The kaolinites produced were studied by X-ray diffraction and electron microscopy. In all samples the morphology of the kaolinite was poor usually showing no sign of hexagonal form and gave weak X-ray diffraction spectra. The majority of clays did not give spectra with sufficient resolution to calculate a meaningful Hinckley[17] crystallinity index. A selection of spectra have been reproduced in Fig. (2.3). Spectra 1 and 2 show kaolinite synthesised at 280°C at pressures of 69MPa



X Ray spectra of kaolinites synthesised at various temperatures and pressures

Fig 2.3

and 172 MPa respectively. Both spectra show a surprisingly small amount of crystalline material but are very similar in appearance. Spectra 3 and 4 show kaolinite synthesised at 320°C at pressures of 69MPa and 172 MPa and again have almost identical form with small amounts of kaolinite. Spectra 5 and 6 show much more crystalline material which was synthesised at 365°C at pressures of 69 and 172 MPa. Here, as at lower temperatures the two spectra are almost identical. These results indicate that the main factor controlling the synthesis process is temperature of reaction and not pressure. In addition to the experiments just described kaolinites were synthesised at various pressures between 20 MPa and 250 MPa and temperatures in the range 260 to 365°C. Without exception it was found that the pressure of reaction made no observable difference to the clay produced. None of the polymorphs of kaolinite were detectable in the samples by X.R.D. Due to the poor morphology of the clays produced it was not possible to gain any useful information from electron microscopy studies.

It should be noted that the kaolinites produced in the platinum reaction vessels were of inferior quality compared to those grown in P.T.F.E. tubes at the same temperatures. The only kaolinites which were similar to those grown in P.T.F.E. were produced when the platinum tubes leaked and the kaolinites were contaminated. This effect will be considered in more detail in sections 2.7.5 and 2.7.7.

2.7.3 Study of the morphology of kaolinite synthesised at various pH-values.

In nature it is thought that kaolinite only forms under acid conditions,[1] the alkali ions being leached from the reaction products before kaolinisation takes place. Acid conditions favour the formation of kaolinite for two probable reasons. Firstly, in neutral or alkaline solutions silica is far more soluble than alumina. Acid solutions could increase the solubility of alumina to the point where it is as soluble as silica. In much of the work which has been done on low temperature synthesis of kaolinite the solubility of the alumina has been increased by the addition of organic acids.[19] Secondly, it has been shown[12] that low pH values tend to stabilise aluminium in six-fold Co-ordination which is identical to the situation for aluminium in the kaolinite structure.

Some reports have been made of synthesis of kaolinite in alkaline media.[20] De Kimpe[20] has grown kaolinite at a temperature of 175°C up to a pH of 12. He reported a drop in pH of the alkaline solutions during hydrothermal reaction and has shown the change in pH to increase with increasing gel/solution ratios. To the author's knowledge a final pH of 8 is the highest reported value of a reaction mixture which has produced kaolinite.

The results obtained in this section, from an undoped

silica alumina gel which was reacted hydrothermally at 280°C ± 5°C for one week in various pH solutions, are summarised in Fig.2.4. The different pH values were obtained by adding either sodium hydroxide or hydrochloric acid to distilled water.

The morphology of kaolinites grown in alkaline solutions was found to be very poor showing no sign of hexagonal form (Fig. 2.5) However, those kaolinites grown in solutions with a final pH of as high as 10 showed a high degree of crystallinity. Reaction mixtures with a final pH of 11 produced a sodium saturated montmorillonite and those with a final pH value of 12 produced analcite. The X-ray diffraction patterns of the minerals synthesised at final pH values of 10,11 and 12 are illustrated in Fig. 2.6. From these it can be seen that for each pH value only one crystalline phase is present. For example the X-ray diffraction spectrum of the sodium saturated montmorillonite grown at a final pH of 11 shows little trace of kaolinite or analcite.

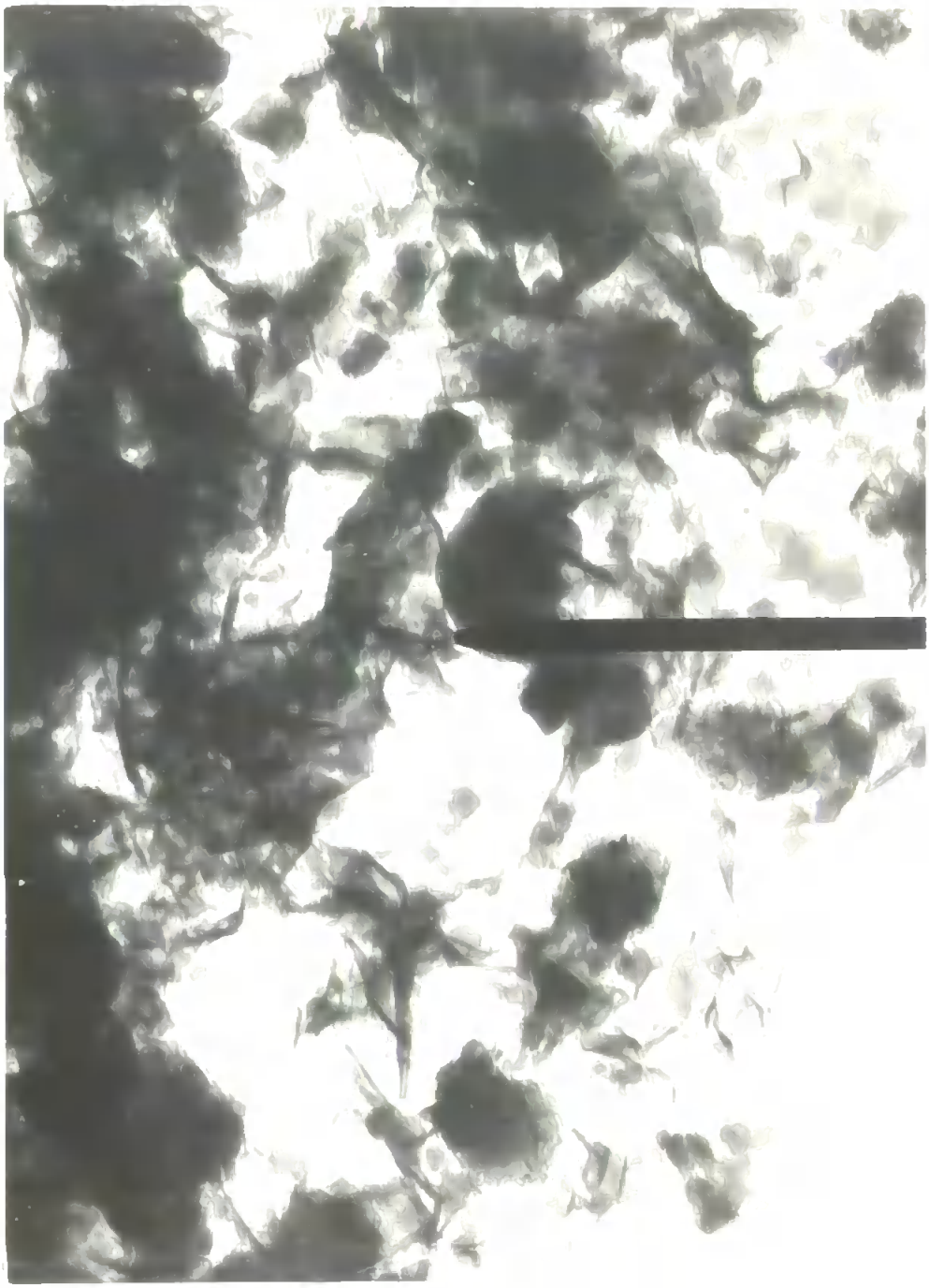
Highly crystalline kaolinites were also grown at low pH values with greatly improved morphology which very closely resembles natural kaolinite (Fig. 2.7) although the particles are rather small being of the order of 0.2 micrometers e.s.d. For final pH values between 2 and 10 there was little change in the Hinckley[17] crystallinity, although an increase in the relative intensity of basal to non-basal reflections was observed in those samples

Fig 2.4

Initial ph	Final ph	Brightness	Crystal-linity	Reaction solution
1	2	0·54	89	HCl
2	5	0·71	88	HCl
3	5	0·52	91	HCl
4	6	0·72	84	HCl
5	6	0·75	83·5	H_2O
6	6	0·66	88	NaOH
7	6	0·78	89·5	NaOH
8	6	0·63	92	NaOH
9	6	0·56	91	NaOH
10	6·5	0·88	88	NaOH
11	8·5	0·76	86	NaOH
12	10	0·76	85	NaOH
13	11	M	86	NaOH
14	12	A	83	NaOH

M=Na saturated montmorrillonite
A= Analcite

Kaolinite synthesised at high pH



x. 44,000

Fig. 2.5

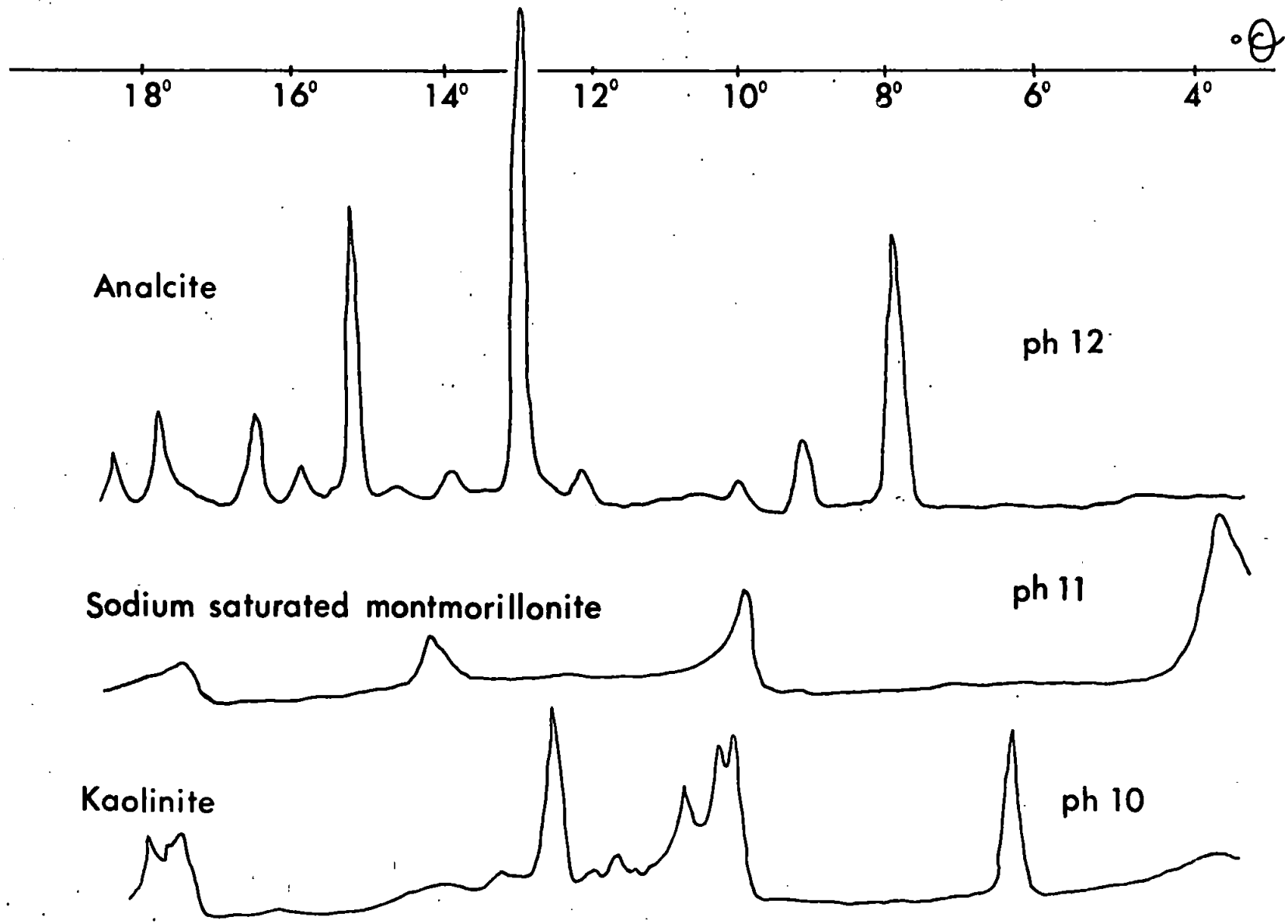
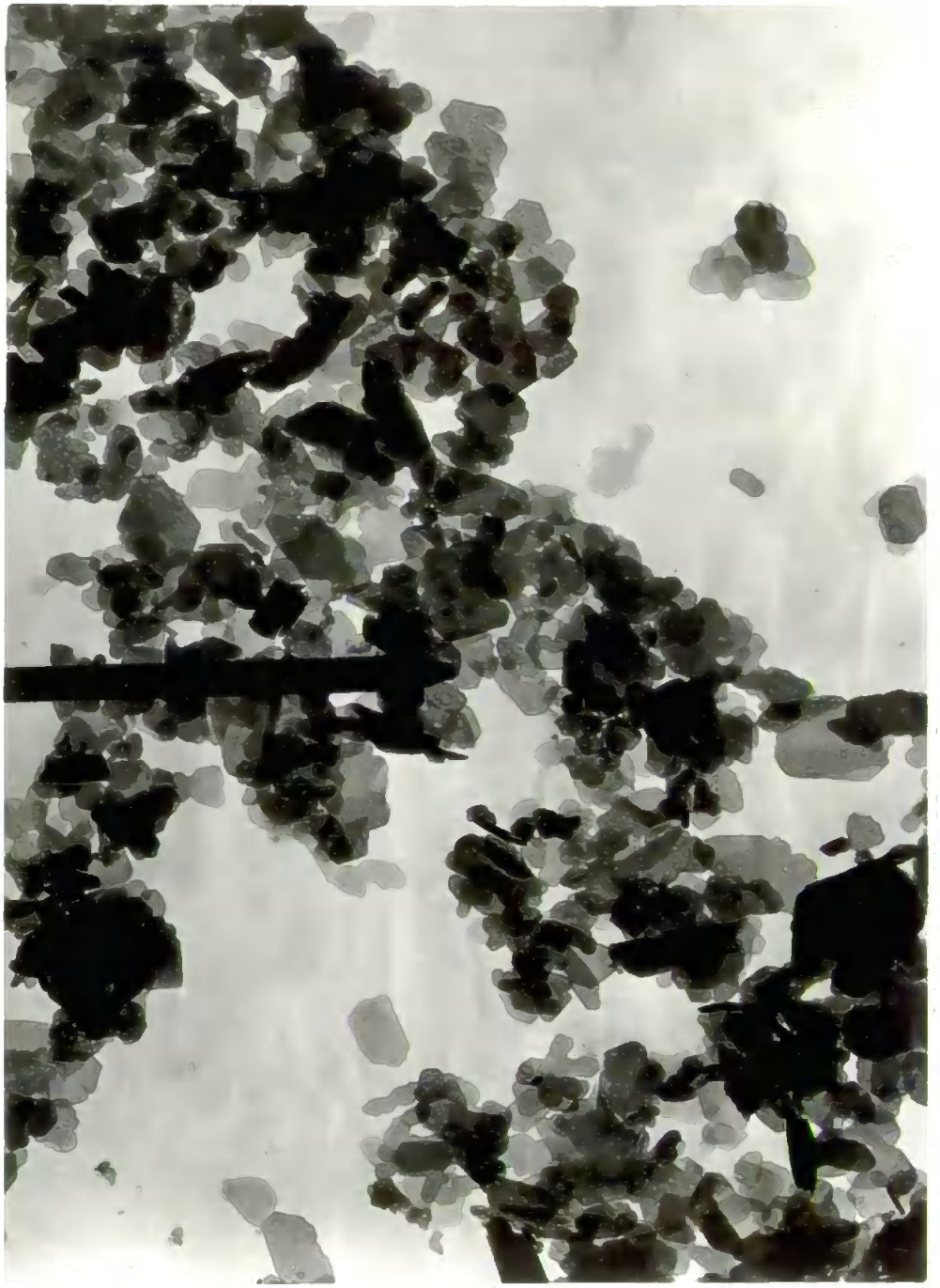


Fig 2.6 X-ray diffraction spectra of samples synthesised at high ph

Undoped kaolinite synthesised at low pH



X 28,000

Fig. 2.7

synthesised at lower pH values also suggesting improved morphology.

The measured values of the pH after reaction, regardless of the initial value, always shifted towards more normal values and the magnitude of the shift was found to depend on the solid/liquid ratio in the reaction mixture. The higher the percentage of solids the greater the pH-change. Alumina is known to act as a buffer because of its amphoteric nature.[21] This probably accounts for the shifts in pH towards more normal values. Also given in Fig.2.4 are the brightness values of the kaolinites produced at different pH values.

In order to measure the brightness of a clay the majority of china clay producers use a commercial instrument manufactured by Zeiss known as an El Repho brightness measuring meter. In general, a fairly elaborate procedure is adopted[22] to prepare the clays for brightness measurement. After being prepared in the form of a disc the sample is placed in the instrument to become part of the inner surface of a sphere. The internal surface of the sphere is coated with barium sulphate. The sample is subjected to radiation with wavelengths from 380nm to 700nm and using a photomultiplier it is possible to measure the total reflectance of the clay surface. By definition the brightness is taken as the percentage reflectance of monochromatic light (usually 458 nm) from a kaolinite sample compared to a

standard, usually magnesium carbonate.

The El Repho instrument is expensive costing about £3,000 and in this work it was not possible to arrange convenient access to such an instrument. An alternative system was built from equipment available within this department. A photograph of the apparatus is given in Fig.2.8. From the diagram it can be seen that the apparatus measures only radiation reflected at about 45^{o} from the clay surface and does not include an integrating sphere. Nevertheless, it was found from preliminary studies using a suite of natural clays of known brightness that the instrument produced comparable results. From the data presented in Fig.2.4. it would appear that the brightness is little affected by the pH value of the reaction mixture. The kaolinites synthesised at various pH's had very different morphology which might have been expected to affect the brightness.

2.7.4 Study of morphology and properties of synthetic kaolinites doped with different impurities.

Numerous past reports[3.23] have suggested that impurities which substitute in the kaolinite structure most probably affect the physical and chemical properties of the material and also might affect its morphology. It has not been possible however with natural products to positively identify any particular impurity as being responsible for a specific crystal form.

In this work particular attention was given to those

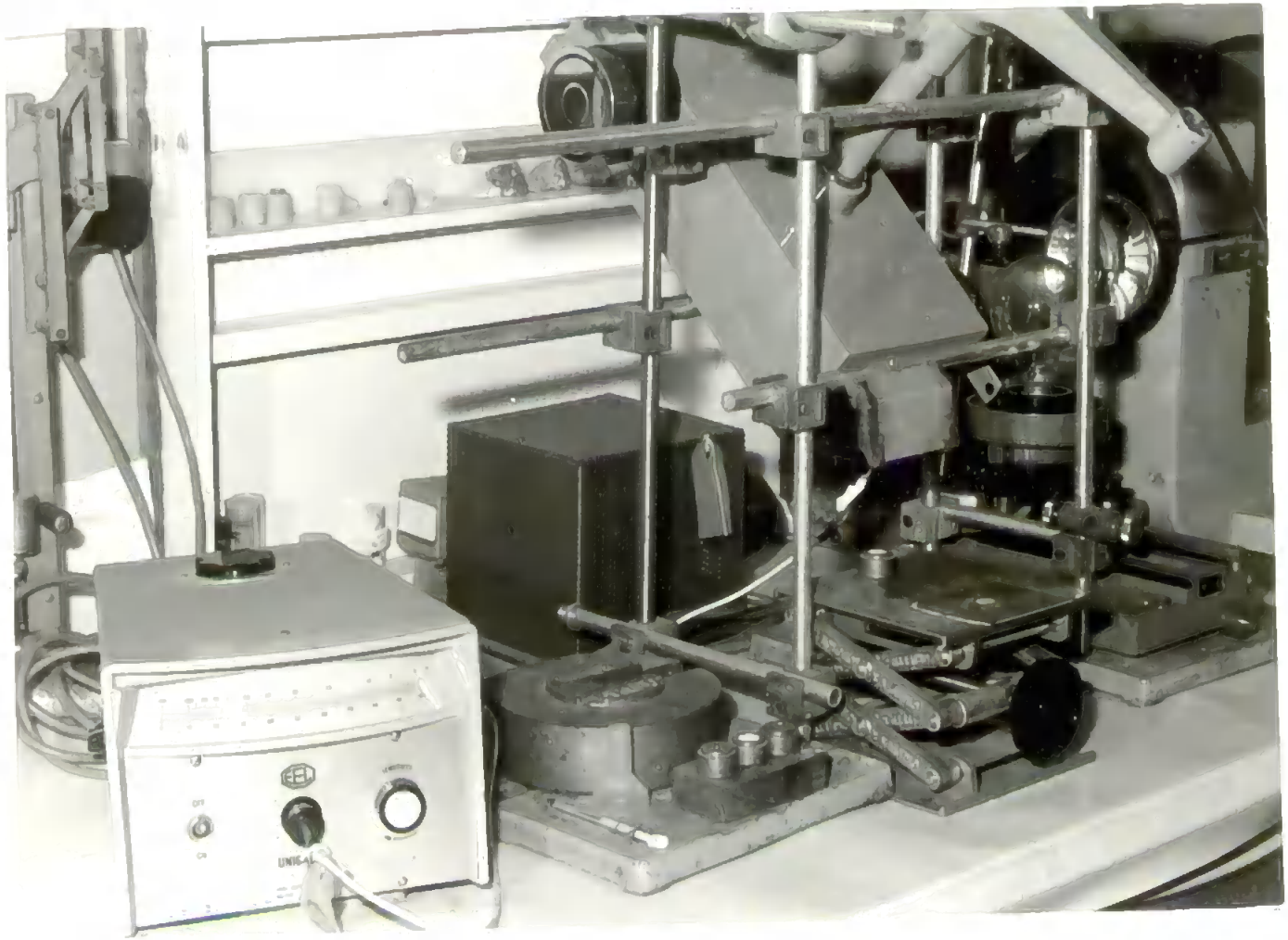


Fig. 2.8. Apparatus used for brightness measurements.

substituted impurities which are paramagnetic and produce an E.S.R. spectrum. The details and background information with regard to E.S.R. in kaolinite are given in the next chapters. It is shown how the E.S.R. technique can unequivocally detect substitution of iron and magnesium in the kaolinite structure. It is for this reason that a study of the effect of substituted ions on morphology of synthetic kaolinites has been limited to those doped with either iron or magnesium or mixtures of both.

2.7.4.1 Preparation of iron doped synthetic kaolinites.

Jones[3] reported that by adding soluble iron salts such as ferric chloride into the water of hydrolysis it was possible to introduce controlled amounts of iron into the gel. From such gels kaolinites doped with iron were prepared. It was considered in this work that anions of the salt used for doping may affect the morphology of the final kaolinite. It was decided therefore to devise a method of preparing iron doped gels which contained only anions relevant to the formation of iron doped kaolinite.

Ferric benzoate appeared to satisfy the requirements for the experiment. On heating at 1,000°C it decomposes to form Fe_2O_3. Ferric benzoate was found to be insoluble in liquid A but a solution of ferric benzoate in di-methyl formamide (D.M.F) mixed uniformly with liquid A, thus providing a convenient method of preparing an iron doped gel.

Solutions of ferric nitrate (40g/litre) and ammonium benzoate (40g/litre) were mixed. A precipitate of ferric

benzoate formed which being insoluble in water was filtered and washed thoroughly with distilled water before being dried at 50°C

$$Fe(NO_3)_3 + 3\,NH_4(C_7H_5O_2) \rightarrow 3\,NH_4(NO_3) + Fe(C_7H_5O_2)_3 \downarrow$$

5g of dry ferric benzoate was then dissolved in 75cc of D.M.F. to form a solution with a concentration of 66.6g/litre. By adding controlled amounts of this solution to liquid A it was possible to introduce known amounts of iron into the resulting kaolinite. For example, consider a doping level of 1% Fe_2O_3 by weight in kaolinite.

100 gms of kaolinite contain 13.95g H_2O
34.42g Al_2O_3
51.63g SiO_2

To form these requires:-

$\frac{204}{102}$ x 34.42 x 2g Aluminium iso-propoxide

and $\frac{208}{60}$ x 51.63g Tetra-ethyl-silicate

i.e. 137g Al-iso-propoxide (Sp.gr 1.03)

and 178.98g Tetra-ethyl-silicate (Sp.gr 0.933)

i.e. 133.7cc of Al-iso-propoxide

and 191.8cc of Tetra-ethyl-silicate

Since liquid A contains 10% by volume of iso-propal alcohol the required volume of liquid A is therefore -

325.5 + 10% = 358cc to produce 100g of kaolinite.

Now 838g of ferric benzoate produce 160g Fe_2O_3, therefore to produce 1g Fe_2O_3 requires $\frac{838}{160}$ = 5.23g ferric benzoate

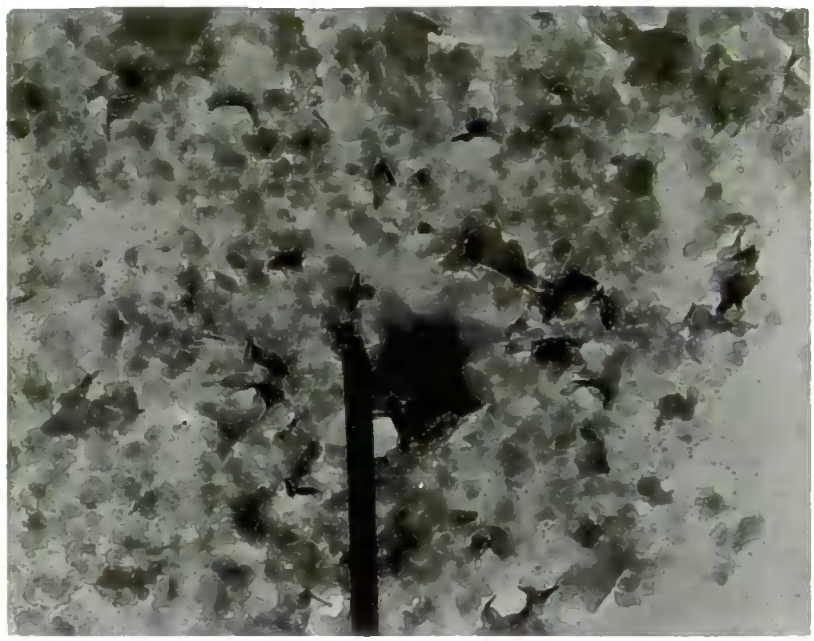
that is $\frac{1000}{66.6}$ x 5.23 = 75cc of 66.6g/litre solution of ferric benzoate in di-methyl formamide.

Therefore to produce a kaolinite with a doping level of 1%, 1cc of 66.6g/litre ferric benzoate in di-methyl formamide solution must be added to every 4.8cc of liquid A.

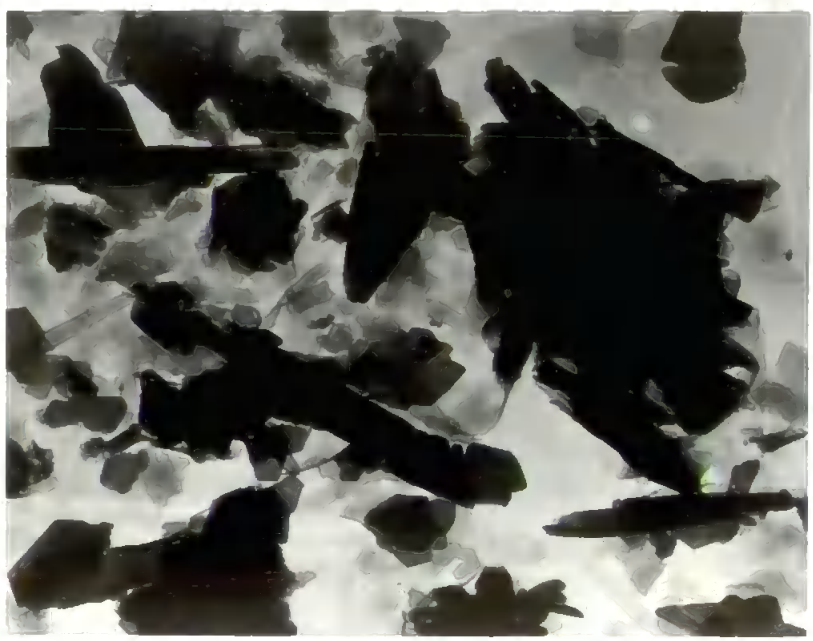
The doped solutions were hydrolised with excess water over a period of one week. Following hydrolysis the excess water was removed by heating in an oven at 110°C and finally the gels were fired at 1,000°C for 48 hours to remove any remaining organic material. The gels were reacted hydrothermally under identical neutral conditions to produce a range of kaolinites doped with differing amounts of iron. Some of the samples produced were subjected to X-ray fluorescence analysis and it was found that the values of the iron concentrations were in agreement with the expected values within the limits of experimental error.

2.7.4.2 Morphology and properties of iron doped synthetic kaolinite.

Although no absolute particle size measurements were made on the final products it was discernable by electron microscopy that the particle size was influenced by the iron concentration (Fig.2.9.and 10). Addition of concentrations as small as 0.05% Fe_2O_3 produced larger kaolinite plates relative to undoped kaolinites. The increase in plate size with iron concentration continued

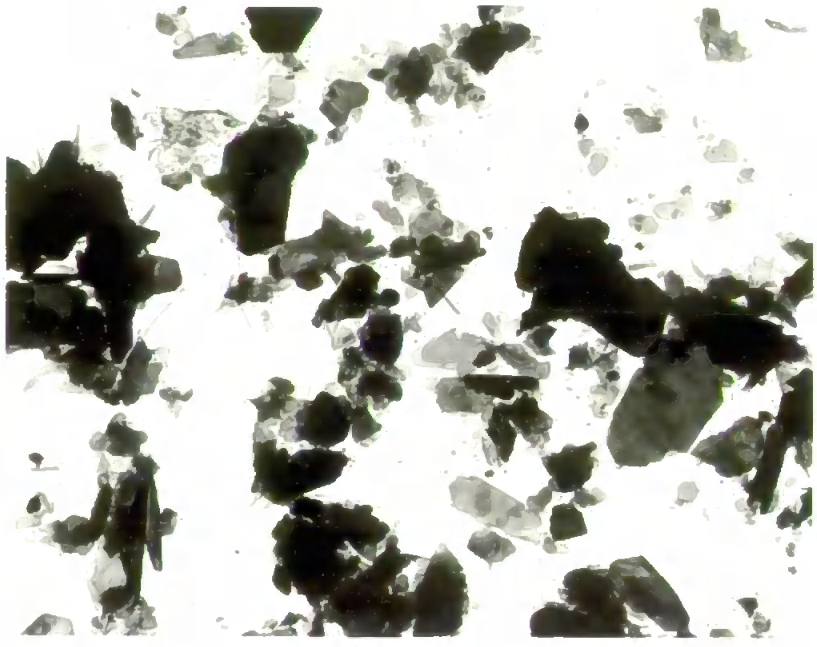


Undoped synthetic kaolinite X 10,400

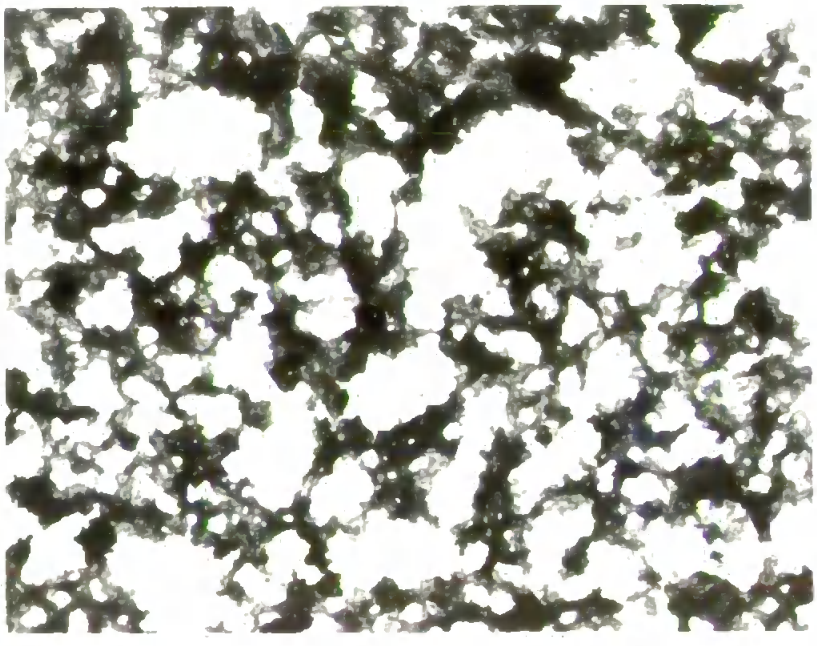


Synthetic kaolinite doped with 0.05% Fe_2O_3
X 10,400

Fig. 2.9



Synthetic kaolinite doped with 2% Fe_2O_3
X 10,400



Synthetic kaolinite doped with 4% Fe_2O_3
X 10,400

Fig. 2.10

up to an iron concentration of 3% Fe_2O_3. Beyond this value the product was no longer recognisable as kaolinite plates and the X-ray diffraction patterns became diffuse. No separate crystalline iron phase was detectable by X.R.D. It is conceivable that iron may promote increased crystal growth to produce larger plates compared with undoped samples. However, the same effect is not readily apparent in natural samples. For example, in Keokuk kaolinite[24] the iron content is only 0.09% and the plates are comparatively large.

Crystallinity of the kaolinites as measured by the method of Hinckley[17] was also found to be dependant on iron concentration. Fig. 2.11 is a plot of X-ray crystallinity against % Fe_2O_3 in synthetic kaolinites and suggests that the most crystalline kaolinites are formed with an iron content of approximately 1.9% Fe_2O_3. However this figure seems remarkably high. Natural kaolinites with high crystallinity rarely contain greater than 1% Fe_2O_3. Repeats of the experiment are represented by points which have been marked with a small circle in Fig. 2.11. Even though in some cases there is considerable discrepancy with previous values the maximum crystallinity was obtained with a doping level of about 1.9% Fe_2O_3. It is possible that a greater proportion of the iron is on the surface of the synthetic kaolinites compared with natural samples.

With the exception of gels reacted at controlled

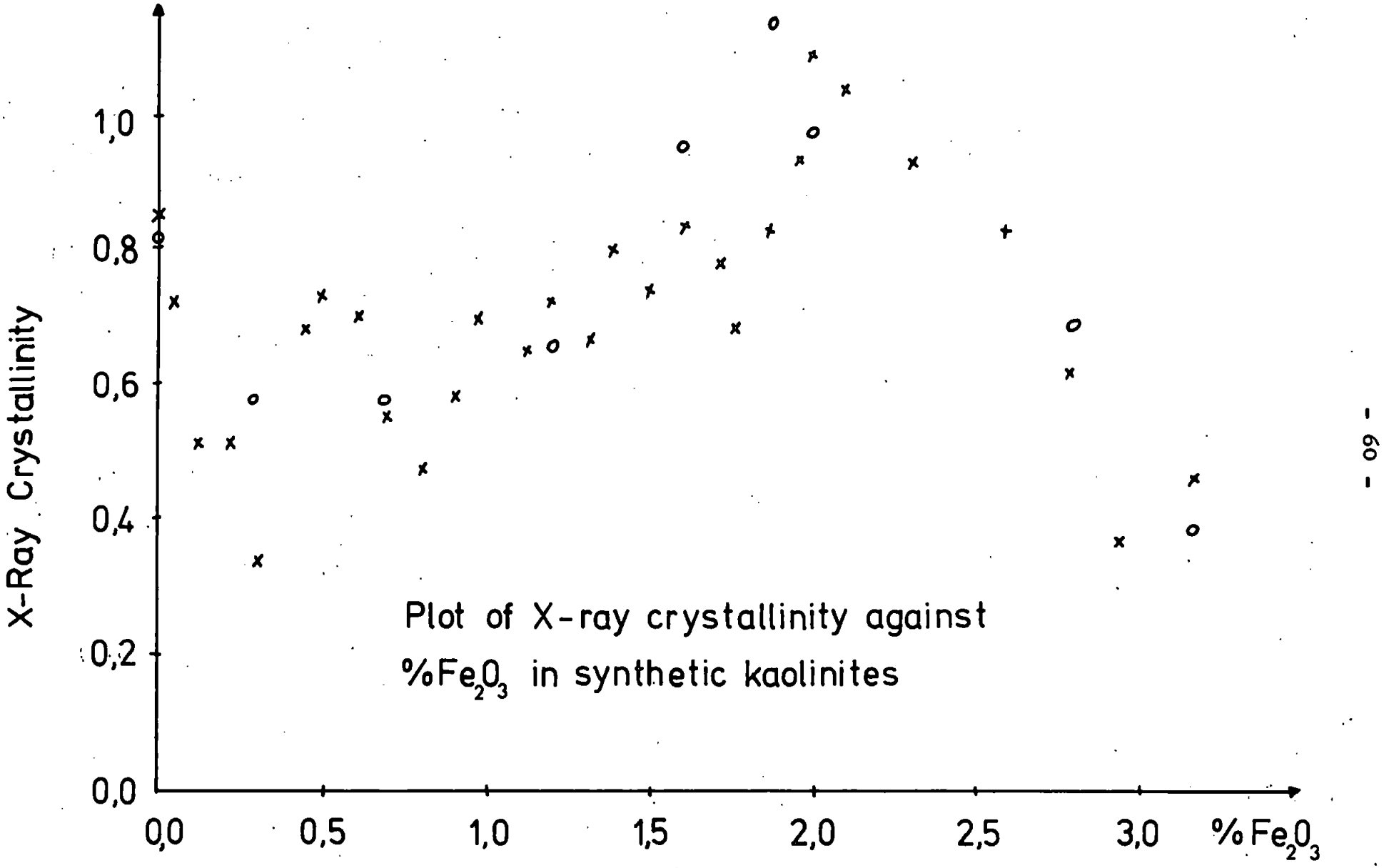

X-Ray Crystallinity
1,0
0,8
0,6
0,4
0,2
0,0
0,0
0,5
1,0
1,5
2,0
2,5
3,0
% Fe_2O_3
Plot of X-ray crystallinity against
% Fe_2O_3 in synthetic kaolinites

Fig 2.11

pressures (sec.2.7.2) in platinum tubes all gels had been reacted in P.T.F.E. liners. With these liners it was noticed that variations in colour sometimes occurred when identical gels were reacted under identical conditions. The effect was attributed to staining by leachings from the stainless steel bombs caused by the end seals of the P.T.F.E. liners leaking. Clearly, effects of this type would destroy any validity in measuring brightness of doped kaolinites so prepared. In order to study brightness it was therefore decided to change the reaction liners to platinum as described in sec, 2.7.2. A series of gels with different iron concentrations were reacted in platinum and the brightness of the resulting kaolinites measured by the method described in sec.2.7.3.

The plot of brightness against % Fe_2O_3 (Fig.2.12) clearly demonstrates the effect of iron on brightness. It should be remembered however that it was shown in sec.2.7.4.2 that the presence of iron appears to increase particle size. Such an effect would reduce scattering effects and hence a lower value of brightness would be measured. It is possible that some of the effects observed in Fig.2.12 may be attributed to particle size variations. Benzoal benzoate has the same refractive index as kaolinite enabling particle size effects to be eliminated. The synthetic kaolinites were placed in small quantities of benzoal benzoate and a darkening in colour was observed in all cases suggesting the presence of particle size effects. However from visual observation

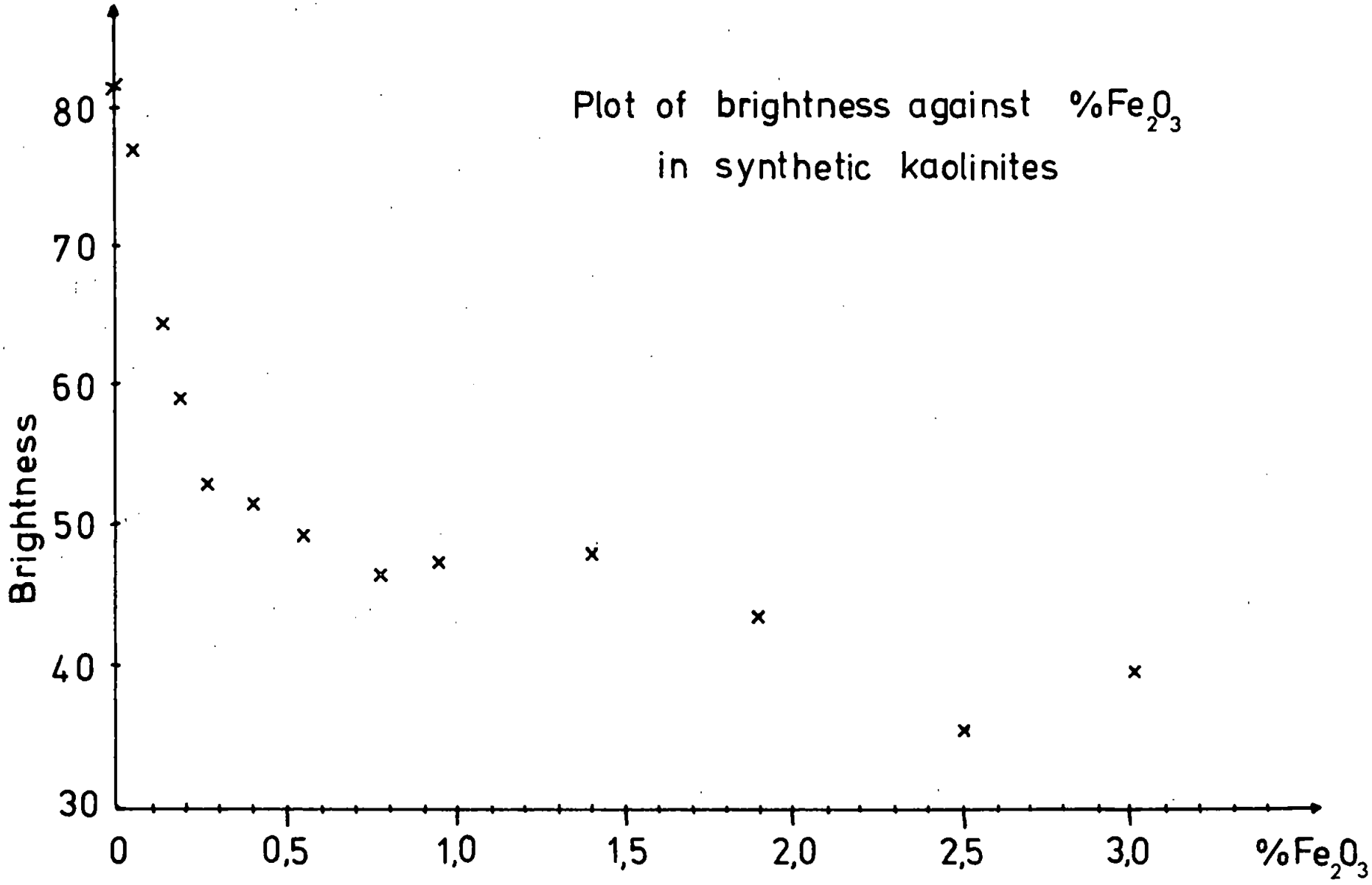

Plot of brightness against $\%Fe_2O_3$
in synthetic kaolinites
Brightness
80
70
60
50
40
30
0
0,5
1,0
1,5
2,0
2,5
3,0
$\%Fe_2O_3$

Fig 2.12

the brightness of the kaolinites followed the same trend as in Fig.2.12. As the kaolinites were in suspension absolute measurements of brightness were not possible.

From these results it would seem clear that the presence of iron has a pronounced effect on the morphology and physical properties of kaolinites. The E.S.R. properties of iron doped synthetic kaolinite are discussed in Chapter 3.

2.7.4.3. Preparation of Magnesium doped synthetic kaolinites.

For magnesium it was not possible to reproduce the technique used for doping with iron as all attempts to produce a magnesium benzoate failed. Doping with magnesium was therefore usually accomplished by the addition of small amounts of magnesium nitrate to the water of hydrolysis. Magnesium sulphate and magnesium chloride were also tried but the addition of more than 0.1% MgO by the sulphate or 0.25% MgO by the chloride prevented the synthesis of kaolinite. This was especially noticeable in kaolinites doped with both magnesium and iron. It was also hoped that the gel would not be contaminated by the nitrate anion as this should be removed on firing the gel at 1,000°C. The gels were dried and hydrothermally reacted in an identical fashion to that described for the preparation of iron doped synthetic kaolinites.

2.7.4.4 Morphology of Magnesium doped synthetic kaolinites.

A number of synthetic kaolinites were produced doped

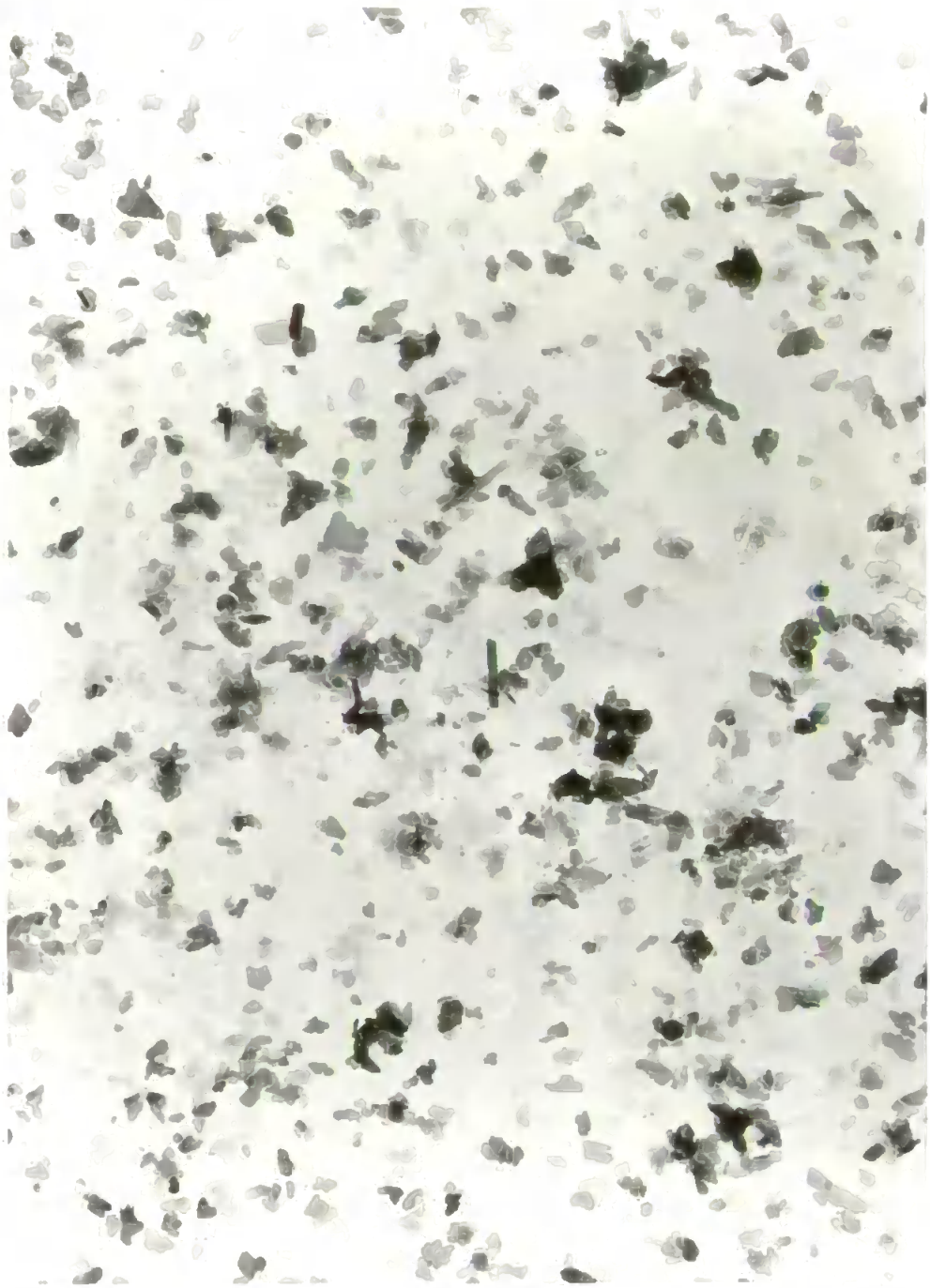
with varying amounts of magnesium and in all cases the most noticeable feature of study by electron microscopy was the formation of very much smaller particles than iron doped or undoped samples (Fig. 2.13). It was also noticeable that the plates though very small and thin were well formed showing better hexagonal form than those undoped or doped with iron.

Some samples were prepared doped with both magnesium and iron by adding ferric benzoate in D.M.F. to liquid A and magnesium nitrate to the water of hydrolysis. From the previous results it seemed that iron alone tended to increase particle size in contrast to magnesium alone which decreased particle size. For the doubly doped samples containing both substituent it was found that larger plates (Fig 2.14) were formed. It would seem therefore that crystallisation processes are more easily affected by iron than Mg. The reason for these effects are unknown. The E.S.R. properties of both magnesium and iron and magnesium doped kaolinites are discussed in Chapter 4.

2.7.5 The possible contaminants from reaction vessels or impurities in starting materials and their affect on the morphology of kaolinite.

Undoped gels reacted hydrothermally in P.T.F.E. liners were often found to produce kaolinites that were rather a dull grey in colour having a brightness value several points lower than kaolinites produced from the same gel reacted in platinum tubes. Although it was expected that the saturated vapour pressure of the water

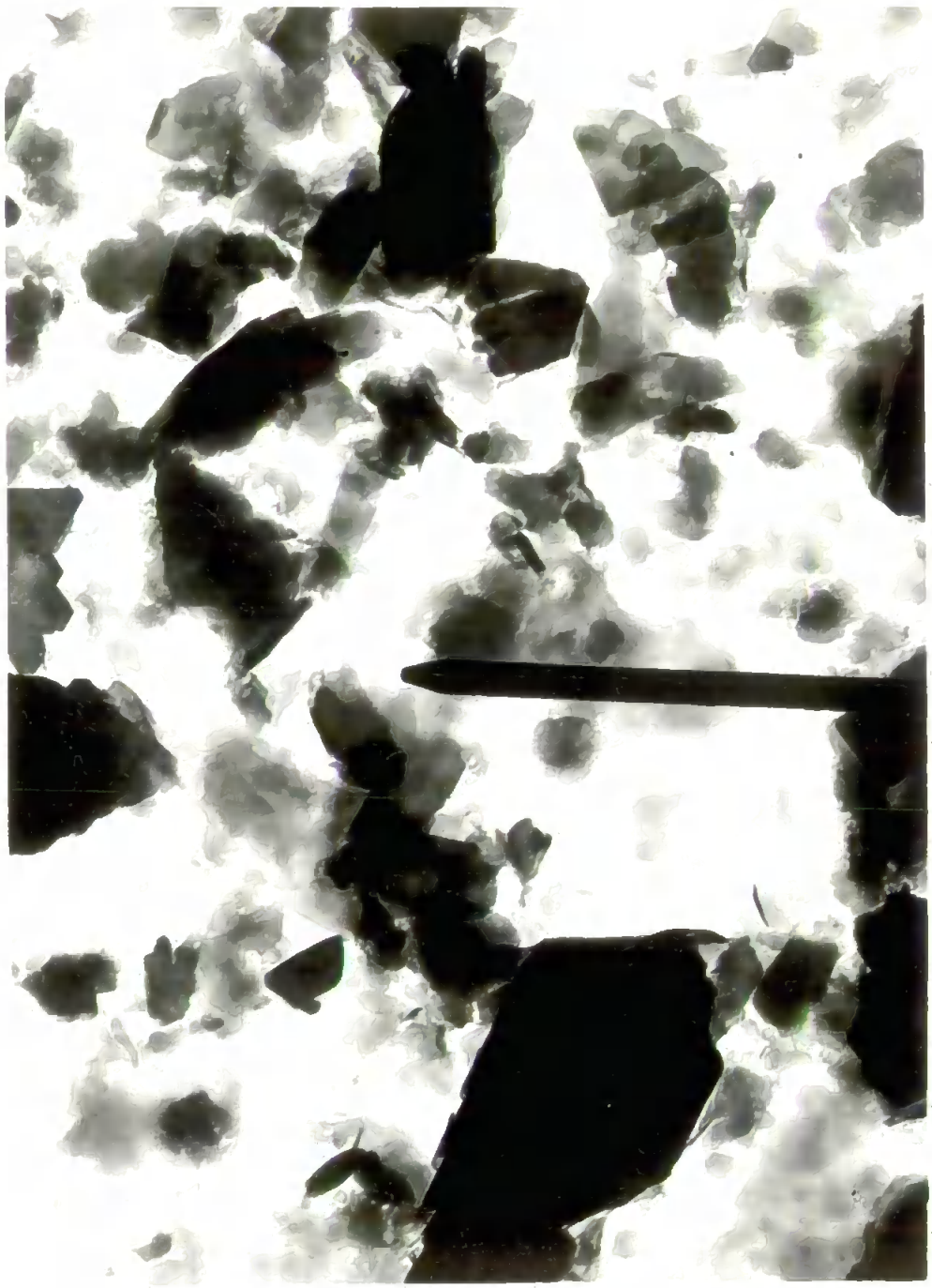
Magnesium doped synthetic kaolinite



X 44,000

Fig. 2.13

Magnesium and iron doped synthetic kaolinite



X 18,000

Fig. 2.14

on either side of the P.T.F.E. tubes would be equal it seemed optimistic to assume that the reaction tube was completely sealed from the water surrounding it. This being so it seems plausable that some contamination of the synthetic kaolinites could be attributed to leaching of the stainless steel Tuttle bomb. The most likely contaminant from the steel was thought to be iron though none was detectable by X-ray fluorescence analysis. However analysis did show that calcium contamination (about 0.02%) was present in the gels and probably originated from the aluminium iso-propoxide.

Fluorine is known to stain kaolinite[25] and being a major constituent of P.T.F.E. was therefore thought to be a possible cause of discolouration. However, personal communication with the manufacturers of the P.T.F.E. indicated that the release of fluorine was extremely unlikely. It has not been possible to date to subject a stained synthetic kaolinite to analysis for fluorine.

Synthetic kaolinites grown under pressure in platinum (Sec.2.7.2) were found to produce very diffuse X-ray patterns and were less crystalline than those produced at the same temperature (but different pressure) in P.T.F.E. reaction liners. However more crystalline kaolinites were produced from the high pressure rig when the platinum tubes leaked and the kaolinites were stained with the 10% soluble oil and water mixture. An identical oil was used in the production of the Tuttle bombs and it was therefore suspected that possibly a component within the machine oil

was acting as a catalyst to produce more crystalline kaolinites.

To test this theory some platinum lined bombs were constructed so that the reactants could only come into contact with platinum and the small area of P.T.F.E. forming the seal. The kaolinites produced were not stained and were well crystalline. In this method it was impossible for the reactants to come into contact with the steel of the bomb or with any machine oil so it seemed unlikely that the machine oil had any effect on the synthesis. From this it would seem likely that the staining was due to leaching from the stainless steel but no reason for the difference in crystallinity of samples grown in platinum or P.T.F.E. was forthcoming. At this stage the most crystalline kaolinites had been produced in the presence of P.T.F.E. either as a reaction liner or as a seal. It was decided therefore to investigate the possible effect of P.T.F.E. on the synthesis. A small amount of P.T.F.E. was ground and added to an undoped gel. This mixture was then sealed in a platinum tube with water and reacted for 7 days at 280°C. An equal amount of gel and water was reacted without P.T.F.E. in another platinum tube to act as a standard. The two resulting kaolinites were equally crystalline and any catalytic effect of P.T.F.E. was discounted.

The results described above give no indication as to why there should be the differences in crystallinity between samples grown in P.T.F.E. at the saturated vapour

pressure and those grown in platinum under pressures greater than the saturated vapour pressure. The effect will be discussed further in Sec.2.7.7.

2.7.6. Cooling and reheating cycles during the synthesis of kaolinite and their affect on morphology.

Many crystal growing techniques involve cycles of cooling and reheating.[2.6] In an attempt to study the effect of heating cycles on the synthesis of kaolinite, undoped gels were reacted for a total of two weeks during which time the temperature was varied from 240°C to 280°C and down to 240°C slowly at a rate of 10° per day. The kaolinites produced had crystallinity indices identical to samples reacted for 1 week at a constant temperature of 280°C. However, electron microscope observations (Fig.2.15) showed a large number of tube like structures of the order of a few microns in length very similar in appearance to halloysite. Electron diffraction measurements confirmed that the tubes were similar in structure to kaolinite. It should be noted however that occasionally samples grown at constant temperature were found to contain small quantities of tube-like structures but in these instances the concentration of the material was much less than that produced by temperature cycling.

2.7.7 Discussion of the properties and morphology of kaolinites synthesised under various conditions.

The previous sections have described some of the effects of pH, temperature, pressure, type and quantity of dopant on the synthesis of kaolinite. The number of

Kaolinite synthesised during cycles of cooling and heating.

X 24,000

Fig. 2.15

experiments performed were limited and were intended to indicate general trends to show how the products vary when synthesised under different conditions.

In section 2.7.2 it was shown that no further reaction takes place after reaction at 280°C for one week. It is possible that improved synthetic crystals might be produced at higher temperatures and longer reaction times but the use of P.T.F.E. liners and time restrictions prevented further study. Results also suggested that pressure appeared to have no effect on the synthesis of kaolinite. However, considering results obtained in Sec.2.7.5 this may only be true for pressures between 35 and 280 MPa. It appears that a kaolinite synthesised at the saturated vapour pressure of reactants at 280°C in platinum is more crystalline than one synthesised at a pressure of 35 MPa. Further increase of pressure does not affect the synthesis. This effect may be due to the collapse of the platinum tube at pressures greater than the s.v.p. changing the filling factor inside the tube, but how this might affect the synthesis is unclear. The solubilities of alumina and silica both depend on pressure so it is feasible that only at pressures around the s.v.p. at 280°C are the solubilities compatible for synthesis. It may also be that large pressures inhibit the production of the hydrogen bonding between layers by holding layers too tightly together.

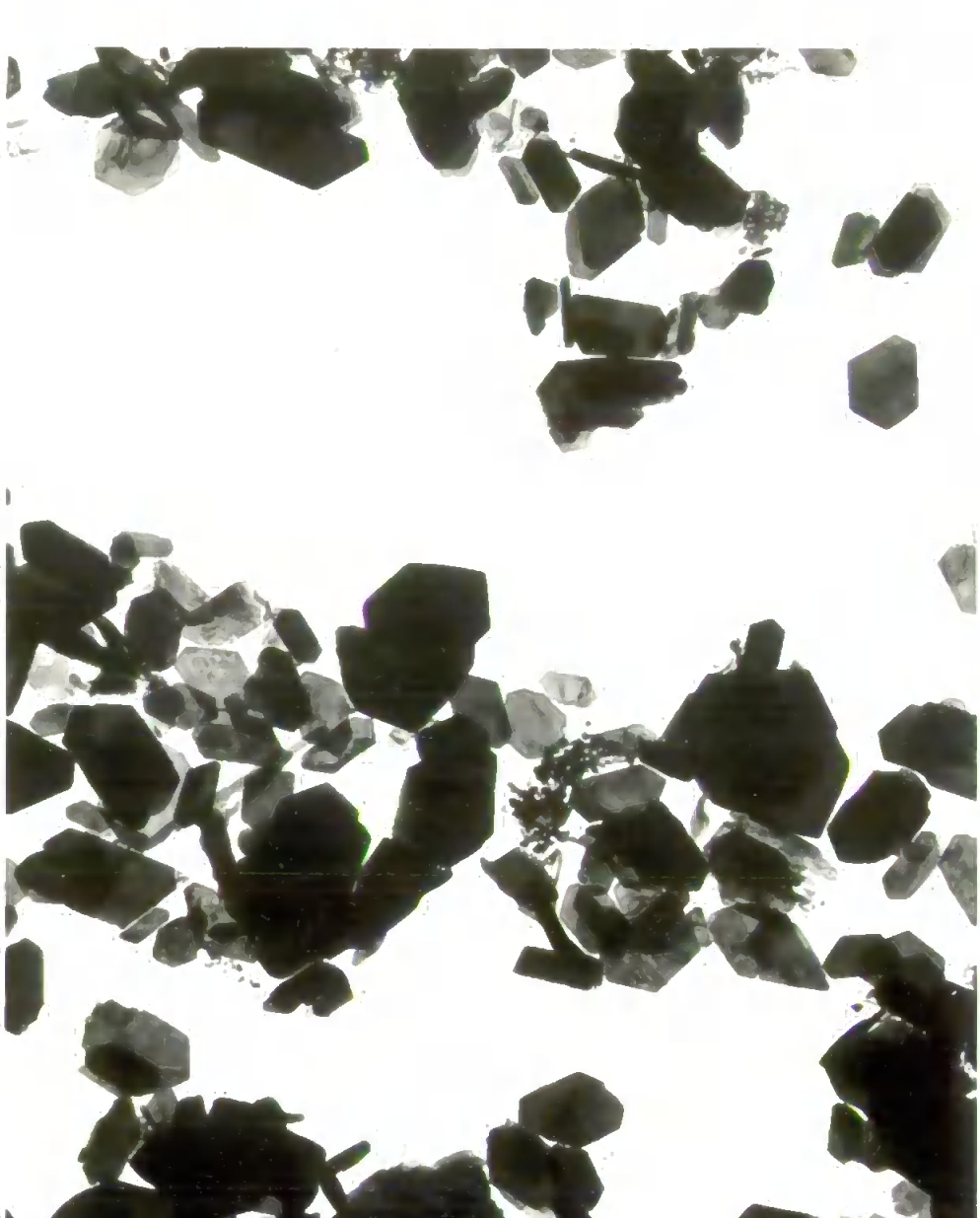
In section 2.7.3. undoped kaolinites prepared using various pH-reaction mixtures were considered. It was

found that well formed hexagonal platelets were only produced at low pH values and that morphological variations had little effect on brightness. However these well formed platelets grown at low pH were rather small compared to natural samples. In section 2.7.4. it was proposed that kaolinites doped with iron comprised larger plates than undoped samples. These results suggested that a synthetic kaolinite consisting of large well formed hexagonal plates might be synthesised by reacting on iron doped gel at low pH. To this end a synthetic kaolinite was produced at a pH of 2 doped with 1.9% iron. Observation of this sample under the electron microscope showed it to be indistinguishable from a well crystalline natural sample. (Fig. 2.16)

The effect of magnesium on the synthesis of kaolinite appeared to be the production of smaller plates than in iron or undoped samples. These plates however were quite well formed. Jones[3] pointed out the detrimental effect magnesium appeared to have on the synthesis of kaolinite. It may be that magnesium slows down the rate of crystallisation and hence produces smaller well formed plates. No experiments have been performed on magnesium doped gels reacted for more than one week.

In nature well formed kaolinites are very widespread and it seems difficult to imagine the right conditions (as described above) for synthesis of such kaolinites always being present. It may be that the synthesis at 280°C is too fast and less definite parameters for synthesis may be necessary at lower temperatures where crystallisation is slower.

Iron doped kaolinite synthesised at low pH



X 8,000

Fig.2.16

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CHAPTER 3

3.1 The basic principles of electron spin resonance (E.S.R.) and its application to the ferric iron in strong crystal fields.

Electronic paramagnetism is created by one or more unpaired electrons in an atomic system. When placed in an external magnetic field the degeneracy of the spin states is lifted to create a number of energy levels. transitions between the energy states may be induced by the application of eledtro-magnetic waves with appropriate energy to produce electron spin resonance.

The simplest system is that of a free unpaired electron where transitions will occur provided the resonance condition is satisfied:

$$h\nu = g_o \beta H$$

Where β is the Bohr magneton

H is the applied magnetic field

and $g_o = 2.0023$

The interaction between the unpaired spin and the applied magnetic field is considerably more complicated when the electron is coupled to an atomic system and even more so when contained within a crystal field. Although it is possible to describe the energy of such an assembly by a General Hamiltonian, Bleaney et al [1] have shown that it is possible to neglect all spin independant terms and formulate a 'Spin Hamiltonian'. In general the spin Hamiltonian contains several terms

representing the effect of crystal field, applied magnetic field and other interactions, each term containing a spin operator which operates on the spin functions of the system.

In this chapter the substitution of Fe^{3+} in kaolinite is considered, for which the spin Hamiltonian for the Fe^{3+} ion in a crystal field may be written in the form.

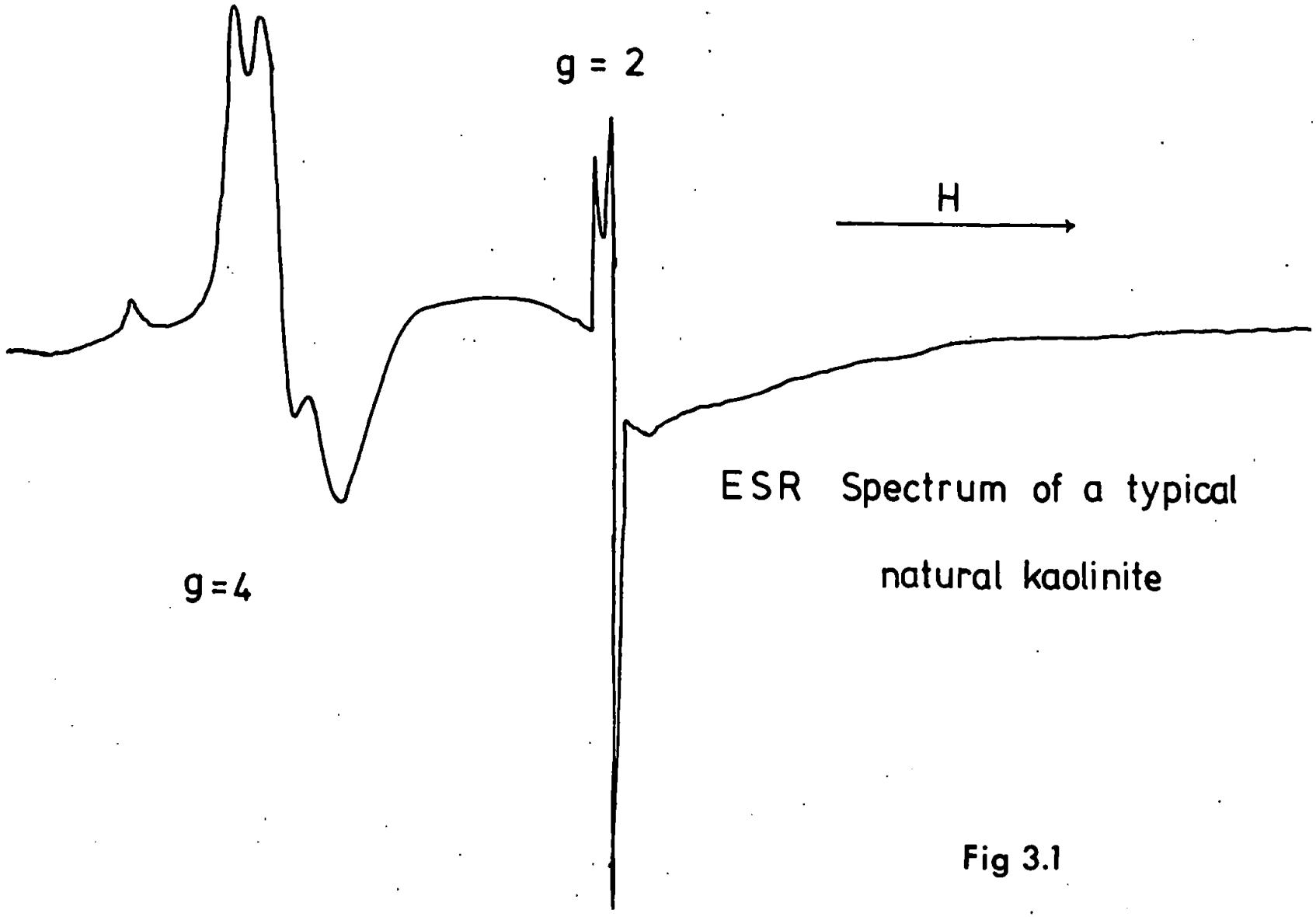
$$\mathcal{H} = g\beta \underline{H}.\underline{S}. + D\left[S_z^2 - \frac{1}{3} S(S+1) \right] + E \left[Sx^2 - Sy^2 \right]$$

The terms D and E effectively represent the symmetry of the crystal field created by the surrounding ligands and spin-orbit coupling. A common method for solutions of such equations is to treat the terms in D and E as a perturbation of the Zeeman interaction term or vice-versa. It has been shown Castner et al[2] that for Fe^{3+} in an environment where Zeeman and crystal field terms are comparable in magnitude, the use of perturbation theory is not valid. A large crystal field lifts the six-fold degeneracy of the $^6S_{5/2}$ ground state of the ferric iron to give three Kramers doublets. The degeneracy of the doublets may be removed by the application of an external magnetic field and thus provide a system for electron spin resonance. However, from computed numerical solutions of the spin Hamiltonian it has been shown that the way in which the energy levels of the three doublets diverges in an increasing magnetic field is particularly complicated. The divergence

depends critically on the ratio of D and E and also on the angle which the applied magnetic field makes with the crystal axis. For a randomly orientated powder it is possible to predict the final lineshape[3] and to assign the resonances observed to transitions within the doublets. These transitions are usually described by a notation of numbers and letters as proposed by Aasa[4]. The eigen-values of energy are labelled 1 to 6 in order of increasing energy. If field variations cause levels to cross, the labelling is changed so that the energy ordering is maintained. A transition quoted as 1-2X is that between the lowest two energy levels, corresponding to the applied field being parallel to the X-principal axis of the crystal.

3.2 Electron spin resonance of kaolinite.

The E.S.R. spectra of natural kaolinites almost without exception contain two groups of resonance lines one of which occurs at g=4, and the other at g=2, as illustrated in Fig. 3.1. The next two chapters deal with each group in turn starting with the group at g=4. Most previous publications[5.6.7.8.9.10.] have all suggested that the lines at g=4 can be attributed to iron substituting in the kaolinite structure. Perhaps the most convincing results to substantiate this argument are those recently produced by Jones[6] in this laboratory using both doped and undoped synthetic kaolinites. The resonances at g=4.0 were only observed in those samples doped with iron. Further refinement of E.S.R. studies by Angel et al[10]



ESR Spectrum of a typical natural kaolinite

Fig 3.1

have shown that the apparent three line signal at g=4 is created by the superposition of two distinct sets of signals which may be attributed to iron in different sites. The first site (centre 1) produces a single isotropic line at g=4.2 and the second (centre 2) a three line spectrum with g values of 4.9, 3.7 and 3.5.

Hall[5] utilized the computer program of Dowsing and Gibson[11] to solve numerically the spin Hamiltonian for Fe^{3+} in kaolinite and found that $\lambda = \frac{E}{D}$ with a value of 0.22 corresponding to a site symmetry between axial and rhombic gave the best fit for the three line spectrum. Fig. 3.2 shows transitions predicted for λ 0.22 for various D values. The isotropic line at g=4.2 was interpretated as Fe^{3+}. occupying a completely orthorhombic site with $\lambda = \frac{1}{3}$.

Although it is possible to find values of λ from the E.S.R. data it is difficult nevertheless to specify the exact nature of the environment of the Fe^{3+} ion in kaolinite and to distinguish substitution either for Al^{3+} in the octahedral layer or Si^{4+} in the tetrahedral layer.

It is known that chemical treatments and heating can affect both groups of resonances and their effects have been used to suggest possible site locations for the paramagnetic species. For example Jones[6] studied the effect on the E.S.R. signals of intercalation of kaolinite with D.M.S.O. The composite g=4 signal was found to collapse to a single isotropic line. This effect

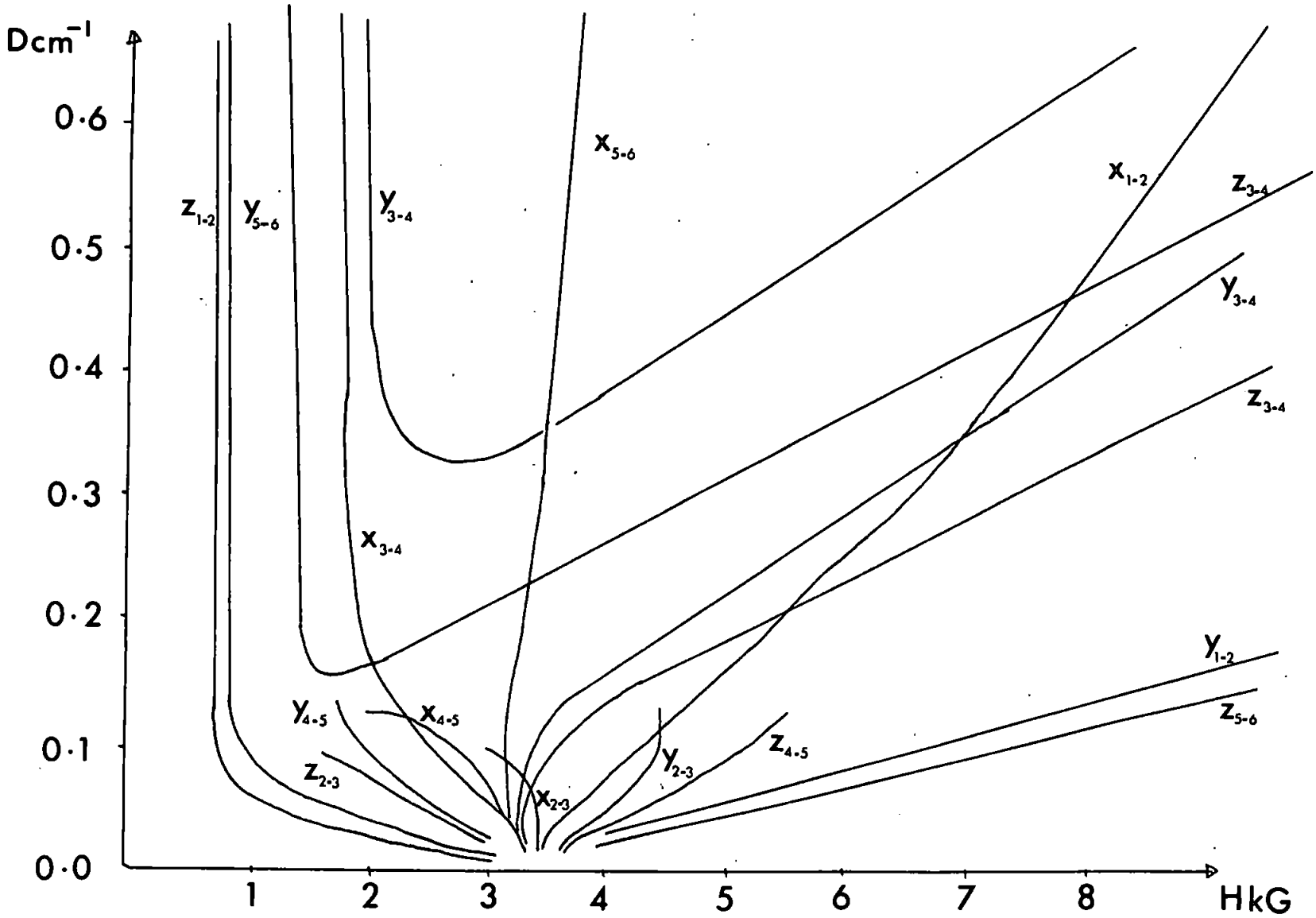
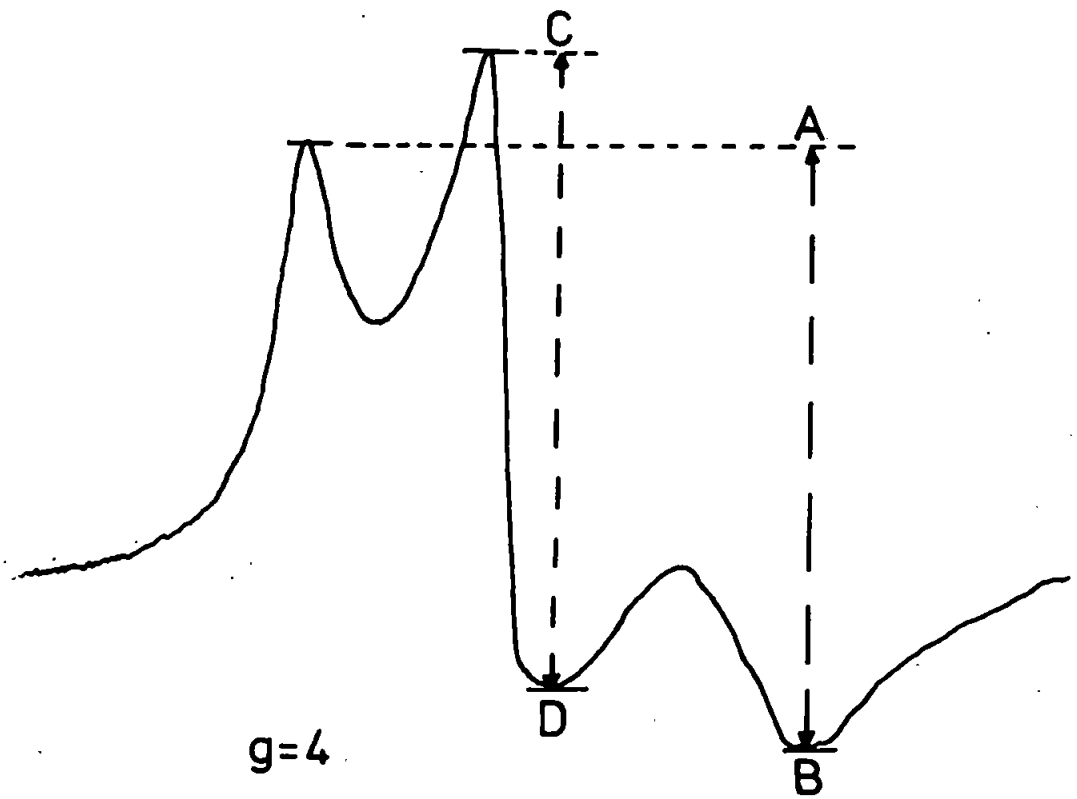


Fig 3.2 Transitions predicted for $\frac{E}{D} = 0{\cdot}22$

suggests that the paramagnetic defects could be in an interlayer site and the intercalation affects their symmetry. However it is thought that intercalation most probably affects the hydroxyl groups in kaolinite and therefore would also perturb the symmetry of the octahedral site. The mineral gibbsite has only octahedral Al^{3+} sites and exhibits an E.S.R. signal at g=4 similar to that observed in kaolinite. On this basis Angel et al[10] preferred to assign the g=4 signal to Fe^{3+} in an octahedral rather than an interlayer site in kaolinite.

In order to distinguish the two resonances which contribute to the g=4 signal and monitor their relative intensities Jones[6] (Fig. 3.3) proposed an "E.S.R. Lineshape parameter" and examined possible correlations of the parameter with sample crystallinity. It was shown from a survey of natural kaolinites with varying crystallinity that the contribution to the g=4 signal by the single isotropic resonance increased with decreasing crystallinity. Since Angel et al[10] had shown previously that similar effects could be obtained by contributions due to mica impurities a separate series of experiments utilizing the same sample were initiated in which the crystallinity was gradually decreased by applying increased strain to the samples. It was found that as the pressure increased and the crystallinity decreased the E.S.R. lineshape parameter also decreased. Hence it was proposed that the application of pressure had

Diagram showing calculation of ESR lineshape parameter



$$\text{ESR Lineshape Parameter} = \frac{AB}{CD}$$

H →

Fig 3.3

reduced the crystallinity and hence changed the symmetry of the site associated with the three line spectrum into the less crystalline site associated with the isotropic line at g=4.2.

As well as substituting in the octahedral layer it is possible that iron atoms might replace silicon atoms in the tetrahedral layer. However for this process to occur some sort of charge compensation is necessary and it might therefore be argued that tetrahedral substitution is less likely than octahedral substitution. Nevertheless, silicate glasses doped with small quantities of iron and in which there can only be tetrahedral substitution produce isotropic signals around g=4. Further evidence for possible tetrahedral substitution in kaolinite is provided by the collapse of the g=4 signals to a single isotropic g=4.2 signal following dehydroxylation by heating to 550°C. Dehydroxylation removes the hydroxyl groups and modifies the octahedral sites to form a new structure which is commonly called metakaolin. If the model suggested by Brindley[12] for metakaolin is adopted then it is possible to suggest that the remaining isotropic line be assigned to tetrahedral substitution there being only tetrahedral sites in the structure of metakaolin. More recent work by Herbillon[9] gives further evidence for both tetrahedral and octahedral substitution of iron in natural kaolinites. A number of natural kaolinites were boiled in concentrated hydrochloric acid in an attempt to preferentially dissolve away the

octahedral layer. The rate of dissolution of iron and alumina were followed by chemical analysis and the E.S.R signals were monitored. It was found that the rate of dissolution of iron closely followed that of the alumina thus demonstrating that the iron is probably associated with the alumina layer and is therefore in octahedral co-ordination. However, for some samples complete removal of the alumina content did not remove all the iron. Herbillon[9] proposed that the residual iron was tetrahedrally co-ordinated. However the presence of other iron bearing minerals made the interpretation of results extremely difficult especially after long dissolution times where the iron in the residue was found to become more concentrated as the acid attack progressed.

When Hall[5] solved the Hamiltonian by the method of Dowsing and Gibson[11] he proposed two octahedral sites but also stated that the isotropic line could be caused by tetrahedral substitution of iron for silicon. If the latter were true one would expect in the work by Herbillon[9] where the alumina layer is dissolved away by acid that the three line spectrum would be removed preferentially leaving behind the isotropic line associated with the tetrahedral silica layer. However, in the E.S.R. spectra published by Herbillon[9] of kaolinites subjected to acid attack it is the central isotropic line that is removed first. This effect would be expected if the isotropic line were associated with a less crystalline site as

proposed by Angel et al[10].

As an alternative to E.S.R. Pott[13] examined a natural clay by phosphorescence spectroscopy in an attempt to identify tetrahedrally co-ordinated Fe^{3+}. However no fluorescence peaks were identified which could be attributed to iron. Pott[13] suggested that either there was no significant quantity of tetrahedrally co-ordinated Fe^{3+} or alternatively that any phosphorescence was effectively quenched by hydroxyl groups which are known to quench phosphorescent emission.

To summarise, the majority of workers in this field would seem to favour the assignment of the three line E.S.R spectrum at $g=4$ to Fe^{3+} substitution in the octahedral layer. The isotropic line at $g=4.2$ may be due to either Fe^{3+} in a distorted octahedral or tetrahedral site. Apart from substitutional iron some iron may exist as a surface contaminant probably in the form of oxides or hydroxides. A chemical analysis of a kaolinite gives the total iron content but gives no indication of the proportions of substituted and surface iron.

Jepson[14] examined the iron in natural kaolinite by electron microprobe micro-analysis. Good agreement was reported between iron concentrations calculated by chemical analysis and electron microprobe micro-analysis of the kaolinite plates, suggesting that most of the iron was associated with the kaolinite phase in the sample. Jepson[14] proposed that, because only six per cent of the total iron could be removed by surface treatments, most

of the iron was in structural sites.

Some industrial processes for the benefication of clay involve the removal of iron. Two main processes are used. Firstly the reduction of surface iron by sodium dithionate and subsequent removal of the resulting soluble ferrous iron. Secondly magnetic filtration which may be effective for the removal of both surface iron and particles high in substituted iron. In the laboratory the most common methods used to remove surface iron are by treating the clay with sodium dithionate as on the industrial scale or with ammonium oxalate. All these methods produce an increase in the brightness of the kaolinite. A typical china clay from St. Austell may start with a brightness of about 87; treatment with sodium dithionate may increase this to 92. This clearly illustrates that surface iron has a detrimental effect on brightness but in no way indicates the effect of substitutional iron on the brightness of a kaolinite.

Surface treatments remove only a small percentage of the total iron content suggesting that the major part of the iron is in structural sites. However, it is clear from the author's numerous discussions with workers in this field that the effectiveness of these methods of iron removal, as well as their mode of action, is in constant debate. Clearly, the amount of iron removed depends not only on the method used but also on the nature of the iron associated with the kaolinite. It is agreed however, that in general, except for kaolinites with excessively

high iron contents the amount of iron removed by these methods is usually of the order of 10% or less of the total iron impurity. A number of kaolinites from Georgia and a few synthetic iron doped samples have been treated with ammonium oxalate in this laboratory and in all cases only a few per cent of the total iron was removed.

By double integration of an E.S.R. spectrum it is possible to get a rough estimate of the number of spins per gram and hence an indication of the concentration of substituted iron. For a natural kaolinite Hall[5] reported reasonable agreement between the iron concentration calculated by double integration of the $g=4$ signal and from chemical analysis. However, Hall[5] did not quote the standard sample used for the E.S.R. calculation. These measurements have been repeated in this work on one synthetic and two natural kaolinites using a freshly prepared copper sulphate standard. In all three samples less than 5% of the total iron appeared to be paramagnetic. These results tend to suggest that a large proportion of the iron is not paramagnetic and not removable by surface treatments. Possible reasons for these results are given below.

Accurate spin concentration measurements are difficult to reproduce and the use of a suitable standard is very important. In the estimation of the iron content by consideration of the $g=4$ signal the standard signal used was at $g=2$. It is known that transition probabilities

vary with applied magnetic field. No corrections were made for differences in transition probabilities. It may be possible that some surface iron is not easily removed or alternatively metallic iron or iron compounds are included within the kaolinite structure and as such are protected from ammonium oxalate treatment.

Previous workers have suggested that surface iron is in the form of oxides or hydroxides.[16] If particulate, these compounds may be ferromagnetic because of strong coupling between adjacent $5/2$ spins. These ferromagnetic contaminants are detected as broad resonances around g=2 (Fig.3.1) and usually can be reduced by treatment with ammonium oxalate. However, it is unusual for all the broad resonance to be removed. For example, in the work by Herbillon[9] described earlier a broad ferromagnetic resonance remained after oxalate treatment followed by extensive acid attack of the alumina layer. It is the author's contention that these broad resonances should be included in the E.S.R. calculations and therefore might account for some of the iron not accounted for previously. To avoid this complication E.S.R. calculations in this work have been on samples which exhibit very small broad resonances.

Some iron may be in a super-paramagnetic state. The spin relaxation time of ferric iron depends on particle size of the host material.[17]. For example in iron oxides or hydroxides the particle size can be sufficiently small

to reduce the relaxation time and destroy the spin coupling and hence produce a change from ferromagnetism to super-paramagnetism. E.S.R. may only be observed if the relaxation time is longer than 10^{-10} sec and hence it is possible for super-paramagnetic iron not to be detectable by E.S.R. Super-paramagnetic states may be studied by Mössbauer spectroscopy.

Some iron may also be associated with a separate mineral phase, in fact it is probable that some iron is associated with the mica content of natural samples, however no mica has been detected in synthetic samples produced in this work.

To summarise, it is clear that the nature and proportions of substituted, surface and included iron associated with kaolinite remains uncertain. A large proportion of iron in some kaolinites is not removed by present methods of surface treatments and is not accountable by E.S.R. measurements as substituted iron. Some iron is detected in a ferromagnetic form by E.S.R. and may be due to surface, or inclusions of, hydroxides, oxides or even metallic iron. It may also be possible for some iron to be in a super-paramagnetic state.

Clearly, additional techniques were required to study both surface and substituted iron. Mössbauer spectroscopy enables the valence states of iron in a structure to be determined and can also distinguish different site symmetries. An account of this work is given in Chapter 5.

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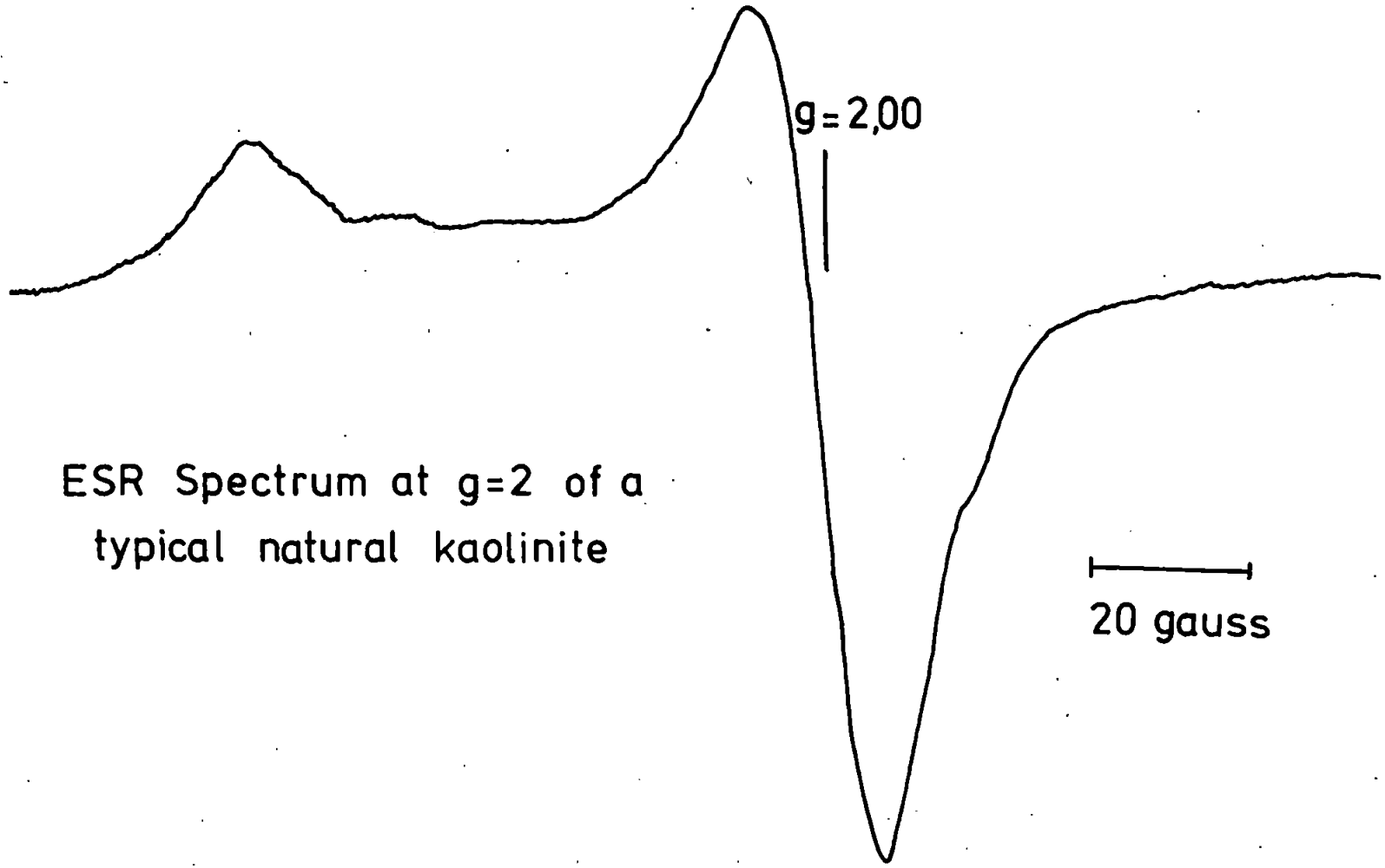
C H A P T E R 4

4.1 Previous E.S.R. studies of the signals at g=2 in kaolinites.

An expanded trace of the E.S.R. signals which occur around g=2.0 in the majority of natural kaolinites is shown in Fig. 4.1. With the exception of work carried out in this laboratory past workers have recorded the signal at g=2.0 under conditions of poor resolution. More precise measurements by Hall[1] demonstrated that the relative intensity of the two principal lines varied considerably in different samples and that on heating the samples to 300°C for half an hour the two lines were more clearly defined. By studying the expanded traces of a series of natural samples before and after heating to 300°C Hall[1] was able to assign the resonances observed at g=2.0 to two discrete centres. A main two line spectrum that remained after heating at 300°C (Centre A) and a number of smaller hyperfine signals (Centres B) that were removed by the heating. The variation in intensity of the main two line spectrum on heating was found to be due to the removal of the hyperfine lines.

The main two line spectrum (Centre A) at g=2.0 is characteristic of an axially symmetric paramagnetic species in a randomly orientated powder, and has the principal g - values

$$g_{\parallel} = 2.049 \pm 0.001 \text{ and } g_{\perp} = 2.003 \pm 0.001$$



ESR Spectrum at g=2 of a typical natural kaolinite

Fig 4.1

Hall[1] prepared a preferentially orientated stack by sedimentation and studied variations in intensity of the two components as a function of orientation in the magnetic field. He concluded that the unique axis of the A-centre lies parallel to the c-axis of the kaolinite crystal. Also it was found that the A centre could be destroyed by heating to 450°C for 2 hours prior to complete dehydroxylation.

A number of theories have been forwarded to explain the occurrence of the main signal at g=2.0. The possible sources of the signal include -

(i) an organic fraction in the clay[2]

(ii) iron substituting for either silica or alumina[3] or

(iii) defect centres.[4]

Angel and Hall[5] removed the organic fraction from some natural kaolinites and found that the g=2 signal remains unchanged. In the work by Jones[4] described in the previous chapter where kaolinites doped with Fe^{3+} ions were synthesised no signal at g=2 was detected. The possibility of the signal being caused directly by Fe^{2+} is very remote due to its very fast relaxation times which precludes detection by E.S.R. at room temperatures. On this basis Jones[4] concluded that the signal must be due to a defect centre. To validate this theory he first of all X-irradiated and subsequently annealed pure synthetic kaolinites. As there was no g=2 signal produced he concluded that the defect centre was not associated with

the intrinsic kaolinite structure but was stabilised by an impurity. For example, substitution of trivalent cations for Si^{4+} or divalent cations for Al^{3+} may produce centres capable of trapping a hole. Hence, synthetic kaolinites doped with Mg^{2+} were produced in which initially no E.S.R. signals were found. However, X-irradiation followed by annealing produced signals at g=2.0 identical to those in natural kaolinites. Jones[4] suggested that a similar hole centre produced by Fe^{2+} substituting for Al^{3+} is less likely because Fe^{2+} has a larger ionic radius than Mg^{2+} and therefore would not be so easily accommodated in the structure. Also the oxidation of Fe^{2+} to Fe^{3+} would be expected to occur during synthesis.

Jones[4] stated that doping the gel with magnesium appeared to inhibit the subsequent synthesis of kaolinite producing poorly crystalline samples. He also noted that the signals produced at g=2 were much less intense than those usually associated with natural samples. Although previous work by Jones[4] had reproduced signals at either g=4.0 or g=2.0 the complete simultaneous reproduction of both resonances had not been achieved and it was not clear from his work the extent to which substitution of one defect might possibly effect the behaviour of the other. Also the kaolinites which produced the g=2.0 resonance were of very poor quality. To make further studies on the g=2 signal in synthetic kaolinite the method of synthesis would have to be improved.

4.2 The synthesis of magnesium doped clays.

In order to understand more fully the synthesis of magnesium doped kaolinite a series of gels were prepared doped with varying concentrations of magnesium salts. As stated in Chapter 2 the addition of magnesium nitrate to the water of hydrolysis of the gel produced more highly crystalline kaolinite than the use of magnesium sulphate or chloride. The use of magnesium nitrate also assisted the production of the g=2 signal and this effect was considered to be due to the higher crystallinity of the magnesium nitrate doped sample. The optimum concentration of MgO for production of the g=2 signal was found to be about 0.04%. This value is surprisingly low being less than one third of the concentration of MgO in a natural kaolinite exhibiting a g=2 signal of about the same intensity. It was considered that in natural samples the signal might be increased by irradiation and annealing. However, this was found not to be so and it was therefore assumed that the 'extra' magnesium in the natural samples was in a form unable to stablise a defect. For example in the mica fraction. Indeed a study of about twenty American and English clays showed no correlation between the intensity of the g=2 signal and their magnesium content.

Double integration of the g=2 signal for both natural and synthetic samples accounted for only a small percentage of their magnesium content assuming one spin per substituted ion. To maintain charge balance in the octahedral layer,

Mg^{2+} would have to substitute trioctahedrally. It seems possible that the defect responsible for the g=2 signal may only be stabilised when a charge inbalance is present, for example dioctahedral substitution of Mg^{2+}.

It is therefore proposed that the g=2 signal (Centre A) is caused by dioctahedral substitution of Mg^{2+}. The reason for the 'discrepancy' in intensities between natural and synthetic samples with similar magnesium contents is attributed to either magnesium in another mineral phase associated with the natural sample or an excess of dioctahedral substitution in the synthetic kaolinites.

4.3 The synthesis of kaolinite doped with both magnesium and iron.

Having established the optimum conditions to produce fairly intense signals at both g=2 and g=4 it was now hoped that the synthesis of a kaolinite exhibiting both sets of signals would be accomplished. Previous attempts by Jones[4] had failed to produce any detectable kaolinite but the main inhibitor of the synthesis employed by Jones[4] seemed to be use of magnesium sulphate. It was hoped that the use of magnesium nitrate which had been successful in improving the synthesis of magnesium doped samples would enable a kaolinite doped with both magnesium and iron to be synthesised.

6cc of ferribenzoate in D.M.F. (67 gms per litre) were added to 25cc of liquid A, and mixed thoroughly. The mixture was then added to 100cc of water containing

about 0.2 gms magnesium nitrate and then shaken thoroughly and allowed to hydrolise for about a week with occasional shaking. The gel was then dried and fired at 1,000°C before being hydrothermally reacted. The resulting sample was subject to X-ray diffraction and E.S.R. and found to be well crystalline kaolinite exhibiting a reasonably intense $g=4$ resonance. Irradiation of the sample produced a broad resonance at $g=2$ and annealing at 200°C produced a signal at $g=2$ identical to those in natural samples.(Fig.4.2)

4.4 B. Centres.

Apart from the main two line resonance (Centre A) Hall[1] also studied the hyperfine lines (B Centres) in natural kaolinites and pointed out that their spacing, of about 7.7 ∓ 0.2 gauss, is in fair agreement with values for a defect centre in which the spins interact with Al^{27} nuclei which has spin $1 = {}^{5}/_{2}$. He observed that the B Centres were less stable than the A centre responsible for the main two line resonance and could be easily annealed at temperatures of 200°C.

From Fig. 4.1 it is clear that it is difficult to make detailed studies of the B centres when resonance lines are superimposed on the lines associated with the A centre. As a possible aid to studying the B centre signals Hall[1] heated a kaolinite to 450°C to remove all signals at $g=2$. By subsequent irradiating he was able to reproduce the B centres superimposed on a broad resonance at $g=2.0$.

The E.S.R spectrum of an iron and magnesium doped synthetic kaolinite after X-irradiation and annealing.

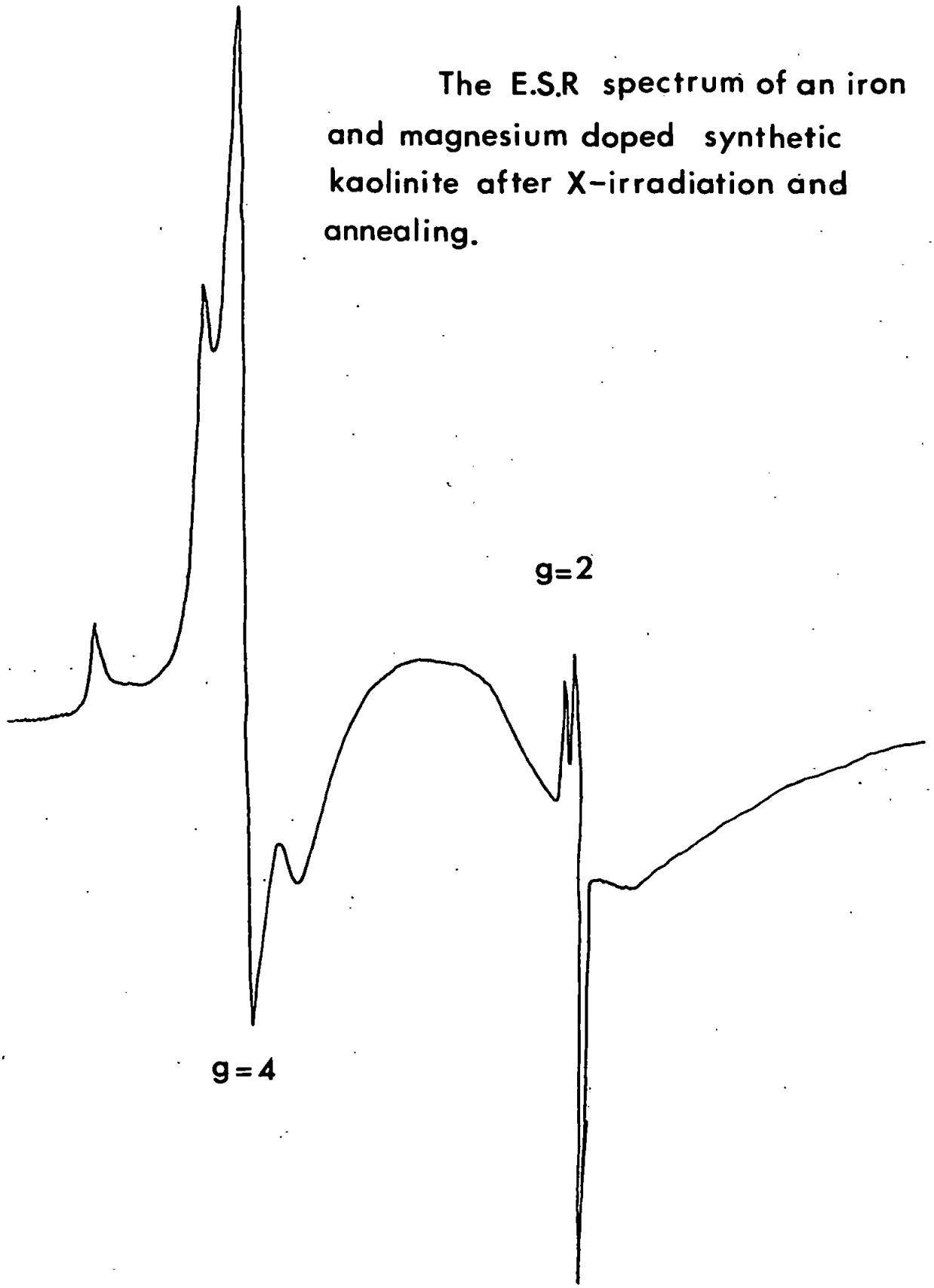


Fig 4.2

It was not established in previous work whether or not the defects were specifically associated with either the silica or alumina layer. It seemed feasible that a possible method of identifying the location of the centres would be to study signals which were reproduced in pure silica or alumina compounds. Initially gels of pure silica and pure alumina were produced doped with small amounts of magnesium. These were hydrothermally reacted to produce boehmite in the case of the alumina gel and an amorphous silica phase in the case of the silica gel. These were irradiated and annealed but unfortunately both failed to produce any signals at g=2. An alternative approach was therefore made by reconsidering natural samples.

Hall[1] had previously noted that it was possible to remove the g=2 resonance (centre A) by heating the sample to 450°C and then by irradiating regrow the B centre signals. Hall[1] noticed that the B centres seemed to give more intense signals than were present before the main g=2 signal was removed. This effect Hall[1] considered to be caused by the absence of the main g=2 signal which previously partly obscured the hyperfine lines.

These experiments have been repeated in this work and it has been shown that after the destruction of the main g=2 signals by heating the main (centre A) resonance may be regrown by irradiation and subsequent annealing at 200°C. This suggests that the g=2 signal associated

with Centre A is annealed before dehydroxylation. Attempts to grow these g=2 signals in dehydroxylated samples were unsuccessful.

Although X-ray diffraction spectra show no detectable change when a kaolinite is heated to 450°C thermogravimetric analysis indicates a small weight loss and suggests that dehydroxylation may have already started. Jones[4] suggested that B centres may be either an aluminium atom substituted in the silica layer or an electron trapped in a hydroxyl vacancy. However, no experimental evidence in support of either assignment was given. Assuming that the two arguments suggested by Jones[4] for the B centres were possible it was thought fruitful to consider what might be expected to happen to the E.S.R. signals for each model when irradiated or annealed in various ways.

It was thought that if the centre was caused by aluminium substituting in the silica layer that the centre may be produced in dehydroxylated samples by irradiation, as the silicate layer is unaffected by dehydroxylation. If, however, the centre was caused by an electron in a hydroxyl vacancy, collapse of the structure upon dehydroxylation would prevent formation of the sites in dehydroxylated samples. In addition partial dehydroxylation may produce more hydroxyl vacancies and it was therefore thought that more intense B centre signals might be produced in samples partially dehydroxylated. It has already been stated that Hall[1] reported an increase in the

intensity of the B centre signals by irradiating after heating to 400°C.

To test these theories a natural kaolinite was completely dehydroxylated by heating to 700°C for two hours and then X-irradiated with a dose of approximately 1 M.Rad. Observation of the E.S.R. signals at g=2 showed only a broad signal with no detectable hyperfine structure associated with B centres. These results provide substantial support for the assignment of B centres to a configuration within the octahedral layer as opposed to the tetrahedral layer. The structure of the silica layer is virtually unchanged by dehydroxylation.

In samples heated at temperatures up to but not including dehydroxylation it was found that increasing the degree of partial dehydroxylation caused a corresponding increase in the intensity of the B centre resonance when subsequently irradiated. Hence, it would seem that the B centres are related to the concentration of hydroxyl vacancies thus giving further evidence for the assignment of the B centre signals to electrons in hydroxyl vacancies.

To summarise; at this stage of the work the main g=2 resonance associated with the A centre was attributed to a hole trapped by magnesium substituting for aluminium and B centres signals were probably caused by electrons occupying hydroxyl vacancies. Previous work has shown that iron may substitute in the lattice as Fe^{3+} to produce resonances at g=4.0. The possibility of the

ferrous ion substituting in the kaolinite to produce the same effects as Mg^{2+} had been considered but dismissed as unlikely because of its larger ionic size and easy oxidation to Fe^{3+}.

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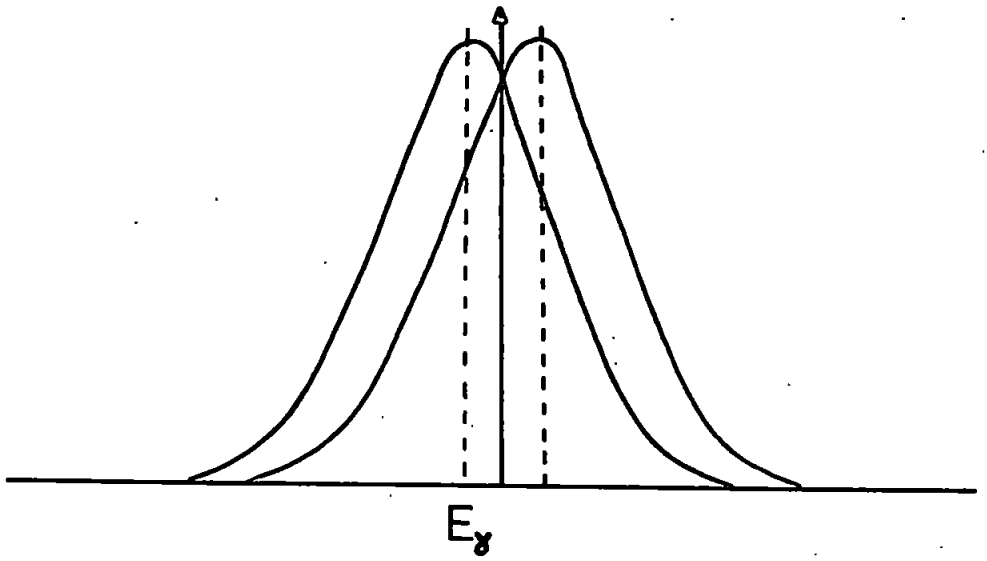
CHAPTER 5

5.1 Basic principles of the Mössbauer effect.

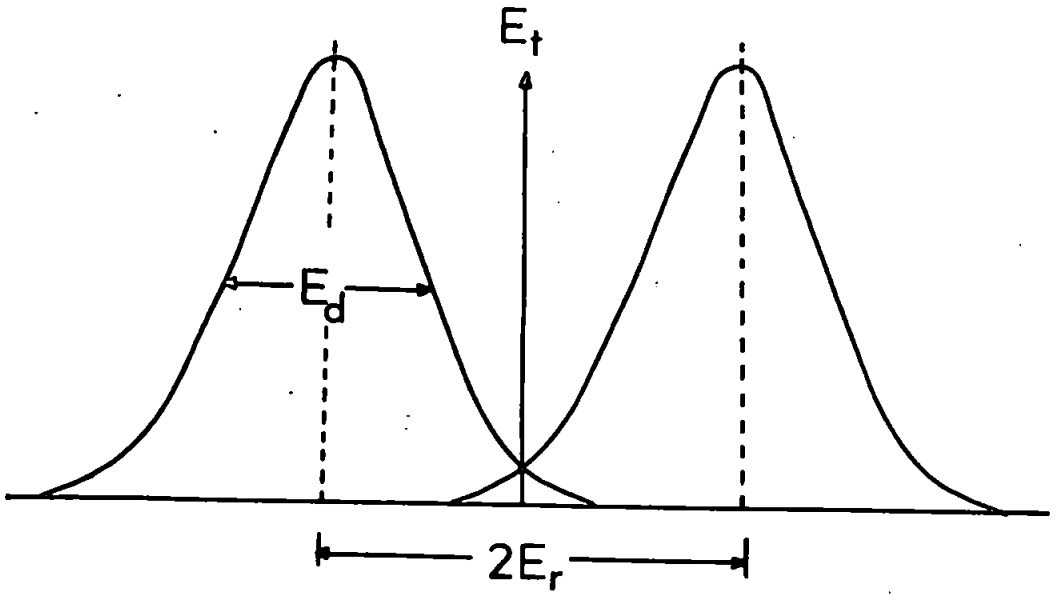
Following its discovery in 1957 the Mössbauer effect has been the subject of many books and papers.[1.2] The technique can distinguish valence states of certain elements and may give valuable information with regard to co-ordination. Iron is the most suitable element for study by the Mössbauer technique.

Resonant absorption of electromagnetic radiation is the prerequisite of the majority of spectrographic studies and when an atom or molecule emits or absorbs an electromagnetic wave it recoils. Hence for resonant absorption to occur between identical systems the electromagnetic wave involved must have an energy equal to the sum of the transition energy and the two recoil energies. The magnitude of recoil is determined by the transition energy. Vibrational transitions in the infra red region of the electromagnetic spectrum are of low energy and the effect of recoil is almost completely overcome by Doppler broadening as demonstrated in Fig. 5.1. In direct contrast gamma ray transitions are very energetic and resonant absorption does not readily occur. The recoil of both the emitting and absorbing nuclei is large compared to the Doppler broadening effects and the amount of resonant overlap is extremely small. Fig. 5.1. It is possible, however, to bring the system into resonance by adding a closing velocity to the absorber and emitter to eliminate the effect of the recoil energies. The

Low energy transitions (eg Infrared)



High energy transitions (eg Gamma ray)



E_r=Energy of recoil
E_d=Average Döppler energy
E_γ=Average energy of emitted γ-ray
E_t=Energy of transition

Diagram demonstrating energy profile overlaps for transitions with recoil.

Fig 5.1

velocity required to produce complete overlap of the source and absorber energy profiles is about 200 m/s. To achieve these values presents considerable practical difficulties. However, by considering in detail the possible ways in which an atom may recoil when bound within a structure the subtle technique of Mössbauer spectroscopy comes to light.

When an atom is bound in a structure there are three ways in which its recoil energy may act. The atom may be ejected from the structure, the energy may be passed to the crystal as a whole or to a lattice vibrational mode. The recoil energy for an atom with mass number A = 100 is about 10^{-2}e V whereas chemical binding energies are of the order of 1 - 10eV. In general, therefore, the recoil energy is not sufficient to eject the atom from the structure. If the recoil energy is transferred to the crystal as a whole, which by comparison with the emitting or absorbing atom has a very large mass, then the process, first recognised by Mössbauer, may be regarded as recoilless.

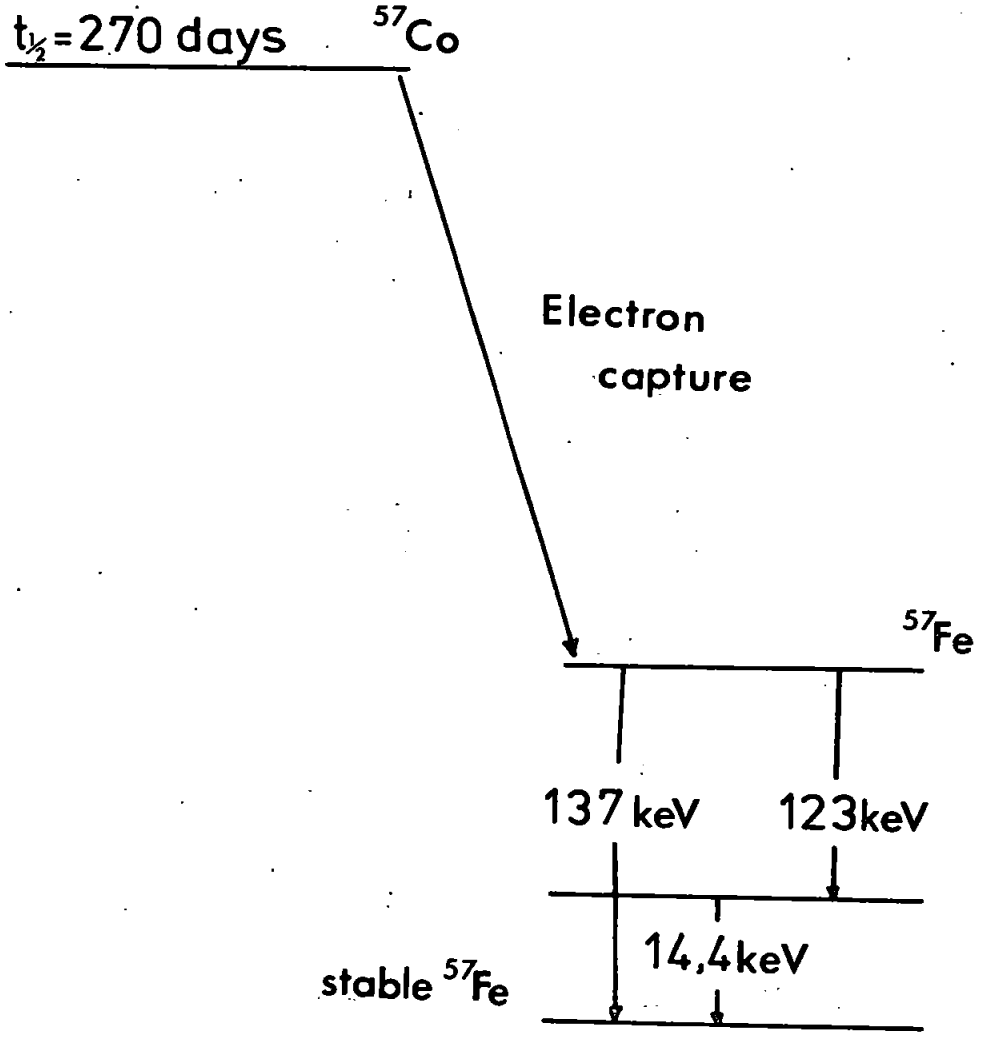
As mentioned above the recoil energy may be passed to a lattice vibrational mode. In the Einstein model for a solid the modes are quantized in multiples of $h\omega$. If therefore the recoil energy is not a multiple of $h\omega$ it will be transferred to the crystal as a whole and the emission and absorption can be recoilless. In the Debye model for a solid the lattice vibrations are allowed a continuous energy distribution but the lower energy modes are difficult to excite. Hence, a fraction of

photons will be emitted and absorbed without recoil. The number involved is termed the recoil free fraction and is usually denoted by the letter f. Mössbauer showed that for some low energy γ-ray transitions the recoil energy and natural Doppler energy become negligible so that emitter and absorber energy profiles completely overlap and linewidths approaching the Weisenberg natural width can be observed.

5.2 Mössbauer Spectroscopy.

The majority of Mössbauer work has utilized iron - 57 as the absorbing species. The resonant γ-ray is produced from the decay of Cobalt - 57 which is illustrated in Fig. 5.2. Because of its low energy the 14.4 keV transition is the transition most commonly observed in Mössbauer spectroscopy.

If the Co^{57} and Fe^{57} nuclei, in source and absorber respectively, have identical chemical environments resonance will be observed for all recoil free transitions. However, in general the nuclear energy levels are perturbed by different chemical environments and resonance does not occur. It is possible however by vibrating the source of γ-rays to modulate the γ-ray energy and hence 'compensate' for the different environments. As the environment of the nucleus determines the relative velocity at which resonance occurs a Mössbauer spectrum is usually presented as a plot of gamma ray transmission against velocity of source.



The decay of ^{57}Co to ^{57}Fe

Fig 5.2

5.2.1 Chemical or Isomer Shift.

The electric field associated with the s-electron density at the nucleus perturbs the nuclear energy levels. Because of shielding effects the extent of perturbation depends not only on the s-electrons but also on the outer electronic shells and the valence electrons. The net result of these effects is a shift in the nuclear energy levels which depends on the chemical environment of the nucleus. The amount of shift relative to a predefined standard is measurable and is termed the chemical or Isomer shift.

5.2.2 Quadrapole Splitting.

Nuclei with spin quantum number $I > \frac{1}{2}$ have a non-spherically symmetric charge distribution and hence possess an electric quadrapole moment given by

$$e\phi = \int \rho r^2 (3\cos^2\theta - 1)\, d\tau$$

where e = charge on proton

ρ = charge density in volume d

r = distance from nucleus centre of charge element

θ = angle r makes with spin quantization axis.

When such a nucleus is in a crystal structure an electric field gradient, caused by the surrounding atoms, can cause a splitting of degenerate nuclear levels and hence produce fine structure in the Mössbauer spectrum. This interaction is known as quadrapole splitting of the nuclear energy levels.

As the quadrapole splitting (Δ) is determined by the electric field across the nucleus the effect can provide valuable information regarding the nature of the co-ordination of the atom.

For nuclei with integral nuclear spins ($I > 1$) quadrapole interaction removes the spin degeneracy of the nuclear levels to produce 21 + 1 levels. This spin degeneracy may also be removed by the application of an external magnetic field but to obtain reasonable splittings, fields of the order of 5 Tesla are required.

Spectra recorded for this work were obtained using a Mössbauer unit constructed within the department of Mathematical Science at Plymouth Polytechnic. The Co^{57} in Pd source was vibrated in the constant acceleration mode and spectra collected by a 400 channel analyser in the multiscalar mode. The drive frequency was derived from a quartz crystal in the multi-channel analyser and was about 25 HZ. The stability of the system was periodically checked using iron foil and over a period of a year the reproducibility has been of the order of 0.3% even though the velocity range has been altered. All isomer shifts are quoted relative to iron foil and all spectra were recorded at room temperature.

The samples were powdered and mounted in plastic trays between sheets of sellotape. The sample thickness was about 1mm. For enriched Fe^{57} samples the sample thickness was reduced to prevent line broadening by saturation effects.

5.3 Mössbauer effect in natural kaolinite.

Naturally occurring Fe^{57} is approximately 2% abundant. Most natural kaolinites which are commercially exploited contain less than 1% total iron and hence less than 0.02% Fe^{57}. Due to the low concentration of Fe^{57} in natural kaolinites the signal to noise ratio is low and the counting statistics required to produce a spectrum are somewhat unreliable. Also natural kaolinites are often contaminated with other iron bearing minerals such as micas which themselves may contribute to and complicate the final spectra. In an attempt to overcome the difficulties introduced by additional mineralogical impurities Meads[3] magnetically refined two natural kaolinites for Mössbauer studies after which no detectable crystalline impurities were present. The kaolinites were then acid washed and were still found to contain 0.5 and 0.8% iron providing evidence for the presence of substituted iron. Mössbauer studies of the refined samples show that most of the iron was substituted as Fe^{3+} and by comparison with results from gibbsite it was suggested that Fe^{3+} was in six-fold co-ordination. Although the values quoted for the isomer shift and quadrapole splitting resembled closely those obtained by other workers for $FeOOH$[1] and Fe_2O_3[4] Meads[3] discounted their presence suggesting that they should be easily removed by the acid treatment. Spin concentration calculations described in Chapter 3 suggest that only a small percentage of the total iron is in a paramagnetic form. Also the recent work by Herbillon[5] would suggest that some non-paramagnetic iron may be

harder to remove by acid treatment than previously expected. Meads[3] also suggested that some iron may be substituted as Fe^{2+} but poor statistics prevented any definite conclusions.

At this stage in the work reported here the methods of synthesising and doping kaolinites with Fe^{3+} had been well established and provided the ideal opportunity to produce a synthetic kaolinite doped with enriched iron 57. Consideration of the counting statistics shows the advantages of Fe^{57} enriched samples not only in improving the resolution and sensitivity of the system but in reducing the time for which samples have to be run. However, for a number of reasons the methods described previously for synthesising doped kaolinite had to be modified considerably. The final results obtained were most significant and in order to appreciate the importance of each step in the work a detailed description is now presented in chronological order.

5.4 Preparation of Fe^{57} doped kaolinite.

The iron - 57 isotope is extremely expensive (about £3,000 per gram) and therefore it was desirable that any method of synthesising the kaolinite should have been previously shown to be successful and repeatable. On a cost basis only 10mg of ^{57}Fe could be made available for the experiment and it was necessary to scale down the methods described in previous chapters on the doping of synthetic kaolinites.

Previous experiments had demonstrated the advantages of using ferric benzoate to produce E.S.R. signals at g=4.0. The benzoate was prepared from commercially available ferric chloride or ferric nitrate. Enriched iron 57 is supplied in metallic form and it was therefore necessary to prepare one of the two appropriate salts from 10mg of metallic iron in order to prepare the benzoate. Initially, experiments to show that scaling down was possible were made with normal unenriched iron. Dissolution of iron in nitric acid can be difficult because the iron tends to become passive. It was therefore decided to prepare the chloride by dissolution of the iron in concentrated hydrochloric acid and then to prepare the benzoate by the addition of ammonium benzoate. The exact method was as follows.

10mg of iron metal were dissolved in 0.4cc of concentrated hydrochloric acid by heating over a water bath. When completely dissolved a solution of sodium acetate in water (1.36 gm/cc) was added until the pH reached about five. A solution of ammonium benzoate in water (0.06 gm/cc) was then added slowly until precipitation of ferric benzoate was complete. The brown precipitate was filtered off in a small sintered Gooch crucible (porosity 4) rinsed with sodium acetate and thoroughly washed with distilled water. The ferric benzoate was then dried at 50°C. At all stages prior to the precipitation of the ferric benzoate the solutions

were tested for the presence of ferric and ferrous ions with potassium ferrocyanide and potassium ferricyanide. Both types of iron were found to be present. It was anticipated that subsequent firing of the gel to remove organic matter would oxidise all the ferrous ions to the ferric state.

The dry ferric benzoate was dissolved in 1 cc of D.M.F. The solution was then added to 5 cc of liquid A and shaken thoroughly before being hydrolised in excess water for one week. The resulting gel was dried at 105°C and fired at 1,000°C for 48 hours to remove any organic matter. Finally the gel was hydrothermally reacted as described in Chapter 2 to produce an iron doped synthetic kaolinite. The development of this method was refined to the extent whereby reproducibility could be guaranteed within the limits of experimental error and it was possible to produce a well crystalline kaolinite exhibiting a well resolved signal at $g=4$.

After a considerable amount of practice with natural iron results were obtained which justified the transfer of the method to the enriched iron 57. An iron - 57 doped clay was produced by the method described and X-ray diffraction and E.S.R. measurements showed the resulting kaolinite to be well crystalline with a crystallinity index of 0.8 and to exhibit a well resolved $g=4$ signal with an E.S.R. lineshape parameter of 0.9. However the signal at $g=4$ was noticeably less intense than in samples

which had been grown using commercially available ferric chloride.

Experimental results.

In marked contrast to previous experiments using normal iron the iron - 57 doped clay when subjected to the Mössbauer apparatus produced intense signals within one hour. However, the numerical values of 1.14 mm/s and 2.53 mm/s for the isomer shift and quadrapole splitting respectively indicated most surprisingly that the majority of the iron was in the form of Fe^{2+} and not Fe^{3+} as expected. (Fig.5.3)

At this stage of the work the results seemed rather contradictory and an immediate explanation was not forthcoming. However, assuming the results to be indisputable an extremely fascinating situation now presented itself. Previously it had been suspected that the synthesis of a clay doped with Fe^{2+} would be very difficult because each stage of the synthesis would tend to oxidize the iron to the ferric state. Having now, for reasons which were not clear, produced a kaolinite which from the Mössbauer evidence, and contrary to the expected results, contained Fe^{2+} it was possible to test the hypothesis that Fe^{2+} should conceivably produce the same effects as Mg^{2+} and stabilise the defect described in Chapter 4 and produce an E.S.R. signal at g=2.0 identical to those observed in natural samples. Accordingly the Fe^{57} doped sample was irradiated

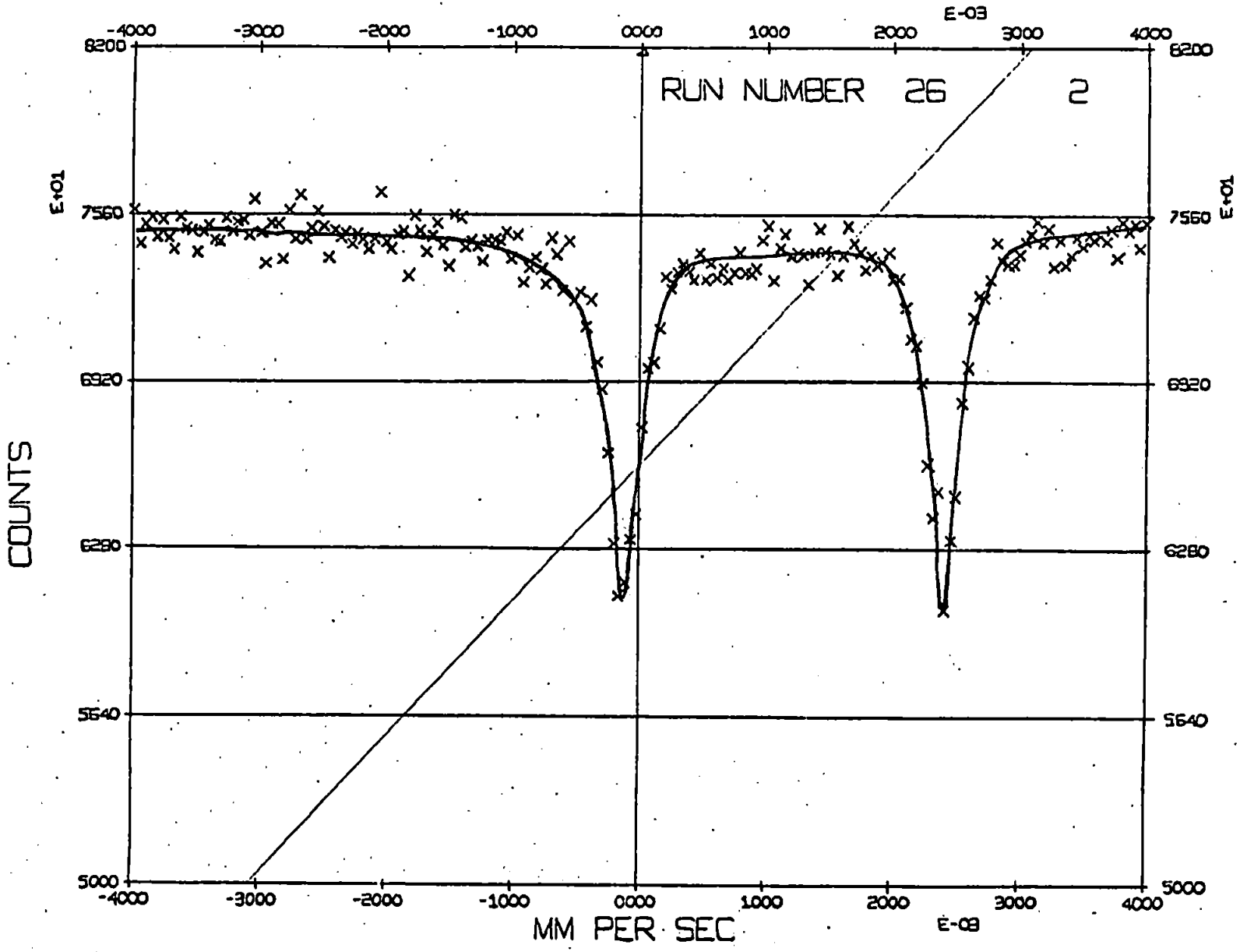

RUN NUMBER 26 2
E-03
-4000
-3000
-2000
-1000
0000
1000
2000
3000
4000
8200
7560
6920
6280
5640
5000
E+01
COUNTS
MM PER SEC
E-03

Fig 5.3

(40 kV, 20 mA, for 4 hours) and then annealed for 2 hours at 200°C. An identical g=2 spectrum was produced in the E.S.R. spectrum as had been produced by the magnesium doped samples there being no measurable difference in g - values. It was also noticed that the isotropic line at g=4 had increased in intensity indicating that some of the Fe^{2+} had been oxidized to Fe^{3+} during irradiation.

These results are very significant. They show unexpectedly that it is possible to interpret both the g=4 and g=2 signals solely in terms of iron impurities. Although the experiments just described had produced some very interesting and significant results the main original aim of the exercise had not been achieved and the reason for iron substituting preferentially as Fe^{2+} and not Fe^{3+} was not clear. Further investigations were made to clarify the situation.

In the initial stages of preparation of the ferric benzoate ferrous ions were formed by the dissolution of iron in hydrochloric acid. It was thought that these Fe^{2+} ions had not oxidized as expected in the subsequent synthesis and hence produced an Fe^{2+} doped clay. Fortunately, part of the Fe^{57} doped gel had been retained and it was contemplated that if the gel contained an abundance of Fe^{2+} ions it should be possible to oxidize them by heating the gel in oxygen. The gel had already been heated to 1,000°C for 48 hours in air. A simple

tube furnace was constructed and a portion of the remaining gel placed in an alumina boat and heated for approximately 2 hours at 1400°C with a continuous stream of oxygen passing through the furnace. This rather rigorous treatment seemed to have no effect on the substituted iron. When the gel was hydrothermally reacted the kaolinite exhibited E.S.R. and Mössbauer spectrums almost identical to those obtained from the previous sample. It was clear that the sample still contained mainly Fe^{2+} ions.

Discussions with a number of experts in the field of mineral synthesis, all of whom expressed some consternation with regard to the fact that the iron had not been oxidized under such extreme conditions, led to the conclusion that the Fe^{2+} must be very closely associated or bound within the gel. An alternative to explain the high concentration of Fe^{2+} in the kaolinite is to suggest that the iron may in fact be in a 3^{+} state in the gel but on hydrothermal reaction is reduced in some way. The ideal structure of kaolinite contains dioctahedral aluminium, that is Al^{3+} occupying two out of every three octahedral sites and the charge is maintained if there are six positive charge to every three sites. Purely from the point of view of charge balance it may be possible for Fe^{2+} ions to substitute trioctahedrally in the structure. If charge balance is not required any combination of Fe^{2+}, Fe^{3+} and Al^{3+} may occupy the sites either trioctahedrally or dioctahedrally.

In order to eliminate the existence of Fe^{2+} ions in the gel a number of different methods of preparation were tried.

Tests for ferric and ferrous ions after the dissolution of iron in hydrochloric acid both proved positive and it was considered that failure of the ferrous ions to oxidize in the subsequent synthesis was the reason for the ferrous ion in the synthetic kaolinite. It was therefore necessary to oxidize the solution of the iron in acid to ensure all the iron was in the ferric state. Although hydrogen peroxide or nitric acid proved successful oxidizing agents, the most convenient method of ensuring complete oxidation was to dissolve the iron in Aqua Rega. Solutions prepared in this way gave negative results when tested for Fe^{2+} ions with potassium ferricyanide.

A gel was therefore prepared by dissolving 10mg of iron in 0.4cc of Aqua Rega. The pH of the solution was then raised to about five by the addition of sodium acetate. Ammonium benzoate was then added to precipitate the ferric benzoate and the method continued as before. The clay formed from this gel however still produced a g=2 signal after irradiation and annealing and indeed the Mössbauer spectrum revealed that the majority of the iron was substituted in the Fe^{2+} form. There seemed now to be a direct conflict with previous results. Originally synthetic kaolinites had been doped with iron by preparing ferric benzoate from commercially available ferric chloride

or ferric nitrate. The two kaolinites produced Mössbauer spectra which indicated the majority of the iron was in the 3+ state. However synthetic kaolinites prepared from gels which were doped by dissolving iron in Aqua Rega in the laboratory and then making the ferric benzoate contained a majority of substituted Fe^{2+}. The only difference in the two methods of preparation, which could be identified to account for the anomoly, was that in the latter the ferric salt solution was prepared from the metal and not directly from a commercially available ferric salt. However, in both cases tests for Fe^{2+} ions prior to the precipitation of the ferric benzoate were negative.

A possible explanation for the apparent anomolies in the results described above might be provided by considering the chemical properties of aluminium iso-propoxide can act as a reducing agent[6] particularly if catalysed by the presence of small amounts of mineral acids. It therefore seemed possible that reduction of the iron might have occurred when preparing the ferric benzoate by either method, but in the case where the iron had been dissolved in acid small traces of the acid remained which were in sufficient quantity to catalyse the reduction reaction. Consequently when the solution of ferric benzoate in di-methyl-formamide was added to the liquid A the aluminium iso-propoxide reduced the iron. In an attempt to combat the possible reducing effect of the aluminium iso-propoxide a gel was prepared by hydrolising the mixture, of ferric benzoate in di-methyl-formamide and liquid A, in ammonia

and H_2O_2. It was hoped that the ammonia would neutralise any acids and that the hydrogen peroxide would oxidize the aluminium iso-propoxide. Unfortunately the clay produced by subsequent hydrothermal reaction of this gel, produced a poorly crystalline kaolinite. Mössbauer results also showed most of the iron remained in the Fe^{2+}state. It is possible that this method failed to produce Fe^{3+} because the iron had already been reduced by the aluminium iso-propoxide and that upon hydrolising the hydrogen peroxide was not effective in oxidizing the iron before the gel was formed. Previous attempts to oxidize the iron in the gel had demonstrated the apparent stability of Fe^{2+} in the gel.

Having not established beyond doubt that small traces of mineral acid might be responsible for the production of Fe^{2+} an alternative method of preparation of the ferric salt was attempted by the direct chlorination of the iron. Ferric chloride was produced by direct chlorination of 10mg of iron in a glass tube heated to about 300°C. The ferric chloride was then dissolved in a small quantity of distilled water and ammonium benzoate added to precipitate the ferric benzoate. The clay was then prepared as described previously. Again the clay produced still contained some iron in the 2+ state though Mössbauer results suggested a large reduction in the Fe^{2+}/Fe^{3+} ratio (Fig. 5.4.) The reason for the failure of this method to produce only substituted Fe^{3+} is not clear. It may well be that some chlorine gas was held in the ferric chloride which following dissolution in water formed hydrochloric

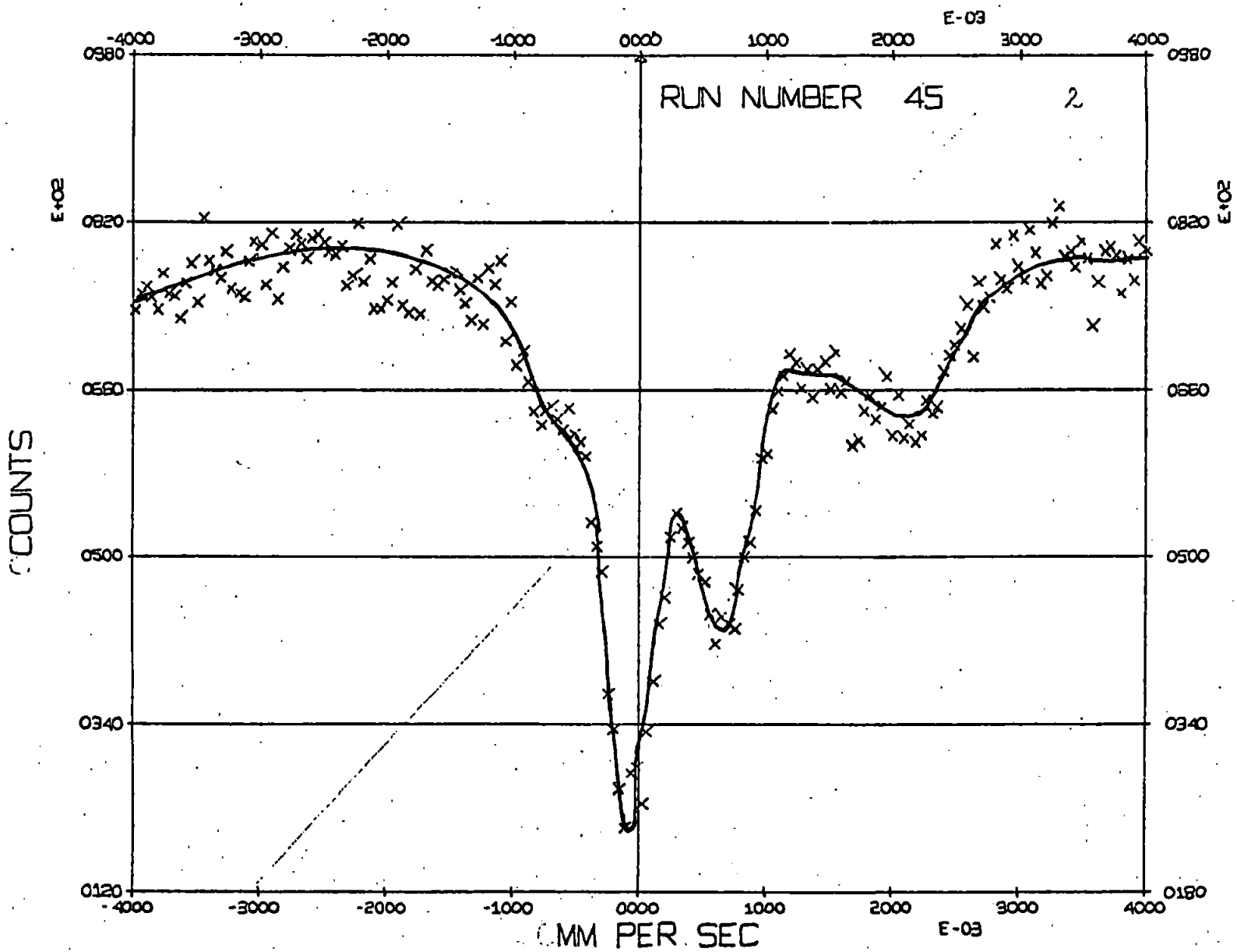

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Fig 5.4

acid which in turn later catalised the reducing effect of the aluminium iso-propoxide.

It is known that in the process of oxidizing organic matter any carbon found may act as a reducing agent.

It was considered that this effect may have been responsible for the reduction of the iron from Fe^{3+} to Fe^{2+} when the gel was fired at 1,000°C. However, if this were so it would not explain why the effect was only detectable in these samples where the ferric benzoate was prepared from the metal as opposed to those which were prepared from commercial ferric nitrate.

In further attempts to reduce the Fe^{2+}/Fe^{3+} ratio in samples doped with ferric benzoate prepared from iron metal, the organic contaminants were removed as far as possible by rotary evaporation under vacuum instead of firing the gel at 1,000°C thereby preventing the formation of carbon and possible reduction of the iron. Unfortunately the kaolinite produced on subsequent hydrothermal reaction contained mostly ferrous ions.

Due to the low concentration of Fe^{57} in synthetic samples doped with natural iron Mössbauer studies had been limited to those doped with concentration greater than 1.5% iron, whereas the doping level in iron - 57 doped samples had been reduced to about 0.4%. It was considered therefore that the difference in iron concentration might possibly account for the different

iron states being present in samples produced by doping with ferric benzoate prepared from metallic iron and from the metal salt. To test this theory a synthetic kaolinite was doped with 2.4% iron by dissolving the appropriate amount of iron metal in Aqua Rega and proceeding as before. The kaolinite gave encouraging results exhibiting an Fe^{3+} doublet in its Mössbauer spectrum. The E.S.R. spectrum contained a well resolved $g=4$ signal and a large broad resonance. It was suspected that a proportion of the iron on the surface of the kaolinite was probably responsible for the broad resonance. It now seemed plausible to suggest that the reason for the difficulties previously encountered in producing an Fe^{3+} doped kaolinite with ferric benzoate prepared from metallic iron were due to the low concentration of iron used in previous methods.

In an attempt to clarify the situation a number of synthetic kaolinites were doped with various amounts of iron by preparing ferric benzoate from commercial ferric nitrate. The resulting kaolinites were subjected to X-ray diffraction, E.S.R. and Mössbauer studies. The results tabulated in Fig. 5.5 are rather disappointing. All the clays were produced under identical conditions yet there is a large variation in the Fe^{2+}/Fe^{3+} ratios. Furthermore no correlation seems to exist between the Fe^{2+}/Fe^{3+} ratio and iron concentration. No reason for the variation in the Fe^{2+}/Fe^{3+} ratio could be found.

SAMPLE No.	Crystallinity Index	E.S.R. Lineshape Parameter	% Total Iron	$\frac{Fe^{2+}}{Fe^{3+}}$
KG 100	0·9	1·6	1·9	< 0·1
KG 99	0·9	0·8	1·7	> 0·9
KG 98	0·8	0·3	1·4	~ 0·5
KG 83	0·4	0·3	0·6	< 0·1

Fig 5.5

Two synthetic iron - 57 doped kaolinites had been produced one of which contained a majority of Fe^{2+} and the other Fe^{3+}. It was decided to study the Mössbauer properties of these samples in more detail.

5.5 A Mössbauer study of Fe^{2+} in kaolinite.

To the author's knowledge no definite account has been made of the existence of Fe^{2+} substitution in kaolinite. Meads[3] studied a natural kaolinite by Mössbauer spectroscopy and suggested the possibility of Fe^{2+} substitution. However because of the low Fe^{2+} concentration and the presence of mica which is known to exhibit an Fe^{2+} doublet only an approximate value of the quadrapole splitting was obtained which was quoted as approximately 2.25 mm/s. Jefferson[7] et al observed Fe^{2+} signals in some iron stained kaolinites but these were found to be partially removed by acid washing and are therefore attributable to surface iron.

The Mossbauer spectrum of an iron - 57 doped synthetic kaolinite containing mostly Fe^{2+} was shown in Fig. 5.3. A computer fit of the spectrum gave a single doublet with an isomer shift of 1.14 mm/s and a quadrapole splitting of 2.53 mm/s. On heating the sample to 400°C for 1 hour it was found that the single Fe^{2+} doublet split to give two doublets with quadrapole splittings of 2.53 mm/s and 1.94 mm/s. Fig. 5.6.

The ratio of the intensities of the two doublets being about 2: 1, the original 2.53 mm/s doublet remaining the more intense. Further heating to 700°C changed the

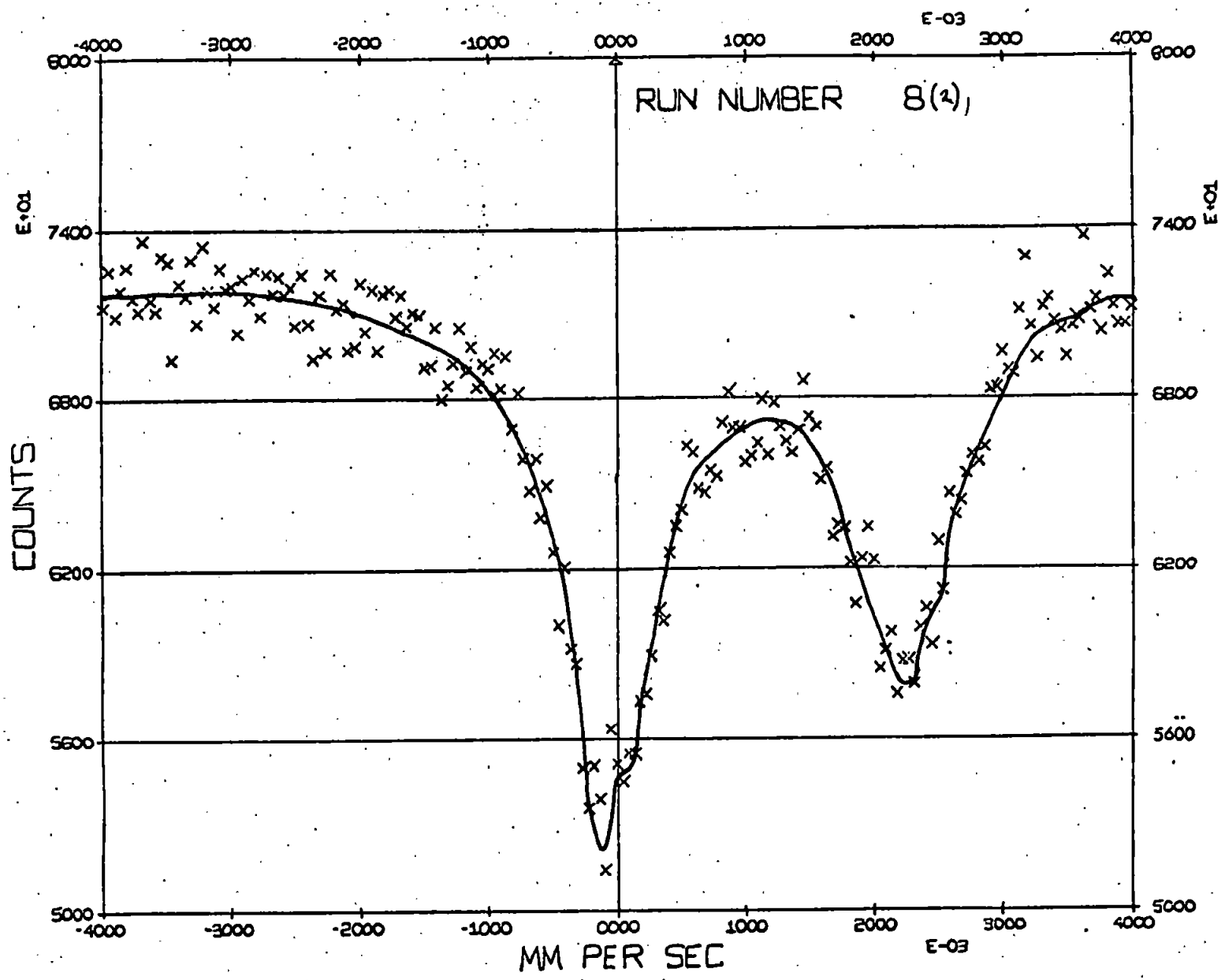
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Fig 5.6

spectrum little though an increase in the Fe^{3+} signal was observed. Washing of the kaolinite with ammonium oxalate did not affect the spectrum so it was assumed the Fe^{2+} was substituted in the kaolinite structure. It is most probable that Fe^{2+} would substitute trioctahedrally to maintain charge balance.

The characteristics of the two Fe^{2+} doublets are very similar to previously quoted values for some trioctahedral biotites.[8] In such samples the octahedral layer consists of both cis and trans sites as opposed to only cis sites in kaolinite. It is generally agreed[8] that the larger outer doublet be assigned to cis sites and the inner to a trans site. In kaolinite the conversion of $\frac{1}{3}$ of the sites from cis to trans on heating to produce the 2: 1 ratio would require the conversion of particular outer hydroxyls groups to oxygen ions. This is demonstrated in Fig. 5.7. A similar effect is known to occur in chamosites.[9]

The average value of the two quadrapole splitting for Fe^{2+} in the synthetic kaolinite after heating is 2.23 mm/s which is very close to the value suggested for Fe^{2+} in natural samples by Meads.[3] This suggests that in natural samples the cis and trans sites may be present before heating and because of poor concentrations of Fe^{2+} previous workers were unable to resolve the two doublets. It is surprising perhaps that the two doublets remain after heating to 700°C for 1 hour, that is after dehydroxylation, as removal of all hydroxyl groups would give three identical

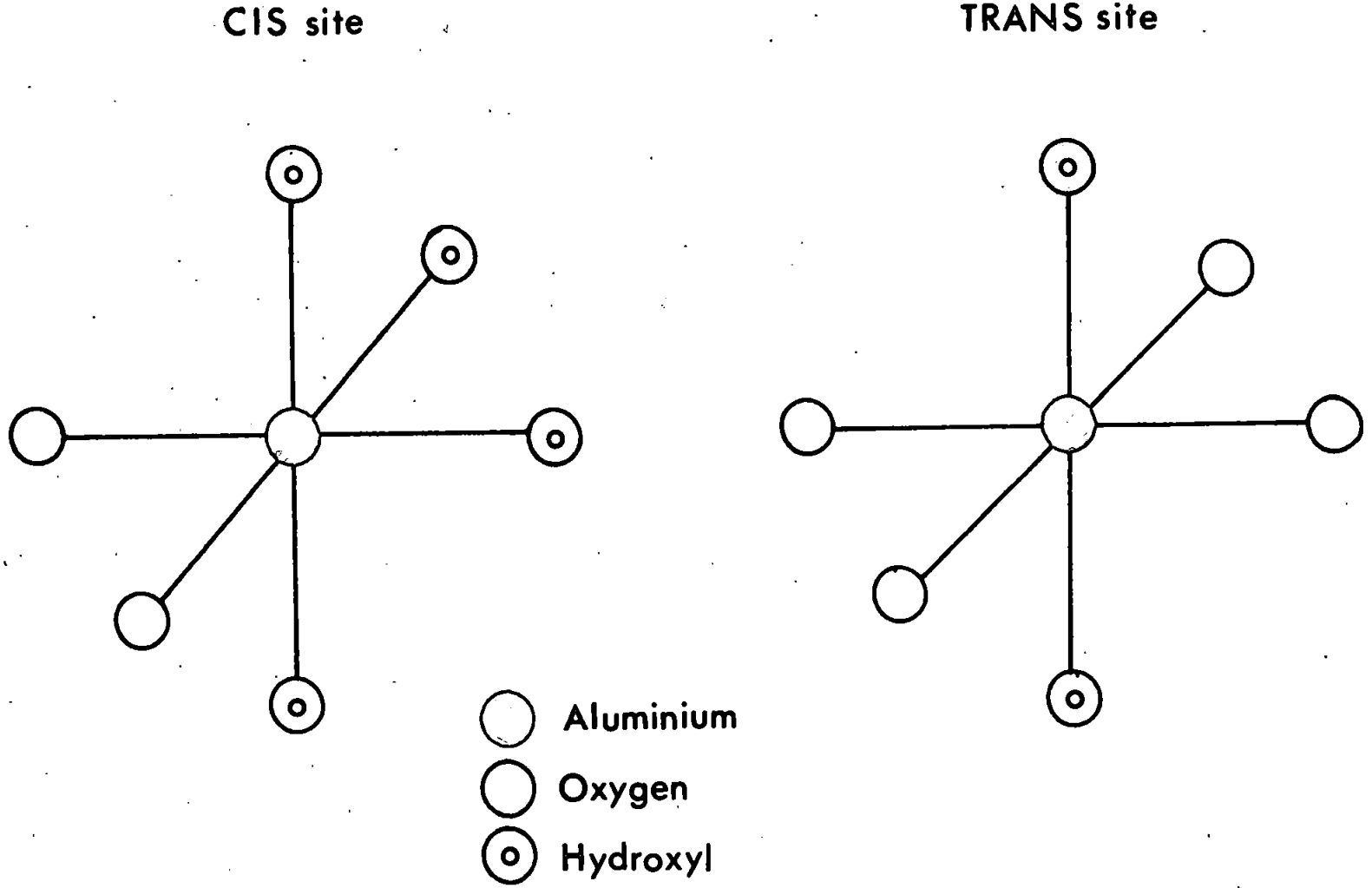

Fig 5.7

tetrahedral sites as in metakaolin. A possible explanation for this anomoly is that the presence of trioctahedral Fe^{2+} may resist the removal of certain hydroxyls.

It may also be possible for the inner doublet created by heating to be caused by Fe^{3+} in an extremely distorted tetrahedral site. However this seems unlikely firstly because of the extreme distortion necessary to produce such a large quadrapole splitting and secondly the conversion of octahedral to tetrahedral sites suggest that dehydroxylation has occurred. It seems unlikely that one third of the sites would be converted at 400°C and no more at 700°C.

5.6 A Mössbauer study of Fe^{3+} associated with kaolinite.

It is likely that Fe^{3+} may exist as a contaminant in natural kaolinites in three main forms. As a ferromagnetic oxide or hydroxide on the surface, as a super-paramagnetic oxide or hydroxide on the surface, or as a substituted paramagnetic ion. Ferromagnetic samples exhibit six line Mössbauer spectrums and as such are easily discernable. However complications arise when trying to distinguish between super-paramagnetic doublets due to small particle size iron oxides or hydroxides and paramagnetic doublets due to substitutional iron. Super-paramagnetic states may be caused by very small particle size. The spin relaxation time decreases with decreasing particle size and may prevent spin-spin coupling in an otherwise ferromagnetic system. Such systems are best studied at low temperatures. By reducing the temperature sufficiently

spin relaxation is slowed so as to allow spin-spin coupling and a six-line spectrum is observed.

Previous reports[3.7.8] on Mössbauer studies of substitutional Fe^{3+} in kaolinite have all quoted values for quadrapole splittings between 0.45 and 0.55 mm/s and isomer shifts of 0.375 mm/s. Fig. 5.4 shows a Mössbauer spectrum of a synthetic kaolinite doped with iron - 57 mainly in the ferric state. The best fit for a single Fe^{3+} doublet gives a quadrapole splitting of 0.7 mm/s and an isomer shift of 0.32 mm/s. The Fe^{3+} doped clay was washed with ammonium oxalate but no change in the spectrum was observed. Several synthetic clays doped with natural iron were also subjected to Mössbauer spectroscopy and although statistics were poor all exhibited a quadrapole splitting of 0.7 mm/s. These were also unaffected by ammonium oxalate treatment. No change in the spectra was observed on heating samples to 400°C.

A natural kaolinite high in iron was also investigated and found to exhibit a ferric doublet of splitting 0.5 mm/s. Treatment of this sample with ammonium oxalate increased the splitting to 0.6 mm/s.

A number of oxides and hydroxides of iron have quadrapole splittings similar to those reported for kaolinite. These are listed in Fig. 5.8. It was reported in Chapter 3 that many conflicting reports about the effectiveness of treatments for the removal of iron made it very unclear as to what types of iron such treatments

Oxide or Hydroxide	Quadrapole Splitting mm/s
α - Fe_2O_3	0·44 → 0·68[4]
α - FeOOH	0·6[1]
β - FeOOH	0·62[10], 0·7[11]
γ - FeOOH	0·55[1]

Fig 5.8

will remove. In this work it was found that in samples exhibiting a six-line spectrum that this was usually easily removed and hence attributed to ferromagnetic surface oxides or hydroxides. The splittings of these magnetic spectra suggested the presence of α Fe_2O_3 and Fe_3O_4.

In direct contrast it appeared that ammonium oxalate treatment had no affect on the 0.7 mm/s doublet in synthetic samples. Furthermore, the increase in quadrapole splitting reported above for the natural sample could be interpreted as the preferential removal of a 0.5 mm/s doublet leaving behind a 0.7 mm/s doublet. Indeed the Fe^{3+} signals were broad and suggested the presence of more than one site.

Reports by Jefferson[7] and Herbillon[5] both suggest that some surface iron may be very difficult to remove. It is possible that some doublets reported as being due to substitutional iron may in fact be due to surface iron which is unaffected by washing. Jefferson[7] cleaned the surface iron with extensive acid treatment and reported that in two samples some iron could not be removed. The values quoted for the quadrapole splittings of these samples was 0.52 and 0.55 mm/s. The sample was investigated at a temperature of 88°K and found not to exhibit a six-line spectrum. These results provided further evidence for substituted as opposed to surface iron. However the values quoted by Jefferson[7] are indicative of α Fe.OOH and much lower temperatures may be needed before this

hydroxide becomes ferromagnetic.[1]

In an attempt to reproduce Fe OOH and Fe_2O_3 on the surface of a natural kaolinite an undoped synthetic clay was soaked in ferric nitrate. Ferric hydroxide was precipitated on the clay surface by the addition of sodium hydroxide and drying at 105°C. Ferric oxide was precipitated on the surface by drying the clay in the nitrate solution at 105°C and then heating to 450°C. The Mössbauer spectrums of both these samples were very similar to that of synthetic kaolinites having a quadrapole splitting of 0.69 mm/s and an isomer shift of 0.37 mm/s. These values are indicative of β Fe OOH. Treatment with ammonium oxalate completely removed the iron on the surface of the undoped clay which casts doubt on the assignment of the 0.7 mm/s doublet exhibited by iron doped synthetics, to surface β Fe OOH as this was not removed by such treatment. No explanation of the larger ferric doublet in synthetic kaolinites as compared to natural samples has yet come to light. So far the only explanation is that previous reports were in error having not sufficiently cleaned the surface and that the 0.5 mm/s doublet is attributable to surface iron and the 0.7 mm/s doublet to substitutional iron.

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CHAPTER 6

6.1 Final summary

Although kaolinite occurs in nature as a relatively pure mineral it is clear that impurities, especially iron, have a pronounced effect with regard to its application in various industrial uses. The impurities complicate studies of natural kaolinite. To avoid unwanted impurities much of the work presented in this thesis is concerned with synthetic kaolinites. The development and use of liquid A as a method for preparing doped synthetic samples has proved extremely convenient. The various parameters affecting the synthesis of kaolinite have been studied and from this work it is evident that the presence of iron and an acid media are most advantageous for the production of synthetic kaolinites with ideal morphology. However it has also been shown that iron has a detrimental effect on the brightness of the kaolinites.

Previous work in this laboratory had shown that the $g=4$ signal in the E.S.R. spectrum of a kaolinite synthesised under neutral conditions could be attributed to Fe^{3+} substitution. In this work samples prepared at low pH did not exhibit a $g=4$ signal and the iron was easily removed by ammonium oxalate treatment. It seems that iron does not readily substitute in the kaolinite structure under low pH but remains as a surface contaminant. It is not clear therefore, how in nature kaolinites occur

with ideal morphology and with substituted iron. For the samples grown in the laboratory it might be argued that iron, being more soluble than alumina or silica in acid media, remains in solution as the kaolinite precipitates. When the clay is dried the iron collects on the surface of the clay.

Jones[1] had previously shown that the g=2 signal in natural kaolinites could be attributed to a hole stabilised by substitution of Mg^{2+} for Al^{3+}. He had suggested that Fe^{2+} as well as Mg^{2+} might replace Al^{3+} but apparently failed to produce an Fe^{2+} doped kaolinite. The work presented here has shown that it is possible to synthesise Fe^{2+} and Fe^{3+} doped kaolinites which therefore permit the interpretation of all the main E.S.R. resonances in kaolinite in terms of iron substitution alone or mixtures of iron and magnesium. Careful examination of the g=2 signals exhibited by samples doped with Mg^{2+} or Fe^{2+} showed no observable difference in their g - values or lineshapes. Hence it was not possible to interpret the g=2 signal observed in natural samples specifically to Fe^{2+} or Mg^{2+} substitution. A method to distinguish between Mg^{2+} and Fe^{2+} substitution in natural samples was studied by observing the variation in the E.S.R. signals in heated natural and synthetic samples doped with Fe^{3+}, Fe^{3+} and Fe^{2+}, Mg^{2+} and Fe^{3+}.

The larger ionic radius of Fe^{2+} compared with Mg^{2+} provided a possible difference which might cause variation

in the ions environment which in turn could possibly be reflected in the observed E.S.R. signals, particularly as dehydroxylation approached. Also it was considered that a defect caused by Fe^{2+} substitution may be less thermally stable than one caused by Mg^{2+} because of the possibility of oxidation from Fe^{2+} to Fe^{3+}. Unfortunately from the study of the heated samples it was not possible to distinguish between g=2 signals created by Fe^{2+} or Mg^{2+} substitution.

Comparison of the intensity of the E.S.R. g=2 signal in an irradiated and annealed Fe^{2+} doped kaolinite with the total Fe^{2+} content estimated from the Mössbauer spectra showed that at least 97% of the ferrous ions had not trapped a hole. Increasing the radiation dose beyond 1 MRad did not change the intensity of the g=2 signal. Even allowing for the possibility of recombination of holes and electrons created by the irradiation it would seem not unreasonable to suggest that a large number of the total Fe^{2+} ions within the structure do not act as 'pre-centres' for trapping holes. The main pre-requisite that a foreign ion should act as a pre-centre is that its valence state should be different from the ion it replaces; in this case Fe^{2+} for Al^{3+}.

A possible explanation of the comparatively high concentrations of Fe^{2+} ions not trapping holes is provided by assuming trioctahedral substitution of Fe^{2+}. Only those ions which substitute dioctahedrally possess the

required charge inbalance and are capable of producing the A centres responsible for the $g=2$ signal.

In addition to the A centres a short study was made of the hyperfine signals around $g=2.0$ (B centres) which are present in natural and synthetic samples. Jones[1] had previously attributed these signals to either aluminium atoms occupying tetrahedral silica sites or an electron in a hydroxyl vacancy. The results presented in Chapter 4 provide evidence which favour the latter assignment.

The results from Mössbauer studies presented in Chapter 5 provide conclusive evidence to show that Fe^{2+} can substitute in the kaolinite structure most probably in a trioctahedral form. It is therefore proposed that Mg^{2+} could also substitute trioctahedrally and therefore not necessarily produce A centres.

Difference in the values of quadrapole splittings of Fe^{2+} in natural and doped synthetic samples have led to the suggestion that the substitution of Fe^{2+} in natural kaolinites involves the removal of some outer hydrogens in the hydroxyl layer producing cells or layers similar in structure to chamosite.

Combined Mössbauer and E.S.R. evidence from doped samples casts considerable doubt on the assignment of the signals by past workers. Also it is shown that the presence of Fe^{2+} in samples may account for further errors in E.S.R. spin density calculations for iron in kaolinite.

The signals associated with Fe^{3+} in the Mössbauer spectra were found to be rather broad and were therefore indicative of more than one site. This may correspond to the two sites as proposed by Hall[2] (α = 0.22 and β = 0.33). It has not been possible to find a satisfactory explanation for the values of quadrapole splittings of Fe^{3+} in synthetic kaolinites which are larger than in natural samples.

6.2 Suggestions for further work.

Vanadium is an impurity in many natural clays but it is not clear in what form it is present or what effects it may have on the properties of kaolinite. There is some evidence that vanadium has an advantageous effect on rheology but this may be due to titanium with which it is usually found. Work is at present being carried out in this laboratory on vanadium in both natural and synthetic kaolinites.

Investigations of super-paramagnetic states in this work were severely hampered by lack of cryogenic facilities for the Mössbauer spectrometer. An extensive survey and study of surface and substituted iron by Mössbauer spectroscopy in natural and synthetic kaolinites at variable temperatures and the effectiveness of surface cleaning techniques will most probably provide results which lead to a clearer understanding of iron impurities in kaolinite.

Due to the combined effects of small particle size and low iron concentration it has not been possible to

identify in detail the optical properties which affect the brightness of kaolinite and the extent to which iron influences the optical properties. In order to establish a new approach to the problem a photon counting system is at present being constructed in this department and an extensive study of the optical properties of various natural and synthetic kaolinites is planned. In this way it is hoped to obtain a clearer understanding of the relative effects the various defects in kaolinite have on its brightness.

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Presented at Symposium for International Correlation Programme - Proceedings to be published.

THE SYNTHESIS, MORPHOLOGY AND GENERAL PROPERTIES OF KAOLINITES SPECIFICALLY DOPED WITH METALLIC IONS AND DEFECTS GENERATED BY IRRADIATION.

Proceedings of International Clay Conference Mexico 1975.

SYNTHETIC KAOLINITES DOPED WITH Fe^{2+} and Fe^{3+} IONS.

To be presented at 25th U.S. Clay Min. Conf. Oregan August 1976.

Proceedings to be published in Clays and Clay Minerals.

A MOSSBAUER STUDY OF SYNTHETIC KAOLINITES DOPED WITH $^{57}Fe^{2+}$.

Draft of paper to be submitted to Clays and Clay Minerals for joint publication with previous paper.

Synthetic Kaolinites - General Comments.

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The main purpose of this paper is to discuss the possible significance of the availability of doped synthetic kaolinites and to present a brief summary of some of the results obtained in this laboratory in recent months. The majority of the results have been treated in detail in papers which have been recently accepted for publication in Clay Minerals.

A broad survey of the methods of production and utilisation of synthetic materials clearly demonstrated the importance of the ability to synthesise pure crystal structures and in particular the advantages of doping materials with controlled impurity concentrations. For many materials the amount of doping which may be as small as 0.01-0.1% impurity concentration can profoundly affect their physical and chemical properties. To quote two specific examples where as a result of successful synthesis and doping, very large industries have evolved which now form very important lifelines in the economy and production in world markets consider semiconductors and synthetic diamonds. Development of the transistor and integrated circuit and their wide application in fields such as communications, medicine, and computers has made a

significant contribution to our cultural and scientific development in recent years. The successful development of synthetic diamond has not produced similar effects but now plays an extremely important role in the engineering industry. By suitable doping and control of the growth conditions it is possible to manipulate the shape and friability of synthetic diamond to produce a wide variety of cutting or grinding machanisms for many different types of hard alloys and ceramics.

In some respects the development since 1959 of the synthesis technique for diamond might easily parallel those which we feel may be possible to explore in future synthesis and doping of kaolinite. It is worth noting for example that the development and subsequent production of synthetic diamond proved to be a very costly process whilst vast reserves of natural material were available. In fact it is probably true to say that political instability in some of the diamond producing regions of the world influenced the investments made for diamond research.

For the successful synthesis of diamond it was found for reasons unknown that the addition of small amounts of transition metal impurity to the graphitic reaction mixture produced a mechanism which allowed the graphite to recrystallise more readily as diamond. Although the results we have obtained so far are not conclusive we suspect that the growth and morphology of kaolinite might possibly be influenced in a similar manner by substituted impurities.

For example consider the electron micrograph 1d of an undoped synthetic kaolinite which compared with that of a natural kaolinite in micrograph 1b shows poor morphology. For reasons unknown it would appear from preliminary studies that synthetic kaolinites with ideal morphology as in micrograph 1c are more likely to be produced when the reaction mixtures are doped with transition metals.

The morphology of kaolinite is very important in determining the rheological behaviour of clay slips. In addition there are a wide variety of physical and chemical properties of kaolinite which are utilised in the production and application of the mineral and which are known to be associated with surface and substituted impurities. For example, the cation exchange capacity of clay minerals which is widely used in the description and classification of clays and controls the defloculation characteristics is influenced to a large extent by surface impurities. In contrast, substituted impurities are known to influence both the optical and magnetic properties of kaolinite. In many samples of kaolinite the whiteness or brightness would appear to be determined in part by impurities but the exact nature of the optical absorption processes are not fully understood. The magnetic susceptibility of clay particles which clearly plays a vital role in the processing of clay minerals by magnetic separation is influenced by the substitution of iron atoms in the lattice.

Numerous publications illustrate the extent to which natural kaolinites have been studied in order to understand more fully their physical and chemical properties. However in general for naturally occurring kaolinites it often proves to be extremely difficult to monitor any possible effects of substituted impurities on cation exchange capacity, optical properties or magnetic susceptibility due to the fact that samples often contain a multiplicity of trace chemical impurities as well as additional mineral species. Consequently, the accurate assignment of a single impurity to a particular physical or chemical characteristic is not possible.

It might be argued that a true synthesis of kaolinite is not recognisable unless a system is manufactured which resembles the natural product in every sense and would therefore contain multiple impurities. Clearly, synthesised systems of this type would not be useful for research purposes.

In our recent work we have synthesised relatively pure kaolinites. In addition we have synthesised kaolinites with known substituted impurities. The impurities we have chosen to investigate are those which substitute in the kaolinite in a paramagnetic form or alternatively can be made paramagnetic by irradiation. The main reason for considering paramagnetic impurities is by virtue of the fact that they are detectable by the technique of Electron Spin Resonance (E.S.R.) E.S.R. is a phenomena with which it is possible to detect very small

concentrations (1 in 10^{12}) of most types of atomic or molecular configurations which contain unpaired electrons and are paramagnetic.

Fig. 2a illustrates a typical E.S.R. spectrum of a natural kaolinite which we discussed in some detail with a possible interpretation at the International Clay Conference in Madrid in 1972. At that time natural samples were the only type available and we tentatively suggested that resonance lines at g=40 were possibly due to the different types of iron substitution in kaolinite in the tetrahedral layer and lines at g=2.0 might be due either to iron in octahedral sites or possibly due to defect centres.

Dehydration of the kaolinite at temperatures up to ~550°C produces very profound effects on the E.S.R. signals (fig. 2b) and in fact very noticeable changes occur in the signals before any change in crystallinity can be detected by X-ray diffraction. It is clear therefore that for the E.S.R. technique valuable information is obtainable provided that the type of impurity responsible for the signals can be identified. It was to this end that our recent work was directed. In Figs. 3a - f and 4a - b the E.S.R. results obtained from synthetic clays doped with known impurities are summarised.

Comparison of the spectra show that it is possible to reproduce the E.S.R. signals of natural kaolinite in suitably doped synthetic kaolinites and thereby draw more

precise conclusions than was previously possible. We have shown from preliminary work that resonance lines at g=4.0 in natural kaolinites can be attributed to Fe^{3+} substitution (c.f. figs 4a and 4c) and lines at g=2.0 can be attributed to a defect centre stabilised by the substitution of Mg^{2+} (c.f. figs 4a and 4f). Detailed discussion of these effects are presented in papers recently accepted for publication in Clay Minerals.

As far as the authors are aware there are no previous reports of synthesis and combined doping of kaolinite. We have made a preliminary study of doped material using only E.S.R. It is felt that the wide variety of techniques now available for the study of clay minerals could be utilised to a greater extent than was previously possible by using doped synthetic kaolinite in order to gain a clearer understanding of the properties of this mineral.

1a

UNDOPED SYNTHETIC
KAOLINITE

1b

NATURAL KAOLINITE

1c

IRON DOPED SYNTHETIC
KAOLINITE

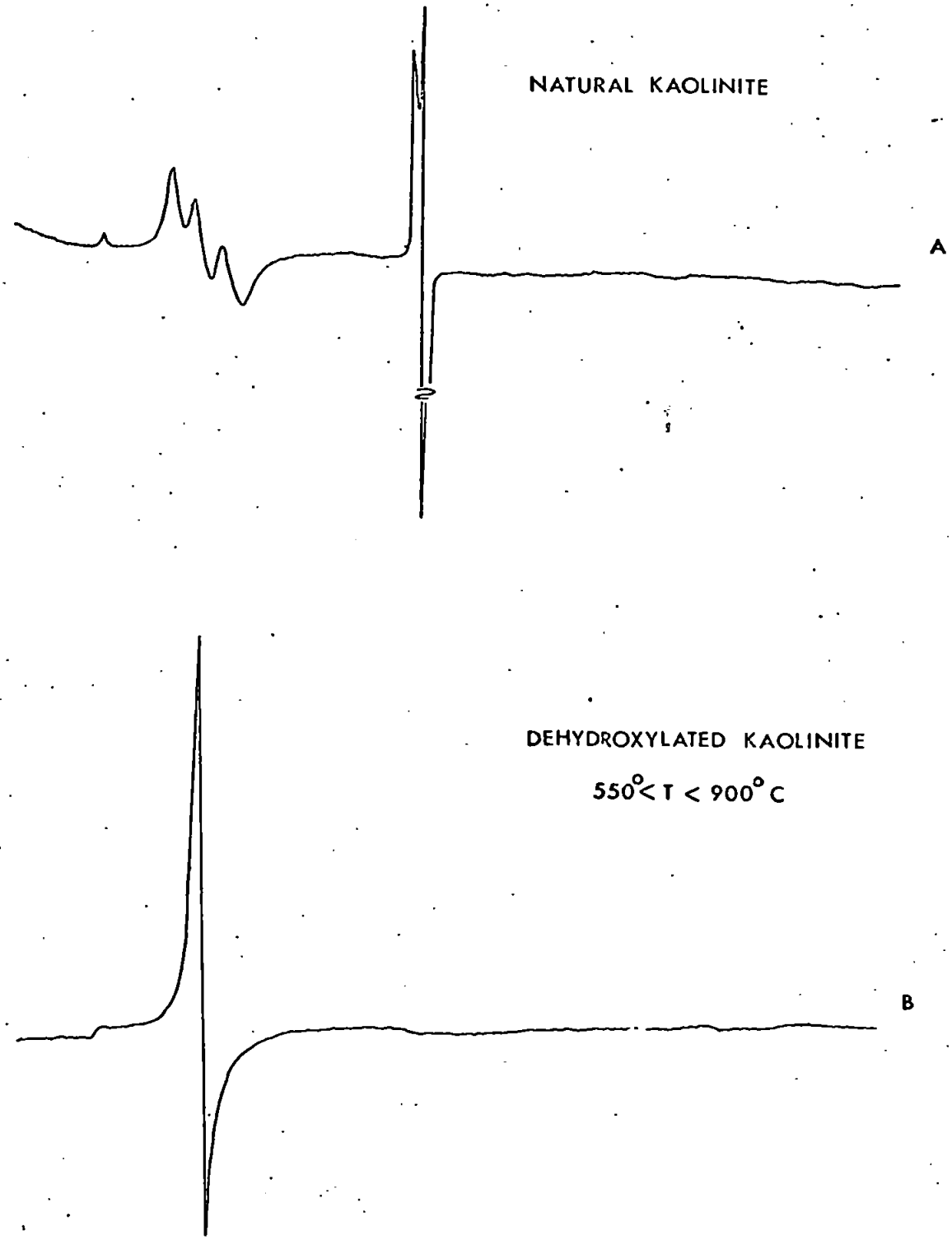

FIG 2

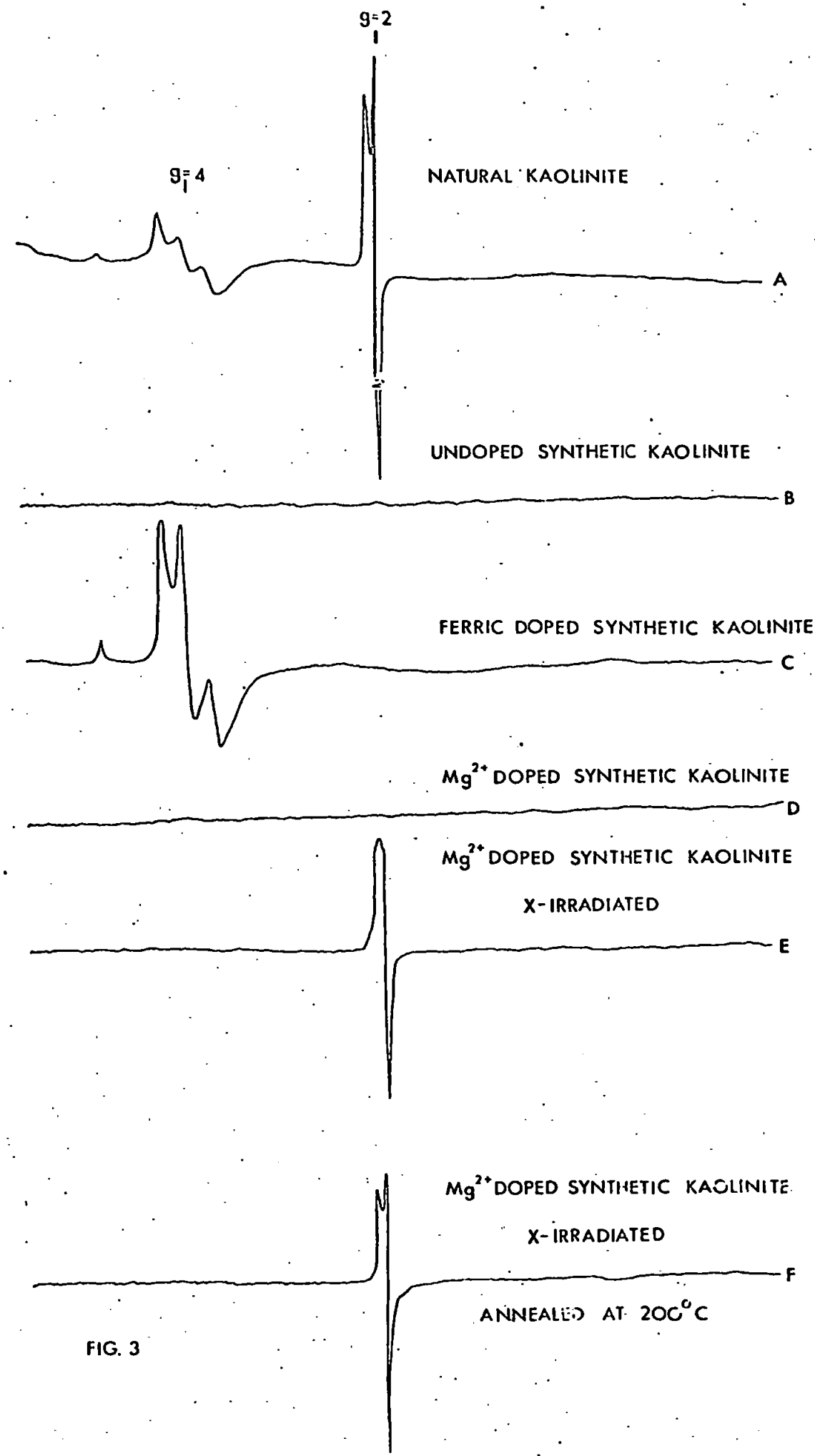
g=2
g=4
NATURAL KAOLINITE
A
UNDOPED SYNTHETIC KAOLINITE
B
FERRIC DOPED SYNTHETIC KAOLINITE
C
Mg2+ DOPED SYNTHETIC KAOLINITE
D
Mg2+ DOPED SYNTHETIC KAOLINITE
X-IRRADIATED
E
Mg2+ DOPED SYNTHETIC KAOLINITE
X-IRRADIATED
F
ANNEALED AT 200°C

FIG. 3

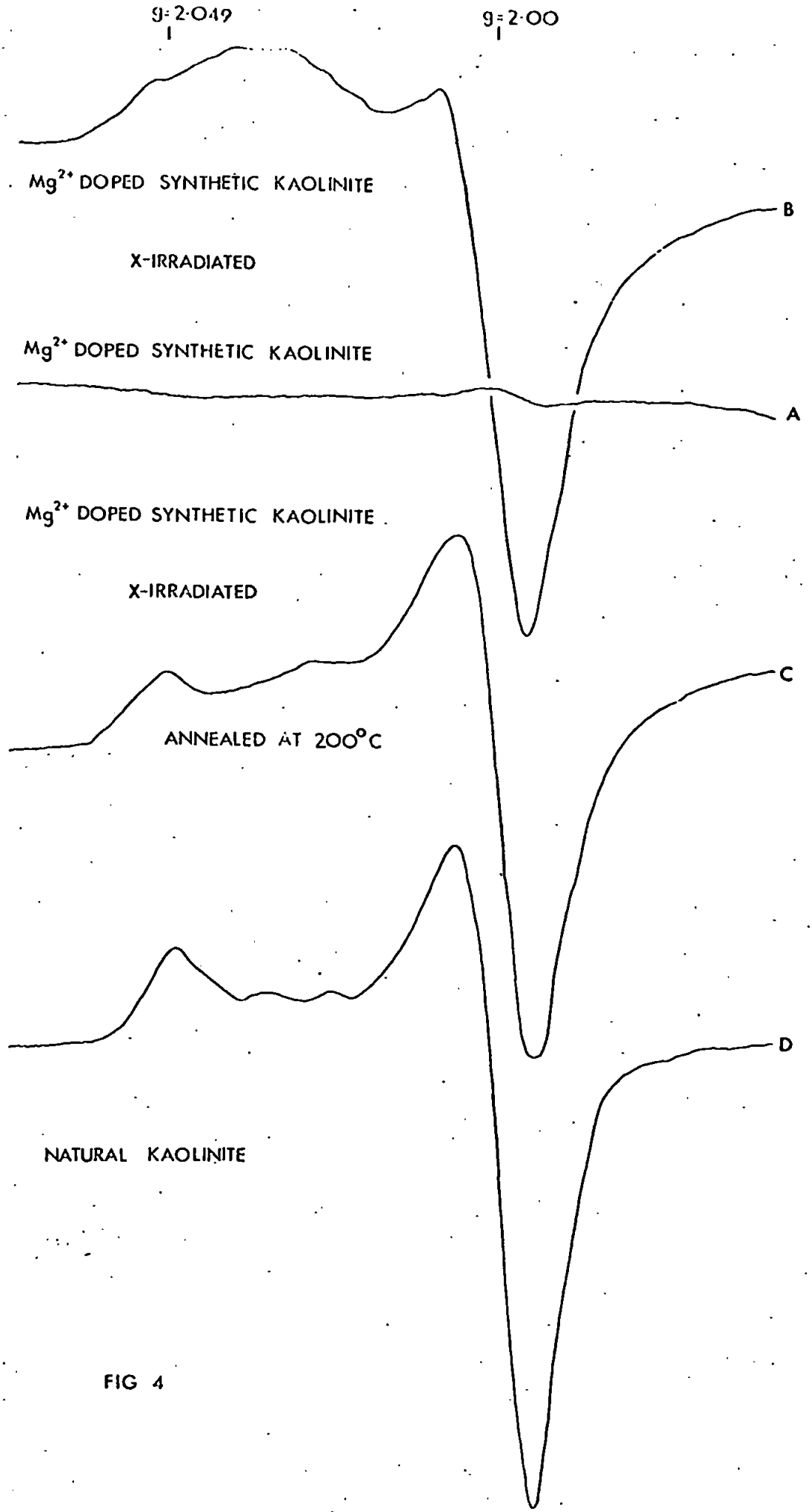
g = 2·049
g = 2·00
Mg^{2+} DOPED SYNTHETIC KAOLINITE
X-IRRADIATED
B
Mg^{2+} DOPED SYNTHETIC KAOLINITE
A
Mg^{2+} DOPED SYNTHETIC KAOLINITE
X-IRRADIATED
C
ANNEALED AT 200°C
D
NATURAL KAOLINITE

FIG 4

THE SYNTHESIS, MORPHOLOGY, AND GENERAL PROPERTIES OF KAOLINITES SPECIFICALLY DOPED WITH METALLIC IONS, AND DEFECTS GENERATED BY IRRADIATION.

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ABSTRACT

Methods of synthesis and controlled doping of kaolinites with the aid of a unique method of gel preparation are described.

A summary of comparative electron spin resonance (E.S.R) measurements, X-ray diffraction and electron microscopical data of natural and purposely doped synthetic kaolinites demonstrate the unquestionable substitution of known types of metallic ions and defects into the lattices of highly crystalline synthetic crystals with ideal morphology. Parameters which are thought possibly to influence the morphology of synthetic kaolins are reported. General trends observed experimentally are illustrated for varying pH values of reaction mixture and dopant levels. The paper is concluded with a description of various experimental investigations which have materialised due to the availability of high quality doped synthetic kaolinites.

INTRODUCTION.

In 1972 at the conference in Madrid a paper was presented by workers from this laboratory which suggested a possible interpretation of E.S.R. signals commonly found in natural kaolins. As in many past experimental investigations of natural kaolin it was difficult at the time to draw definite conclusions because the results were complicated and influenced by a multiplicity of trace impurities, defects and additional mineral species. Considerable progress, in the understanding of the observed physical phenomena,

has been achieved since 1972 by synthesising pure and doped high quality kaolinites. The production of kaolinites with various known substituted dopants as well as providing a sound foundation for E.S.R. studies can also be used in a wide range of experimental investigations. We report in this paper the development of methods of synthesis and doping and some of the applications of the doped kaolinites in the continued study of this mineral.

Development of methods of synthesis and doping of kaolinite.

Although a vast amount of literature dating from approximately 1887 is available which descfibes wide ranges of experiments associated with the synthesis of kaolinite, as far as the authors are aware no reports exist which refer to methods of doping synthetic kaolinites. The references listed represent a very small fraction of the total papers available on kaolin synthesis and are quoted to provide typical examples of past work. The methods of synthesis employed in the past can be broadlay classified into three main categories. These are basic hydrothermal alteration of an alumino-silicate gel or glass at temperatures up to 400°C, the direct hydrothermal alteration of minerals (particularly feldspars) at elevated temperatures and the formation of kaolinite at low temperatures.

It is known (Biggar and O'Hara 1969) that in hydrothermal reactions the nature and pretreatment of the starting materials can affect the phase finally formed. In this work a number of different previously attempted techniques of synthesis

were reinvestigated for preparing controlled doping of synthetic kaolinite which included synthesis form albite, montmorillonite, silico alumina gels and mixtures of pre-gibbsitic gels, gibbsite and silica. For those techniques which involved the use of naturally occurring minerals it was found in general that substituted impurities were detectable in the starting materials and it was not possible therefore, to control the doping processes satisfactorily. Considerable emphasis was placed on the development of doped silico-alumina gels through which it was possible to achieve greater purity in starting materials and controlled doping.

Initially, gels were prepared by the cohydrolysis of tetrachyl silicate and aluminium isopropoxide. The aluminium isopropoxide was added to the water at a slower rate compared with the tetrachyl silicate and continuous stirring was applied for approximately 24 hours. The gels were recovered as powders by removing excess water in a rotary evaporator and drying at 110°C prior to hydrothermal reaction of typically 0.5g of gel with 3ml of water. Although the method excluded ionic impurities it was dificult to determine the degree of mixing of the silica and alumina. It was likely that poor yields of kaolinite with high proportions of boehmite were sometimes formed by the aluminium isopropoxide hydrolyzing sufficiently rapidly to remain in the gel as a separate alumina phase. Aluminium isopropoxide varies in its rate of hydrolysis because it behaves in some instances as a viscous supercooled liquid, which, not having crystallised fully hydrolyses more rapidly than usual.

We found that when the aluminium isopropoxide was well crystallised and solid the reacted gels produced improved quality kaolinites with no traces of boehmite. In view of the unpredictable behaviour of aluminium isopropoxide redistillation followed by solidification in a dessicater for at least one week was carried out before it was used and in addition a variety of temperatures for synthesis were utilised in attempts to produce consistent results. In general, it was found that no rigid control of the nature of the final product was possible although on average excellent yields of kaolinite were obtainable by using freshly prepared aluminium isopropoxide.

For ions which are stable in neutral solutions doping of the gel can be achieved by adding the relevant soluble salt as the mixture is hydrolising. However, Fe^{3+} which is known to substitute in natural clays and is of particular interest[1.16.17] is extremely insoluble under neutral conditions[18] and only becomes soluble if the pH is less than 1.5. Attempts to introduce Fe^{3+} into synthetic kaolinite by hydrothermally reacting gels in the presence of Fe_2O_3 were unsuccessful. The gradual addition of small amounts of $FeCl_3 . 6H_2O$ during hydrolysis of a gel resulted only in the subsequent production of a poorly crystalline kaolinite with a single E.S.R. line at g=4.0. It was found however, that when the ferric chloride was added as a single lump half way through the hydrolysis the reacted gel produced a higher quality kaolinite with a 3 line E.S.R. spectrum at g=4.0 very similar to that observed in natural samples of kaolinite. It is probable that Fe^{3+}

ions remained in solution in the vicinity of the ferric chloride long enough to become bound in the gel during its hydrolysis.

A number of gels were doped with iron by using Ferric ethoxide, a metal alkoxide, as are tetraethyl silicate and aluminium ixopropoxide or liquid tetraethyl silicate separately prior to cohydrolysis. However, it was found that aluminium isopropoxide hydrolysed more rapidly when doped with ferric ethoxide thereby producing greater phase separation and resulted in the production of poor kaolinites together with boehmite. Results obtained from the doped tetraethyl silicate were slightly better but precise reproduction of signals observed from natural kaolinites were difficult to obtain and were often not reproducible. After attempting many combinations of the techniques just described a method of gel production and doping was established which as far as the authors are aware is quite unique and is proving to be of great value in our work.

Gel production and doping with liquid A

By adding an appropriate amount of tetraethyl silicate to hot liquid aluminium isopropoxide a clear liquid forms which remains liquid at room temperature. It is known[19] that metal alkoxides easily exchange their alcohol groups and in the mixture formed it was assumed that such an exchange had taken place. The liquid formed will be referred to as liquid A. The hydrolysis of liquid A occurs fairly rapidly and if left in an open container absorbs water from the air and slowly hydrolyses with the gel precipitating as a white powder.

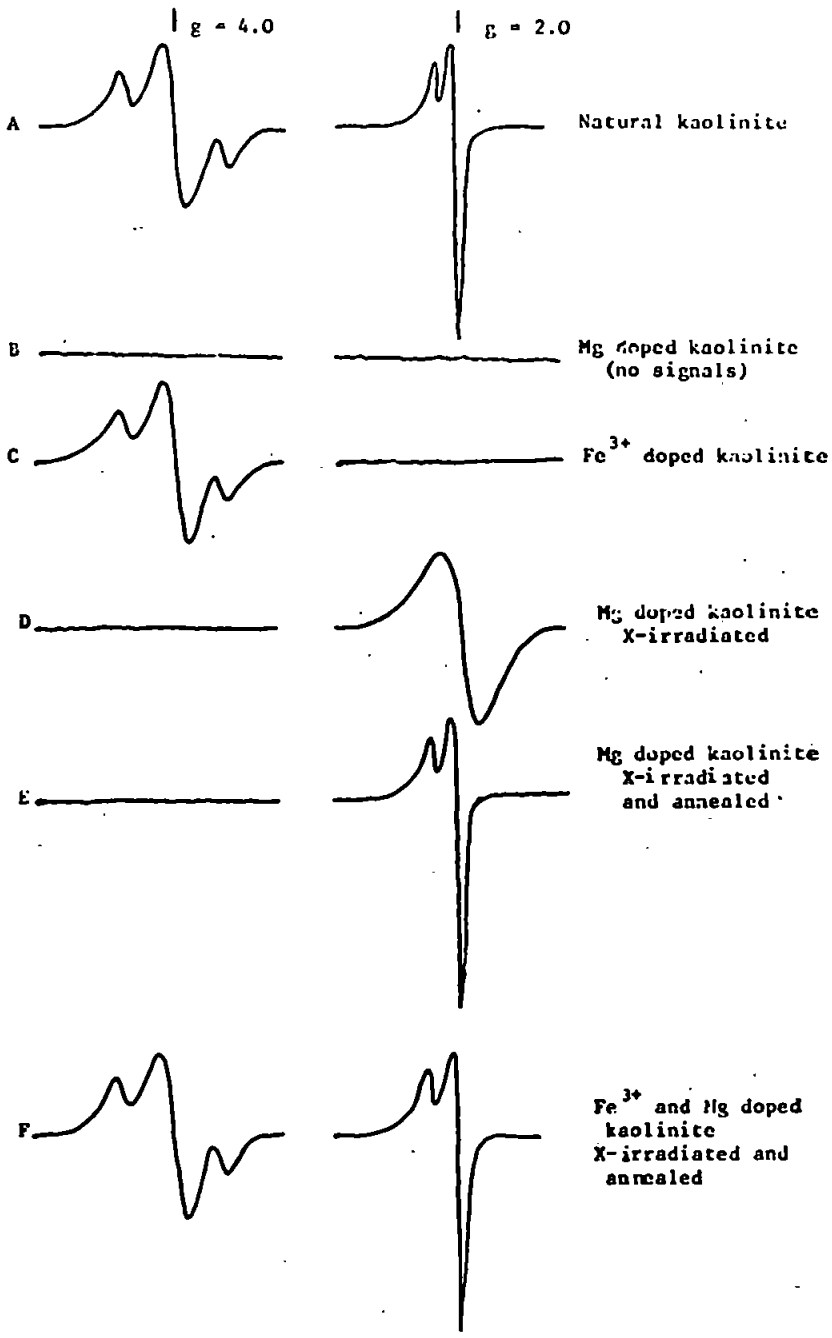
The addition of isopropal alcohol to liquid A in an open vessel prevents precipitation and the liquid eventually sets to form a clear solid gel.

Doping with Fe^{3+} can be achieved either by adding ferric ethoxide to freshly prepared liquid A more conveniently and equally as effective by adding ferric benzoate dissolved in dimethyl formamide. (D.M.F.) Ferric benzoate is much easier to prepare and does not hydrolise as rapidly as ferric ethoxide. The production of a clear silico-alumina gel from liquid A doped with ferric benzoate makes it possible to visually check the homogeneity of the gel and ensure that the Fe^{3+} ions are uniformly distributed throughout the mixture. When the liquid A isoproponal mixture ages slowly in air it becomes progressively more viscous and if at some point immediately prior to gelling a mixture of water and ethanol is added no precipitation occurs. Thus, for water soluble ions doping of the gel can be readily achieved and at the same time the rate of gellation can be increased. Doping of kaolinites with magnesium can be achieved simply by dissolving a soluble salt in water and adding the solution to liquid A.

The usual method adopted in the past by other workers, for producing comparable clear silico-alumina gels has been to mix solutions of sodium silicate and sodium aluminate and neutralise with acid. This technique suffers the disadvantage of contamination of the gel by sodium ions and anions from the acid which even after washing remain in the gel at relatively high concentrations.

It has been suggested[20] that impurity ions of this type inhibit the synthesis of kaolinite. By using liquid A contamination does not occur and after drying the gels further heating at temperatures up to 1000^{o}C can be used to remove any organic matter. Using liquid A we are able to produce abundant well crystallised kaolinites and it is possible to dope under controlled conditions. In general results are easily reproducible.

In view of our particular interest in E.S.R. phenomena in kaolinites the bulk of our work has so far concerned itself with the reproduction of signals in synthetic samples which are common to natural samples. The results obtained to date are conveniently demonstrated by referring to the E.S.R. spectra A-F in Fig 1. Comparison of the E.S.R. spectra of natural and selectively doped samples demonstrate how it is possible to unequivocally assign signals to specific types of paramagnetic centre in a more precise manner than was possible previously. For example, in 1972 using only natural samples we were only able to speculate on possible mechanisms being responsible for the two groups of main signals which are centred at g-values 2.0 and 4.0. Spectrum C demonstrates the unquestionable assignment of signals at g=4.0 to Fe^{3+} ions substituting in the lattice with no effects observable at g=2.0. In contrast, signals at g=2.0 with no signals at g=4.0 have been obtained from samples doped with magnesium followed by irradiation and annealing (Spectrum E). A detailed discussion of the way in which we have been able to assign


g = 4.0
g = 2.0
A
Natural kaolinite
B
Mg doped kaolinite
(no signals)
C
Fe^{3+} doped kaolinite
D
Mg doped kaolinite
X-irradiated
E
Mg doped kaolinite
X-irradiated
and annealed
F
Fe^{3+} and Mg doped
kaolinite
X-irradiated and
annealed

the signals to particular types of crystal lattice sites is given in papers recently published[16,17]. It is interesting to note that at the time of publication of the papers quoted above we were unable to reproduce both groups of signals simultaneously at g=2.0 and g=4.0 in a synthetic kaolinite. We found that although it was possible to reproduce signals at g=2.0 by doping with magnesium chloride (followed by irradiation and annealing) the combined addition of magnesium chloride and ferric benzoate failed to produce any crystalline phase in subsequent reactions. At the time of writing this paper we have reproduced both groups of signals by using magnesium nitrate and ferric benzoate as dopants (Spectrum F) and it will now be possible to study in more detail the effect of dehydroxylation on the E.S.R. signals in kaolinite.

Morphology of synthetic kaolinites.

Although there have been numerous reports of the successful synthesis of kaolinite, in general the basis of identification of the products has been almost exclusively by X-ray diffraction and frequently the morphology of the products has not resembled natural kaolinites. We have found that the possible number of variable parameters encountered in synthesis and combined doping experiments which possibly influence the nature and morphology of the final product can include

(i) The nature and composition of the starting materials of gel production.

(ii) The temperature and time of reaction.

(iii) The pH of the reaction mixture.

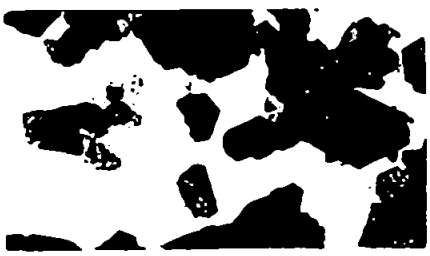
(iv) The concentration and type of dopant.

(v) Possible contamination from reaction vessels depending on the experimental techniques used.

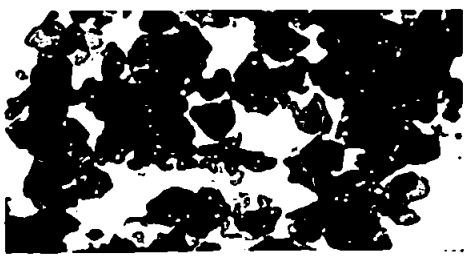
(vi) The pressure of reaction which is known[20] to influence the solubility of the reaction products and which may be determined by the s.v.p. at the temperature of reaction or which may be controlled externally with the aid of more sophisticated types of apparatus.

(vii) Cycles of cooling and reheating during synthesis.

Also, it is possible that some of the parameters quoted above might be interrelated, for example the dopant could affect the pH. Assuming minimum interrelation it is clear that a very large number of experiments would have to be completed in order to survey the influence of all variables i-vii. To date we have synthesised approximately 500 kaolinites without being able to control factors (v) and (vi) for reasons discussed in detail in the papers recently published.[16.17.] We make no rigid claims therefore, as to factors which produce definite types of morphology but report here some general trends and observations which we feel will be of interest. The features to be discussed are illustrated in electron micrographs A - F of synthetic kaolins which were grown from liquid A. In general it has been found that with no dopants involved acid conditions with pH values between 2.0 and 6.0 favour the growth of highly crystalline kaolins with hexagonal morphology. The particles tend to be thinner than most natural samples and particle size is usually less than 0.5 microns. It is also perhaps surprising that regardless of the value of pH



A (X 27000)



B (X 35000)

C (X 35000)

D (X 7,700)

E (X 44000)

F (X 7,700)

A Natural kaolinite

B Undoped synthetic kaolinite

C 0.0.5% Fe^{3+} doped synthetic kaolinite

D 0.1% Fe^{3+} doped synthetic kaolinite

E Mg doped synthetic kaolinite

F Undoped synthetic kaolinite produced by slowly cooling reaction products.

the initial reaction mixtures the shift in pH always tends towards more normal values. For an initial pH value of 12.0 after reaction the pH drops to values between 8.0 and 10.0 and a highly crystalline kaolinite is still produced but with very poor morphology. Similar results are obtained from samples grown with normal solutions for which the pH value does not change.

The main trend in samples grown from ferric doped liquid A is to produce kaolinites with improved morphology under acid conditions. Ferric doped gels with high pH values have not been investigated. The variation of concentration of iron dopant for a fixed pH starting value produces noticeable changes in crystallinity and morphology. Small concentrations of iron $\sim$0.05% decreases crystallinity but with higher concentrations $\sim$0.5- 1.0% crystallinity increases and the aspect ratio changes considerably. (Micrographs C & D). For magnesium doped kaolinites the most noticeable feature regardless of the pH value of reaction is the tendency of formation of very small particles but again acid conditions produce better morphology (Micrograph E). Increasing the level of magnesium doping above 0.5% prevents the formation of kaolinite.

As well as the general observations mentioned above a number of interesting phenomena have been observed which it is hoped will be investigated in more detail in the future. Micrograph F demonstrates the effect of allowing reaction products to cooll slowly from 280°C to room

temperature over a period of 3 or 4 days by gradually reducing the temperature of the furnace. The folding or curling of the particles is very evident and does not occur when a similar gel is cooled over the same temperature range in a period of 3 to 4 hours.

To date no quantitative measurements with regard to optical properties in the visible region have been made on our synthetic kaolinites. However, it is very noticeable that many of the synthetic kaolinites vary in their apparent whiteness. It is perhaps surprising to find that some undoped kaolinites with high crystallinity and ideal morphology appear very dark compared with similar samples which contain concentrations of substituted iron as high as 1.0%. We suspect that a possible explanation of the synthesised products from the P.T.F.E. liners which have been used in the reaction vessels. It is hoped that in the near future the synthetic clays will be analysed for possible organic contamination and larger tuttle bombs with platinum lines are being constructed which will also possibly provide sufficiently large samples for rheological measurements. In addition, an experimental rig has been constructed which will produce small samples of synthetic kaolinites in platinum ampules under externally controled pressures.

The development of liquid A and process of doping clays with Fe^{3+} has provided the facility of being able to

synthesise a kaolinite doped with enriched Fe^{57}. Past experimental studies of substituted iron in natural kaolinite using Mössbauer spectroscopy which depends on the existence of the iron 57 isotope have been limited to some extent because of poor statistice involved in the detection process. Iron 57 is 2.245% naturally abundant and consequently natural clays with typically 0.3% total iron contain of the order of 0.006% Fe^{57}.

At this stage our results from Mössbauer studies of the Fe^{57} doped samples before and after dehydroxylation are not sufficiently refined to warrant detailed discussion.

The same may be said for preliminary studies which have been made on the magnetic susceptibility of synthetic kaolins doped with iron and the possible influence of substituted vanadium on the physical and chemical properties of kaolinite.

We conclude from the small number of results so far obtained that the continued development of synthesis of kaolinites with known substituted impurities will provide valuable information to elucidate unknown factors which would appear to influence the behavioural characteristics of this mineral and provides sufficient incentive to continue this approach in future work.

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FIGURE CAPTIONS

Fig. 1 X-Band E.S.R spectra of natural and selectively doped kaolinites.

Fig. 2. Electron micrographs of natural and selectively doped synthetic kaolinites.

SYNTHETIC KAOLINITES DOPED WITH Fe^{2+} AND Fe^{3+} IONS

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Abstract

Previous studies by Electron Spin Resonance (E.S.R.) have established the substitution of Fe^{3+} and Mg^{2+} in the kaolinite structure. It is shown that Fe^{2+} can substitute in kaolinite and stabilise defects which are detectable by E.S.R. in a manner identical to Mg^{2+}. The development of methods of preparing a synthetic kaolinite doped with Fe^{2+} is described in detail. It is shown that the main E.S.R. signals, which occur at g = 4.0 and g = 2.0 in natural kaolinites and which previously have been interpreted in terms of iron and magnesium, can be attributed to iron alone.

Introduction

The general E.S.R. characteristics of naturally occurring kaolinites were first examined in this laboratory in 1968 and a survey of a large number of samples established, without exception, the existence of fairly intense signals[1] The E.S.R. spectra usually contained two main groups of resonance lines centred at about g = 2.0 and g = 4.0 respectively (Fig. 1). However, some samples exhibited only one of the main groups of resonances either at g = 2.0 or at g = 4.0. On this basis it seemed reasonable to suggest that the paramagnetic species responsible for the two groups of signals were not necessarily related or connected in any way and could exist as separate entities.

A series of experiments was carried out to establish that the E.S.R. signals associated with kaolinite could be attributed to impurities substituted within the crystal structure and not to mineralogical impurities or surface

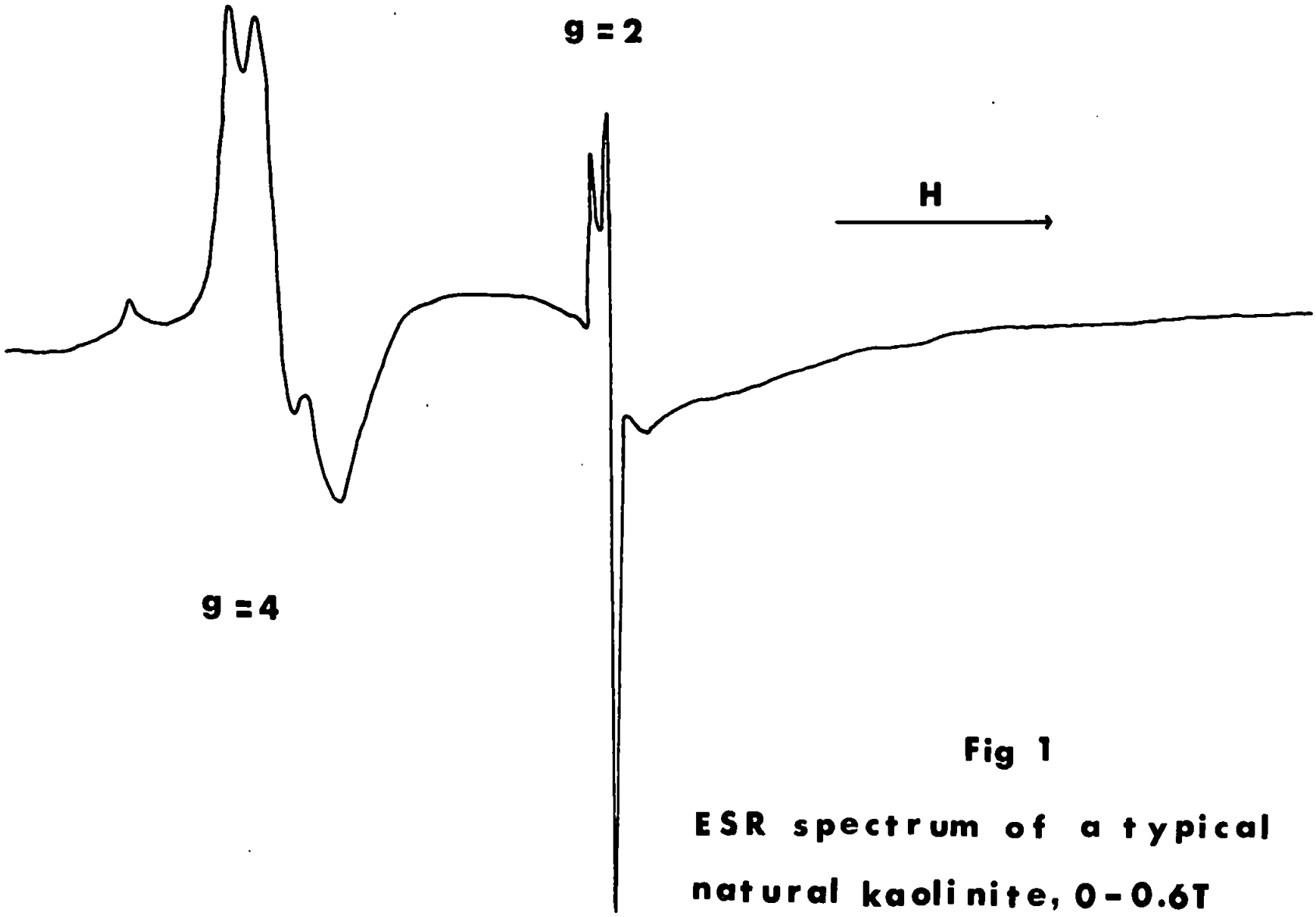


Fig 1

ESR spectrum of a typical natural kaolinite, 0 - 0.6T

contaminants.[2] For the signal at g = 2.0 it was clear that, with the exception of ball clays which contain relatively high concentrations of organic matter, there was no measurable contribution to the signal from the organic fraction.[3] This being so, it seemed feasible to seek the source of the resonances from comparison of the chemical analysis of natural samples with the known structure of kaolinite and the results indicated that iron was most probably responsible. It is well known that glasses doped with iron produce intense resonance signals at g = 4.0[4] similar to those found in kaolinites. In fact, it has been established that the g = 4.0 resonance in kaolinite can be assigned to iron substituted in the structure.[5,6] However, the signals at g = 2.0 are less easily attributed to iron.

The g = 2.0 Resonance

The resonance at g = 2.0 is stable at temperatures up to about 400°C. The collapse of the signal on dehydroxylation suggests that the paramagnetic species is more closely associated with the octahedral layer than the tetrahedral layer, which is virtually unchanged by dehydroxylation.[7] Furthermore, it is found that intercalation of kaolinite with dimethylsulphoxide[6] leaves the g = 2.0 signal unaffected, which indicates that the signal is not due to an interlayer defect.

The spin relaxation time of Fe^{2+} is extremely short[8] and liquid helium temperatures are required to detect it directly by E.S.R. Hence it would seem unlikely that Fe^{2+} could be responsible for a signal at g = 2.0 at room temperature. It is also difficult to attribute this resonance to Fe^{3+} substitution. The five unpaired electrons associated with the free ferric ion, either through spin orbit coupling or interaction of surrounding ligands or both, can be shown to stabilise in a number of different ways, depending on the relative strengths of the interactions and the geometry of the crystal field. It has been found that at room temperature either groups of lines at g = 4.0 are observed or at least five lines at g = 2.0.[8] However, in

kaolinite only two lines are present at g = 2.0, which is indicative of a paramagnetic system with an effective spin S = ½ and in axial symmetry. Therefore, it is difficult to see how such a resonance could be produced directly by iron.

A considerable volume of literature is available describing the various defects which have been identified in minerals.[9,10,11,12] In particular, it has been suggested that the production of a stable paramagnetic centre (such as that which might account for the g = 2.0 signal in kaolinite) usually requires the presence of some sort of "pre-centre", which, when irradiated, subsequently traps a hole or an electron.[9,10] The pre-centre often takes the form of a foreign ion substituting within the crystal structure and requiring charge compensation. For kaolinite it was proposed that divalent magnesium or iron substituting for trivalent aluminium might provide the necessary pre-centre for the production of a stable defect.

To test this hypothesis kaolinites doped with magnesium were synthesised. These samples did not exhibit E.S.R. signals, but when irradiated by X-rays with a dose of the order of 1 MRad a fairly intense broad resonance around g = 2.0 with a positive g-shift was observed. By annealing the samples at 200°C for two hours the majority of the resonance disappeared to leave a signal at g = 2.0 identical to that observed in natural kaolinites.[5,6]

These results suggested that Fe^{2+} might be able to perform the same function as Mg^{2+}. Hence, it now seemed possible that both groups of resonances at g = 4.0 and at g = 2.0 might be caused by iron impurities. Clearly, evidence for Fe^{2+} producing the g = 2.0 signal in kaolinite could be obtained from a synthetic sample which was known to contain a reasonable amount of substituted ferrous iron.

In order that Fe^{2+} could be detected directly in kaolinite samples, Mössbauer spectroscopy was considered as an alternative to E.S.R. The Mössbauer technique has the advantage that both Fe^{2+} and Fe^{3+} can be

detected and easily distinguished at room temperatures. The main disadvantage of this method is that only the ^{57}Fe isotope, which is 2.245% abundant, is detectable. A typical clay, which might contain up to 2% total iron impurity, will contain a relatively small amount of ^{57}Fe and consequently the statistics of results obtained from past studies on natural clays have placed restraint on their interpretation. Therefore, it was decided to attempt the synthesis of a kaolinite doped with iron-57. Although from previous work it was thought that the iron would substitute predominantly as Fe^{3+}, it was anticipated that sufficient Fe^{2+} would also be present to provide a kaolinite suitable for detailed Mössbauer studies.

Synthesis of ^{57}Fe - Doped Kaolinite

In order to dope a kaolinite with ^{57}Fe a number of practical difficulties arise. In previous experiments the method of doping with iron was to utilise commercially-available ferric chloride, from which ferric benzoate was prepared.[13] This was dissolved in dimethylformamide and could be added to the mixture of aluminium isoproproxide and tetraethylsilicate prior to hydrolysis. Reaction of the gels so formed produced Fe^{3+} doped kaolinite with resonances at g = 4.0.

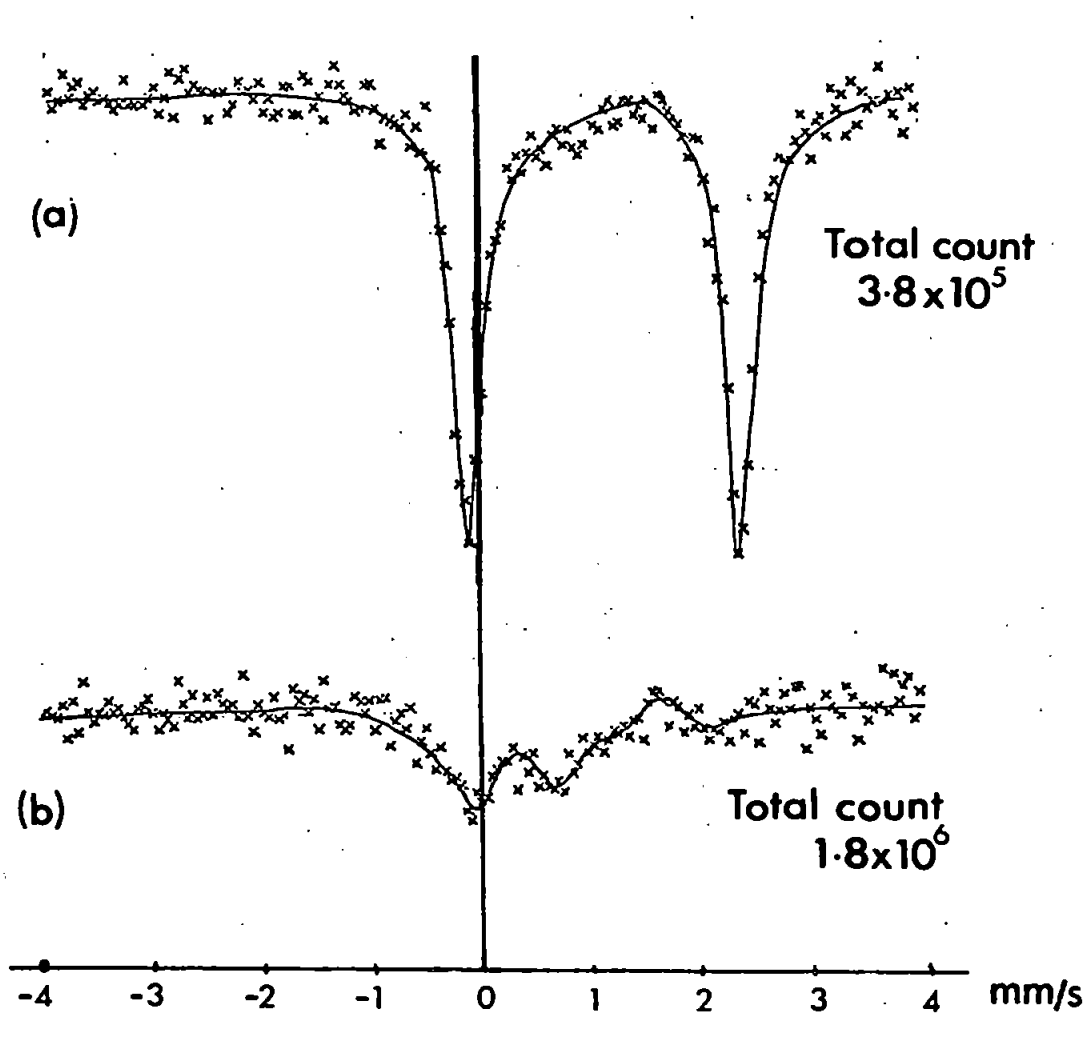
To repeat the process in an identical manner with ^{57}Fe is more difficult. Firstly, it should be noted that ^{57}Fe is very expensive (approximately £10^6/kilo) and so only small amounts could be used. Secondly ^{57}Fe is available only in the form of metallic filings or chips. Therefore a method had to be devised to produce ferric benzoate from a few milligrams of metallic iron. Initially, a method was established using natural iron. The iron was dissolved in concentrated hydrochloric acid and then oxidised by the addition of a small quantity of nitric acid. The pH of the solution was raised to about five with sodium acetate before adding ammonium benzoate solution. The precipitate of ferric benzoate formed was filtered, washed with sodium acetate solution and distilled water, and dried at 50°C.

Although the E.S.R. spectra of Fe^{3+} in the kaolinites produced were fairly weak compared with those of kaolinites produced from commercially-available ferric chloride, the technique was sufficiently refined to initiate experiments with ^{57}Fe. Accordingly, a sample of kaolinite was grown and doped with ^{57}Fe. Most surprisingly the Mössbauer spectrum (Fig 2) showed that the iron was substituted in the kaolinite structure as Fe^{2+} with very little indication of Fe^{3+}. Although a fairly weak g = 4.0 resonance could be identified in the sample by E.S.R. it should be noted that the E.S.R. technique is probably at least an order of magnitude more sensitive than Mössbauer spectroscopy.

It seemed, therefore, that during the course of the preparation of the ^{57}Fe-doped kaolinite the iron had been reduced to the ferrous state. In an attempt to ensure complete oxidation of the iron in the gel prior to hydrothermal reaction to form kaolinite, some of the ^{57}Fe-doped gel was heated in oxygen to 1400°C. However, it was found that the kaolinite produced still contained an abundance of Fe^{2+} with very little Fe^{3+}.

An intriguing situation presented itself. The E.S.R. signals at g = 4.0 and g = 2.0 in kaolinites had so far been attributed to Fe^{3+} and a defect stabilised by Mg^{2+} respectively. Now a sample had been produced which from the Mössbauer study was known to contain iron, predominantly in the ferrous state. This kaolinite was therefore irradiated and annealed in a manner identical to that which had been used previously for samples doped with Mg^{2+}. It was found to exhibit a g = 2.0 resonance identical to that observed in natural kaolinites. Hence, a synthetic kaolinite had been produced doped only with iron, but exhibiting both the g = 2.0 and the g = 4.0 signals present in natural samples. It must be emphasised, however, that for the g = 2.0 signal substituted Fe^{2+} does not in itself produce the signal, but acts as a centre for the paramagnetic defect which is produced on irradiation.

The availability of an $^{57}Fe^{2+}$-doped kaolinite has provided a facility whereby the Mössbauer spectrum of Fe^{2+} in natural clays has been



Mössbauer spectra of (a) $^{57}Fe^{2+}$-doped kaolinite
(b) a typical natural kaolinite

Fig 2

interpreted in more detail. The results of this study are presented in a separate paper.

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A Mössbauer Study of Synthetic Kaolinites Doped with $^{57}Fe^{2+}$

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Abstract

An $^{57}Fe^{2+}$ doped synthetic kaolinite has been studied by Mössbauer spectroscopy. By thermal treatment of this kaolinite and comparison with trioctahedral biotite it is proposed that Fe^{2+} substitutes trioctahedrally, as expected by consideration of charge balance. Furthermore, it is proposed that this substitution may in some cases, involve alteration of the hydroxyl layer to form two distinct trioctahedral sites.

Introduction

The existence in natural kaolinites of a multiplicity of trace impurities tends to complicate the interpretation of experimental results. Work in this laboratory has been directed towards the synthesis of pure and selectively doped kaolinites. For example, Angel et al[1,2,3] have shown that only synthetic kaolinites doped with Fe^{3+} ions and defects stabilised by Mg^{2+} or Fe^{2+} substitution can reproduce the main E.S.R. signals which are common to the majority of natural kaolinites.

The ability of Fe^{2+} as well as Mg^{2+} to stabilise irradiation induced defects was established by combined E.S.R. and Mössbauer studies of an $^{57}Fe^{2+}$ doped kaolinite. The nature of substituted iron in natural kaolinites and other minerals has been studied fairly extensively by previous workers[4,5,6,7] using Mössbauer techniques. A summary of available data is presented in Table I. The values of the isomer shifts and quadrapole splittings obtained for Fe^{2+} and Fe^{3+} are imprecise due to the low concentration of substituted iron in natural kaolinite.

The reported linewidths are approximately twice the value of those for natural iron or ferric oxide with sufficiently large particle size to produce magnetic splitting. The poor statistics normally encountered when studying iron in natural kaolinite have been considerably improved in this work by producing

	Fe^{2+}		Fe^{3+}	
	σ mm/s	Δ mm/s	σ mm/s	Δ mm/s
Dioctahedral Kaolinite 1:1	—	—	0.36	0.48
Trioctahedral Chamosite 1:1	1.14	2.57	0.38	0.78
Dioctahedral Muscovite 2:1	1.13 1.13	2.98 2.21	0.37	0.75
Trioctahedral Biotite 2:1	1.13	2.46	0.45	0.70

TABLE 1

^{57}Fe doped kaolinites.

Experimental Apparatus and Techniques

The Mössbauer drive system used in this work was similar to that described by Clark et al[8]. The stability was checked periodically using an iron foil standard. Over a period of a year the reproducibility on setting the drive amplitude has been better than 0.3% . The source was ^{57}Co in Pd and all data is quoted relative to iron foil. The drive frequency was derived from a quartz crystal in the multichannel analyser.

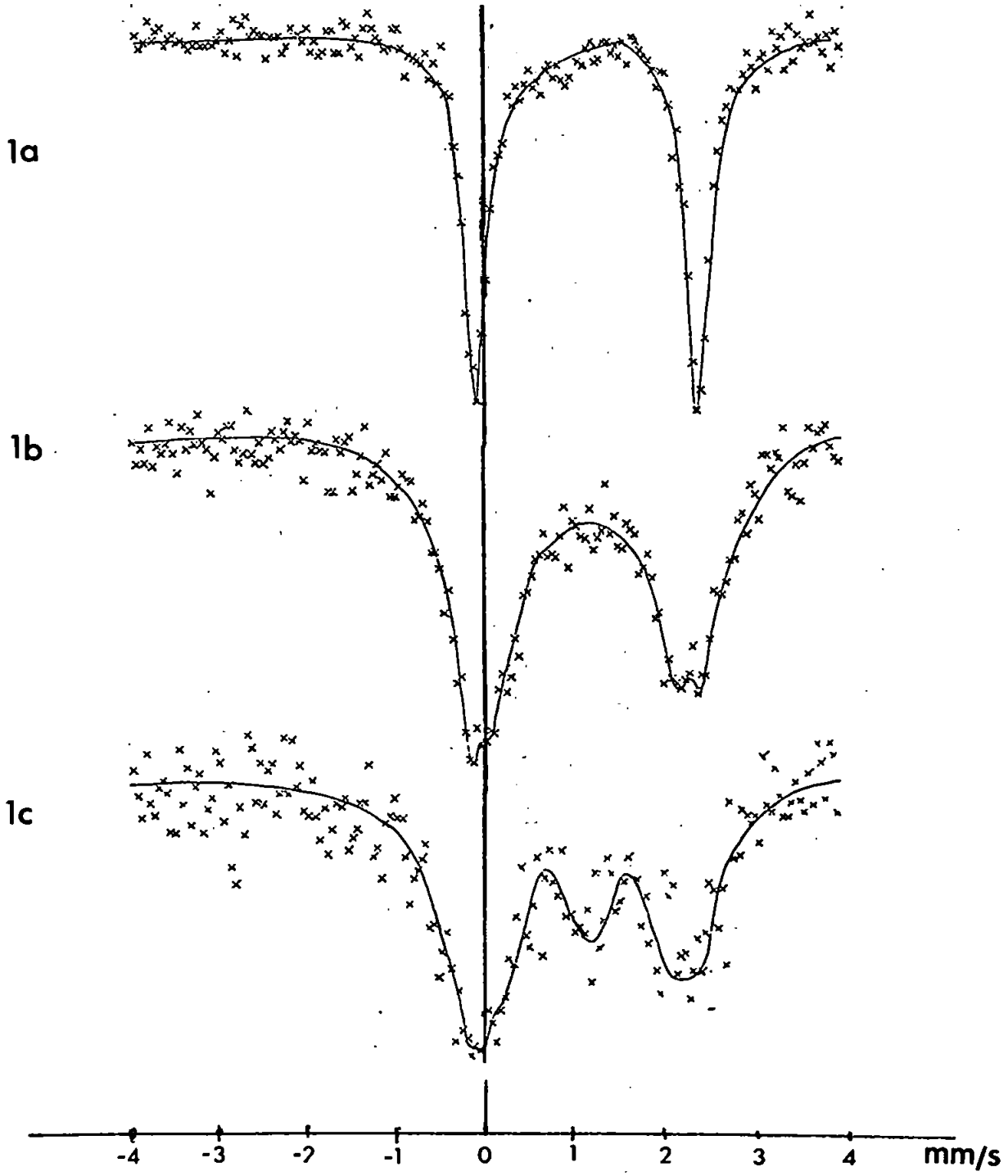
Samples were powdered and mounted between two sheets of sellotape. The sample thickness was about 1 mm for natural iron samples and 0.1 mm for samples containing enriched iron.

Experimental Results

The Mössbauer spectra of a synthetic kaolinite doped with 90% $^{57}Fe^{2+}$ before and after heating at 400°C for 30 minutes are given in Figs. 1a and 1b. Fig. 1c shows the effect of further heating to 700°C. A synthetic kaolinite doped with $^{57}Fe^{3+}$ as well as $^{57}Fe^{2+}$ and contaminated slightly with Fe_2O_3 produces a Mössbauer spectrum as in Fig. 2a. The spectrum of the same sample after treatment with ammonium oxalate in order to remove the Fe_2O_3 is given in Fig. 2b. The spectrum in Fig. 3 was obtained from a synthetic kaolinite doped with normal iron and is very similar to those obtained from natural samples. This sample contains mainly Fe^{3+} and a weak Fe^{2+} doublet which is not clearly defined due to poor statistics. For comparison, spectra obtained from a mica (biotite) containing ferrous ions are given in Figs 4a and 4b. The mica was heated under the same conditions as the kaolinite which produced the spectrum in Fig. 1b.

Discussion

Comparison of Figs. 1 and 4 shows that separate and distinct changes occur in the Mössbauer spectra of Fe^{2+} in kaolinite but not in the mica when heated under identical conditions. In contract to the mica, the kaolinite



Mössbauer spectra of a synthetic $^{57}Fe^{2+}$ doped kaolinite

(a) Untreated

(b) After heating at 400° C for 30 minutes

(c) After further heating at 700° C

Fig 1

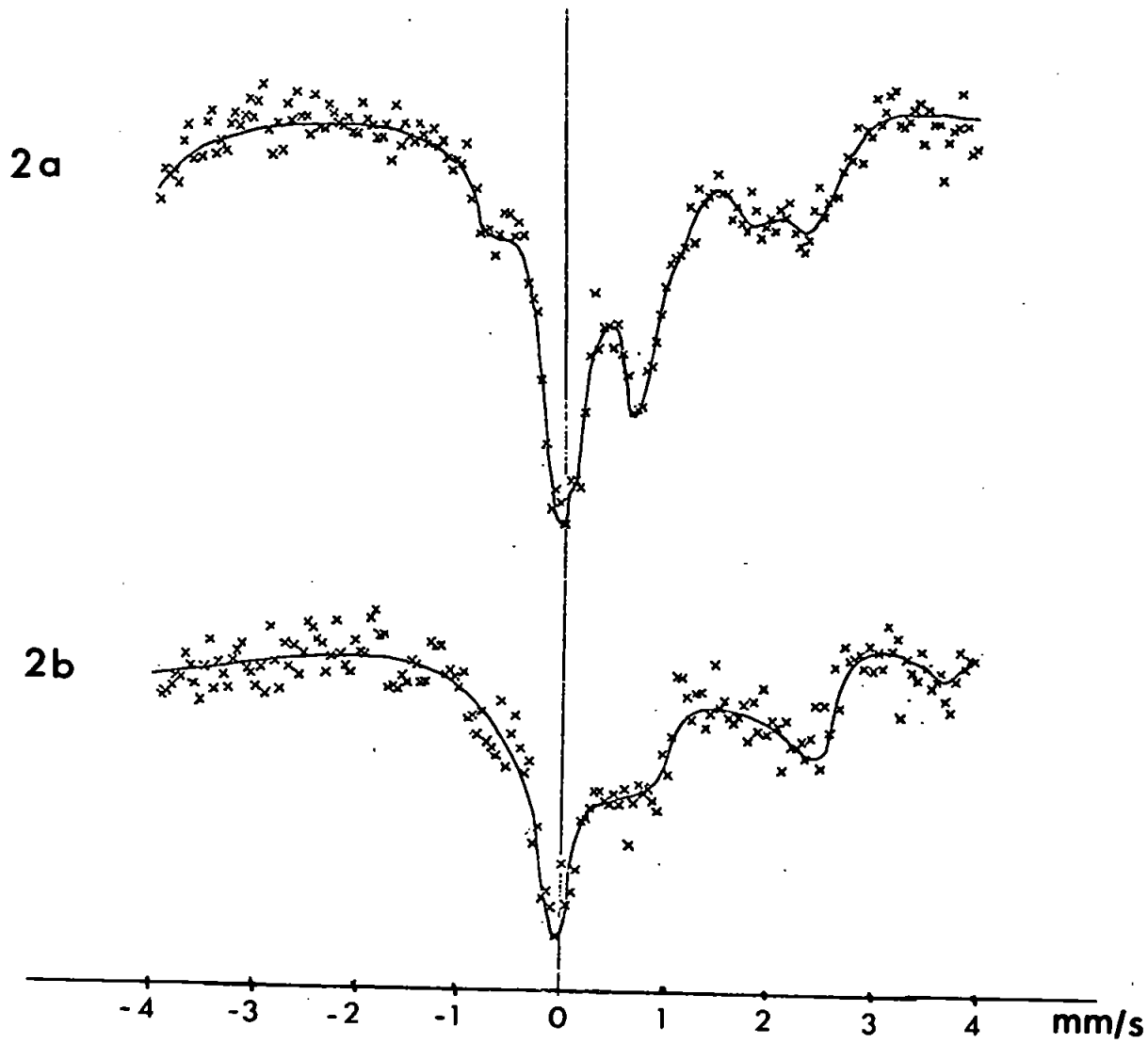


Fig 2

Mössbauer spectrum of a synthetic $^{57}Fe^{3+}$ and $^{57}Fe^{2+}$ doped kaolinite contaminated with Fe_2O_3, (a) untreated, (b) after treatment with ammonium oxalate.

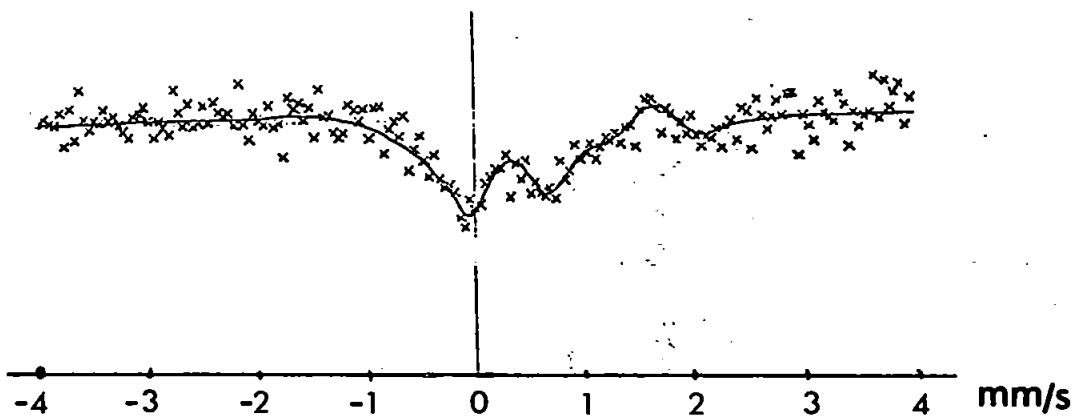


Fig 3

Mössbauer spectrum of a synthetic kaolinite doped with natural iron.

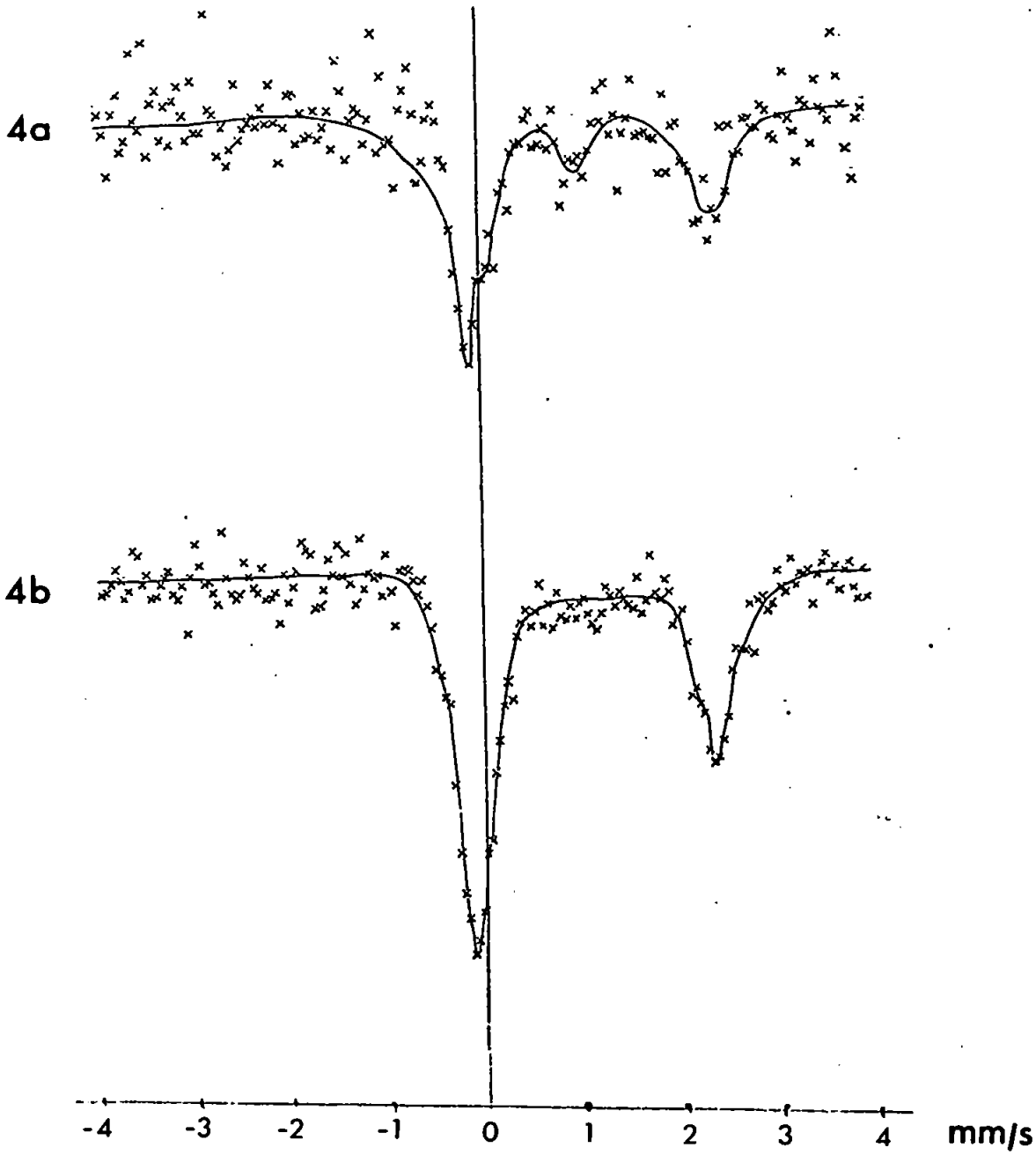


Fig 4

Mössbauer spectrum of biotite. (a) untreated, (b) after heating at 400°C for 30 minutes.

Fe^{2+} doublet at room temperature splits to give two clearly resolvable Fe^{2+} doublets after heating at 400°C for 30 minutes. There is no evidence of oxidation before further heating at 700°C. Although there also appears to be no evidence of oxidation in the mica when heated to 400°C for 30 minutes (Fig. 4a and 4b), Hogg et al [9] have shown that oxidation of Fe^{2+} occurs in some biotites when heated to 400°C for 12 hours or more. The possibility that similar effects might occur in kaolinite is being studied in this laboratory.

The production of two clearly resolved Fe^{2+} doublets from the synthetic kaolinite heated to 400°C suggests that two distinct sites for Fe^{2+} are created. This behaviour is in direct contrast to the effects observable by E.S.R. for Fe^{3+} substitution in a kaolinite. The effect on the room temperature E.S.R. spectrum at g = 4 is to transform the composite spectrum to an isotropic line. The effect has been interpreted [10] in terms of Fe^{3+} occupying two distinct sites prior to heating which are transformed to a single identical site. For Fe^{2+} it would appear that one site is transformed into two.

The value obtained for the quadrapole splitting of the Fe^{2+} doublet in the synthetic kaolinite prior to heating is greater than the value published previously by Malden and Meads [4] for a natural kaolinite but the linewidths are narrower. A value of quadrapole splitting similar to that obtained by Malden and Meads may be found from the average of the quadrapole splittings of the two Fe^{2+} doublets in the heated synthetic sample. It would seem feasible to suggest, therefore, that Malden and Meads may have failed to resolve two Fe^{2+} doublets in natural samples. The lack of resolution is due to the combined effects of the low concentration of iron and overlap in the spectra from Fe^{3+} doublets. (Fig. 3)

The following model and mechanisms are suggested as a possible explanation for the splitting of the Fe^{2+} doublet in the synthetic kaolinite.

Comparison of the structure of mica and kaolinite show that for ions such as Fe^{2+}, Fe^{3+} and Al^{3+} which are held in six-fold co-ordination within the octahedral layer, the surrounding ligands have slightly different configurations.

In micas the ligands comprise four oxygens and hydroxyl groups with cations in either cis or trans sites. For kaolinites only cis sites are present formed by two oxygens and four hydroxyl groups.

It is proposed that the synthetic kaolinite contains trioctahedral units, in the octahedral layer, in which three Fe^{2+} ions replace two Al^{3+} ions maintaining charge balance. It is suggested that the trioctahedral units within the kaolinite are similar in structure to those in a ferrous chamosite. Furthermore, it is suggested that the effect of heating these kaolinites at 400°C is to cause the release of hydrogen. Brindley [11] has proposed that the effect of heating chamosite at 400°C is to cause oxidation of Fe^{2+}

If it is assumed that the effect of heating the synthetic kaolinite at 400°C is to remove two hydrogen atoms from the hydroxyl layer, without any accompanying oxidation of Fe^{2+}, the effect is to transform one third of the cis sites into trans sites similar to those in biotite. It has been shown [7] that the iron in a trans site produces a smaller quadrapole splitting compared with that in the cis site.

The mechanisms proposed above would produce two distinct ferrous doublets with an intensity ratio of 2:1. Without refining the Mössbauer spectra by computer fitting it is clear from Fig. 1b that such an intensity ratio and the nature of the proposed sites could exist within the heated kaolinite. Furthermore, the assignment of the cis and trans quadrapole splittings is consistent with results obtained for micas by Goodman[12] and Annestern[13].

The existence of units or sub-layers of trioctahedrally co-ordinated iron in sufficient quantity could possibly affect the crystallinity of the kaolinite. A number of kaolinites containing various ferrous/ferric ratios has been examined by X-ray diffraction. However, no significant correlation between ferric/ferrous ratios and crystallinity has been discovered.

The possibility that the ferrous doublets might be due to a separate mineral phase is minimised by consideration of the results from samples treated with ammonium oxalate (fig. 3). No change in the Mössbauer spectra

of Fe^{2+} could be detected.

More detailed measurements are being made to gain a deeper understanding of the phenomena described.

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