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AN EXPERIMENTAL STUDY OF IRON AND VANADIUM ASSOCIATED WITH KAOLINITE

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VINCENT, WENDY E.J.

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AN EXPERIMENTAL STUDY OF
IRON AND VANADIUM
ASSOCIATED WITH
KAOLINITE.

BY

WENDY E.J.VINCENT, B.Sc., (LONDON)

A THESIS SUBMITTED FOR
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July, 1977.

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My grateful thanks are due to my supervisor, Dr.B.R.Angel, for his encouragement, guidance and support; to the members of the technical and academic staff of the Department of Mathematical Sciences, Plymouth Polytechnic, for their assistance; to English Clays Lovering Pochin and Company Limited, the U.S. Georgia Kaolin Company and to Professor U.Schwertmann for their kind provision of samples used in the research; to Mrs.J.V.Foster for typing the script and, last but not least, to the Board of Governors of the Plymouth Polytechnic for the grant of a Research Assistantship which made this work possible.

The work described in this thesis was carried out in the Department of Mathematical Sciences at Plymouth Polytechnic, Plymouth, Devon in the period between October, 1974 and June, 1977.

This is to certify that, unless stated otherwise, the results presented here were obtained by Mrs. W.E.J. Vincent under my supervision.

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July, 1977.

ABSTRACT.

This thesis is divided into six chapters. In the first chapter relevant previous studies of kaolinite are summarised and in particular a review of past electron spin resonance studies of kaolinite is included.

The experimental results are presented in four chapters. Chapter 2 describes an investigation of the vanadium impurities associated with natural kaolinites from Georgia, U.S.A. By following the changes in the electron spin resonance spectra of these samples with magnetic separation, thermal and chemical treatments, preferential orientation and relative humidity, it is shown that vanadium is substituted in the kaolinite structure, probably in the octahedral layer, as V^{4+} ions.

The synthesis and electron spin resonance study of vanadium-doped kaolinite is reported in chapter 3. It is shown that vanadium is substituted in the tetrahedral layer of these kaolinites and also that vanadium may be adsorbed on the surface of kaolinite. It is demonstrated that the comparison of electron spin resonance spectra of kaolinite samples equilibrated in atmospheres with low and high values of relative humidity provides a convenient method to distinguish between vanadium substituted in the structure and vanadium adsorbed on the surface.

Chapter 4 describes the synthesis of kaolinites doped with iron (II) ions. It is shown that ions of this type can stabilise paramagnetic defects produced by X-irradiation and reproduce the asymmetric two-line resonance at $g = 2$ which is common to most natural kaolinites.

An investigation using electron spin resonance that identifies different types of iron oxide phases associated with the surfaces of two groups of kaolinites from England and the United States is described in chapter 5. It is shown that the English kaolinites are coated with a lepidocrocite-like phase which is readily removed by de Endredy's method of deferrification. In contrast the American kaolinites are coated with a hematite- or goethite- like phase which is not removed by similar treatment.

Throughout the course of this work, the effects of the various physical and chemical treatments on the brightness values of the kaolinites were examined. The results are summarised and discussed in chapter 6 and ideas for further work are suggested.

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

INTRODUCTION

It is well known that kaolin is used extensively in the ceramics industry and is an important ingredient in paints, plastics, medicines, cosmetics and some catalysts applied in the petrochemical industry. Its major use, however, is in the filling and coating of paper.

Paper is essentially a thin sheet of interlaced cellulose fibres which has many voids and surface irregularities. To make the sheets smoother they are coated with a slurry of kaolin which becomes trapped between the fibres. For high quality papers a thin film of pure refined clay is spread on the surface of the filled sheet thus improving its brightness, smoothness and ink absorption.

The value of a kaolinite used in the paper-coating industry depends mainly on its brightness and its rheological characteristics. It is not surprising, therefore, that considerable expenditure has been incurred by industrialists to develop physical and chemical methods for the beneficiation of kaolinite.

It should be noted that, in general, the kaolins of the South-West peninsula of England have higher brightness values compared with those of Georgia, U.S.A., but are inferior with regard to rheological properties. These differences between the two kaolin deposits may be connected to the origins of the clays. The English kaolinites are residual in nature whereas the Georgia kaolinites are sedimentary. Residual clays are those which have not been transported by natural agencies and are found in the same area as the altered igneous rocks from which they were formed. Clays of this type can usually be separated from the parent rock and obtained in a comparatively pure state. In contrast, sedimentary clays are known to have been removed from their origin by currents of air and water, and, during their transportation, may have acquired and retained impurities which are more difficult to remove.

It is known that iron- and titanium-bearing impurities have a deleterious effect on the brightness of kaolins.[1] Processes often used to remove these impurities and thus improve brightness include bleaching, froth flotation and magnetic refining. Also, it has been suggested that, for unknown reasons, the concentration of vanadium impurities in a clay are probably related to the viscosity of the clay suspension at high sheer rates.[1]

The work described in this thesis has been directed towards a more detailed study of iron and vanadium impurities associated with kaolinites using electron spin resonance spectroscopy. It is shown that this technique may be applied to study some properties of kaolins which are related to matters of industrial importance and, in particular, improves the understanding of the contrasting nature of English and American kaolins.

CHAPTER 1.

PREVIOUS STUDIES OF KAOLINITE.

1.1 Introduction.

It is beyond the scope of this thesis to review the very large volume of available published work on kaolinite. In order to facilitate interpretation of the results of this work in terms of the known structure and fundamental properties of kaolinite, it is considered necessary to consider only a relatively small number of the previous studies which have been made on this mineral.

1.2. 1 The Structure of Clay Minerals.

The structure of all of the clay minerals may be regarded as being built up from two basic units,[2,3] which are often referred to as the octahedral and tetrahedral layers. The octahedral layer consists of divalent or trivalent cations such as Mg^{2+} or Al^{3+}, each coordinated with six hydroxyl groups. The octahedra are linked by sharing edges. When Al^{3+} ions are present, only two-thirds of the available cation sites are occupied in order to maintain charge balance. This type of structure is known as dioctahedral and may be regarded as a derivative of gibbsite ($Al_2(OH)_6$). When Mg^{2+} ions are present, all the available sites are occupied and the structure, which resembles that of the mineral brucite ($Mg_3(OH)_6$), is said to be trioctahedral.

The tetrahedral layer contains silicon atoms, each one of which is surrounded by four oxygen atoms arranged in the form of a tetrahedron. The tetrahedra are connected at three corners in the same plane thus forming a hexagonal, two-dimensional network with the apices of the tetrahedra all pointing in the same direction. The octahedral and tetrahedral layers may be linked through the oxygen atoms at the tips of the tetrahedra projecting into the plane of hydroxyl groups in the octahedral layer and replacing two-thirds of them.

Clay minerals can be divided into two main groups on the basis of the type of combinations of tetrahedral and octahedral layers.[2,3]

(a) The two-layer or 1 : 1 clay minerals consist of one tetrahedral layer condensed with one octahedral layer and include the kaolinite group minerals, which are dioctahedral.

(b) The three-layer or 2 : 1 clay minerals, which include micas and smectites, consist of two tetrahedral layers between which is sandwiched an octahedral layer.

The members of the kaolinite group of minerals are kaolinite, dickite, nacrite and halloysite. Dickite, nacrite and halloysite are polymorphs of kaolinite differing mainly in the manner of the stacking of the layers and in the location of the vacant octahedral sites.[4] Halloysite differs from the other members of its group in its water content[5] and its crystal habit.[6] Nacrite, dickite and kaolinite exist as platy crystals, but halloysite exists in a tubular form.

1.2. 2 The Structure of Kaolinite.

The structure of kaolinite was first established by X-ray diffraction using the material in powder form[7,8] and was later refined both by X-ray[9] and electron[10] diffraction techniques using single crystals. It has a triclinic unit cell of dimensions[9]:

$a = 5.14 \times 10^{-10}$ m; $b = 8.93 \times 10^{-10}$ m;

$\alpha = 91.8^\circ$; $\beta = 104.5^\circ$;

$c = 7.37 \times 10^{-10}$ m.

$\gamma = 90.0^\circ$.

The basic structural unit of kaolinite consists of one octahedral, or gibbsite, layer bonded to one tetrahedral, or silica, layer (see Fig.1.1). However, interionic repulsion between adjacent Al^{3+} ions results in lateral distortions of the octahedral layer, which account for the a and b dimensions being higher than those expected for regular octahedra. To compensate for this effect, the silica tetrahedra rotate slightly in both clockwise and anticlockwise directions about the c-axis of kaolinite.

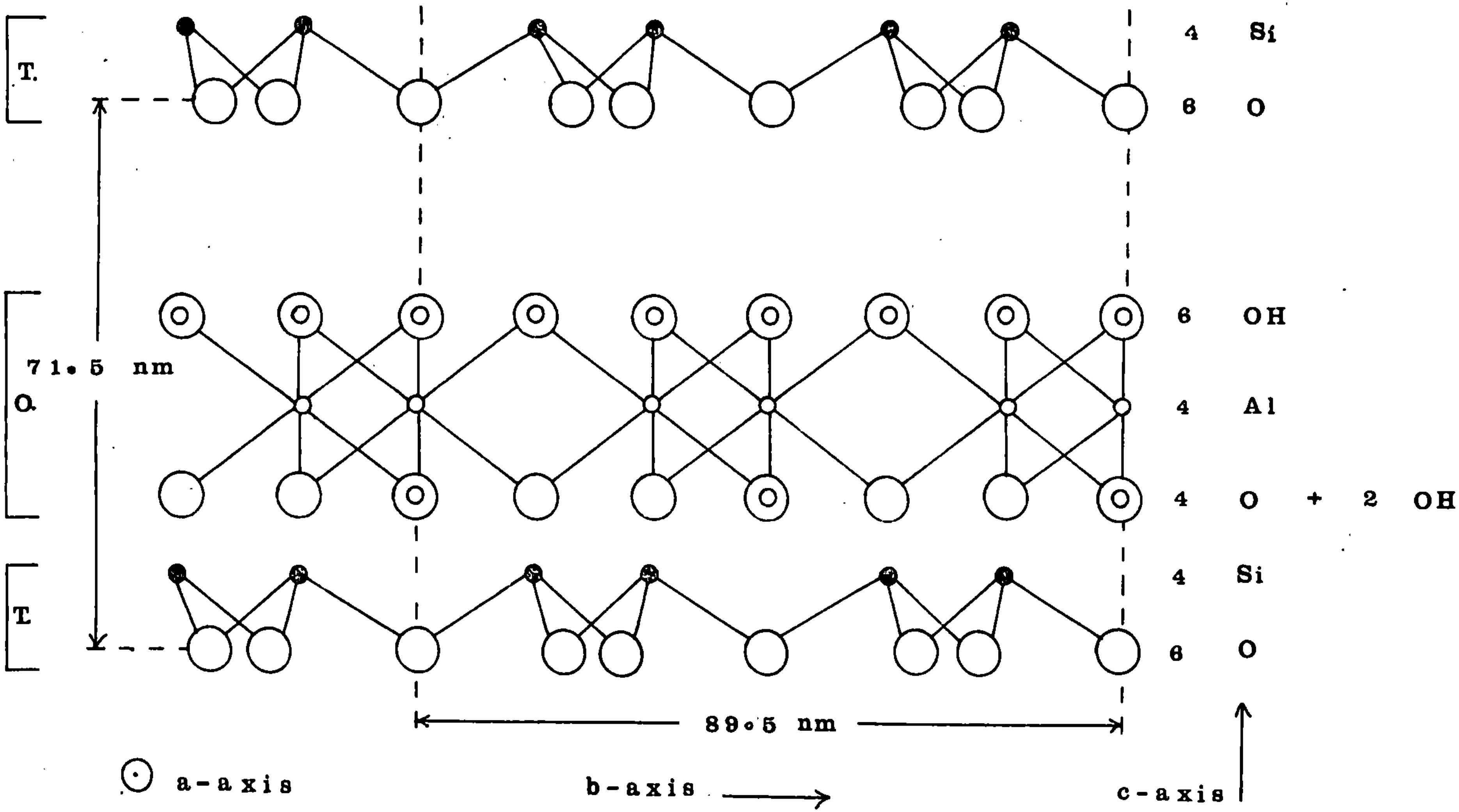

FIG. 1.1. Diagram to show the structure of kaolinite, $Al_4 (Si_4O_{10})(OH)_8$.

Key: T = tetrahedral layer,
O = octahedral layer.

A crystal of kaolinite comprises a large number of the basic structural units, which have been considered by some people to be held together by hydrogen bonding.[2,5] Indeed, the structure of kaolinite, in which successive structural units are shifted by (-a/3) is such that the hydroxyl groups at the surface of the gibbsite layers are adjacent to oxygen atoms at the surface of the silica layer in the next unit. However, more recent work has demonstrated that the type of bonding between successive layers may be predominantly electrostatic.[11]

1.3 X-ray Diffraction Studies of Kaolinite.

X-ray diffraction (X.R.D.) is used extensively for the identification of kaolinite. An X.R.D. spectrum of a typical natural kaolinite is shown in figure 1.2. It is often found that identification of kaolinite is complicated by the presence of ancillary minerals which have similar X-ray patterns. For example, kaolinite is sometimes indistinguishable from chlorite. However, these two minerals can be recognised either by treatment with warm hydrochloric acid which removes the chlorite or by heating at 873 K which changes the structure of kaolinite.[5] The identification of additional clay mineral impurities associated with kaolinite has been aided by a process known as intercalation whereby some minerals selectively absorb organic molecules between

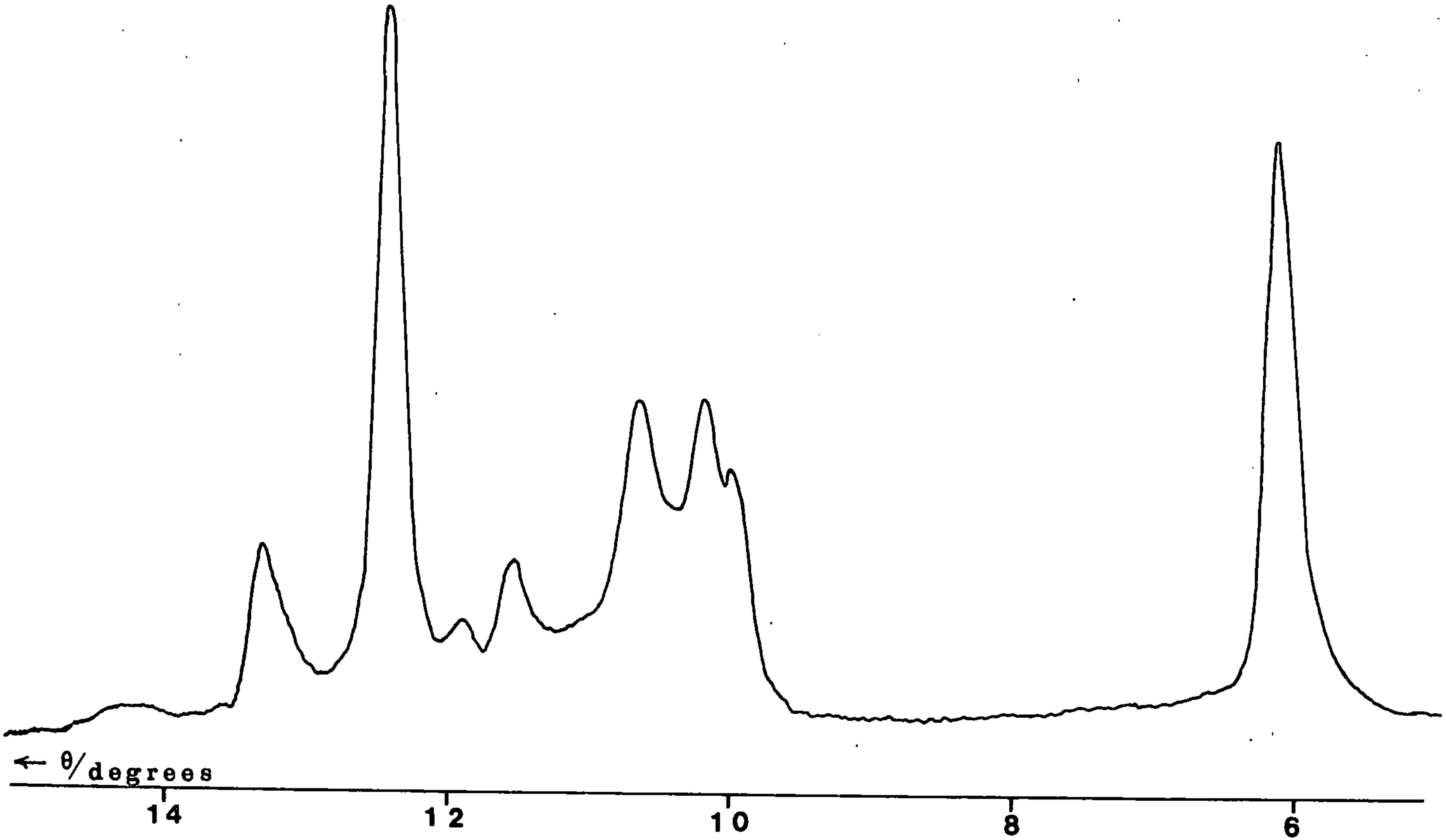

FIG. 1.2. X.R.D. spectrum of a typical natural kaolinite.

their layers producing shifts in the peaks of their X.R.D. spectra. For example, treatment with ethylene glycol permits the identification of small amounts of smectites which would otherwise not have been detected.[2]

Quantitative analysis by X.R.D. of kaolins in a mixture of minerals is seriously hindered owing to the tendency of kaolinite particles to assume a preferred orientation when normal techniques are used to prepare powdered samples. Kaolinite consists of small hexagonal platelets with large aspect ratios. The particles, therefore, tend to become aligned with their basal planes parallel to the base of the specimen holder thus greatly enhancing the intensity of the basal reflections. The degree of preferred orientation varies from sample to sample and is not reproducible. Orientation of a specimen depends on factors such as the crystallinity, particle size and the relative amounts of impurities, which may, or may not, have a plate-like structure similar to that of kaolinite. Various methods have been proposed for the preparation of randomly oriented specimens.[12, 13, 14]

For kaolinites X-ray methods also demonstrate the variability of crystallinity which is often found in different samples. This variation has been attributed to random layer displacements parallel to the b axis of nb/3 [5] and to cation vacancies not always occurring in the same octahedral site in each layer.[4]

Hinckley[15] has proposed a method for determining the crystallinity from measurements made on selected non-basal reflections thus permitting evaluation of a parameter which is independent of the preferred orientation of the sample. Figure 1.3 indicates the relationships of the measurements involved. Noble[16] has shown that the resolution and intensity of the selected reflections are influenced by the degree of misstacking of the layers in the kaolinite structure.

1.4 The Chemical Composition of Kaolinite.

The ideal chemical formula for kaolinite is $Al_4(Si_4O_{10})(OH)_8$ corresponding to the composition: 46.54 % SiO_2, 39.5 % Al_2O_3 and 13.96 % H_2O. However, this exact composition is seldom, if ever, found in nature.[3]

Common impurities determined by chemical analysis include Fe_2O_3, TiO_2, MgO, CaO, Na_2O and K_2O (see Table 1.1).

Also most samples contain an excess of either silica or alumina. By combining the results of chemical analysis with X.R.D. analysis and selective chemical dissolution studies, it is possible to identify the ancillary minerals which are often associated with kaolinite. Such impurities include mica, smectite, quartz, anatase, rutile, feldspar and various types of iron oxides.[3] In addition to these mineralogical impurities, certain foreign ions have been found to be

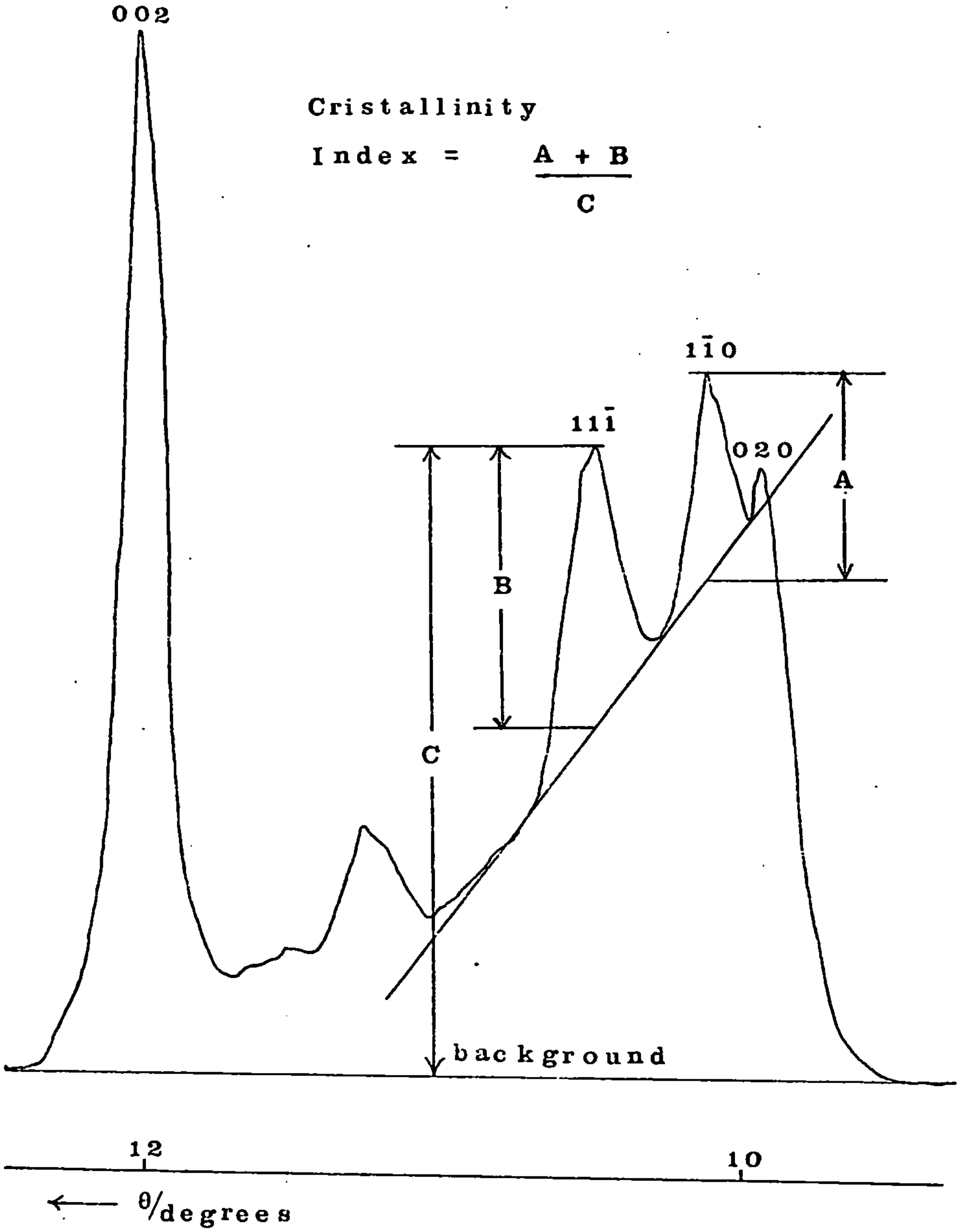

FIG. 1.3. Diagram to show Hinckley's crystallinity index for kaolinite.

substituted within the kaolinite structure.[17,18,19,20]

The impurities coexisting with kaolinite can easily lead to misinterpretation of experimental data. This being so, great care must be exercised when interpreting results from studies of naturally occurring samples.

TABLE 1.1 : X-ray Fluorescence Analysis of Typical Naturally Occurring Kaolins from Georgia, U.S.A., and from Cornwall, England.

	Kaolin from Georgia	Kaolin from Cornwall	Theoretical Composition
% Al_2O_3	38.46	36.55	39.50
% SiO_2	45.62	48.58	46.54
% TiO_2	1.56	-	-
% Fe_2O_3	0.34	0.42	-
% MgO	0.04	0.13	-
% CaO	0.08	0.03	-
% Na_2O	0.11	0.03	-
% K_2O	0.01	0.73	-
% ignition loss	13.78	13.53	13.96

1.5 The Morphology of Kaolinite.

Electron microscopy has shown that kaolinite exists as platelets with pseudo-hexagonal borders. There are, however, considerable variations in the morphological forms of kaolinite.[6] Some particles show elongation in one direction; some show deviations in the angularity of corners and others have irregular outlines. In addition, particle sizes vary from approximately 0.3 to 4 μm and thicknesses from 0.05 to 2 μm.

The possible relationship between crystallinity and morphological development of crystals in natural kaolinites has not been studied in detail. It has been found that poorly-crystallised kaolinite often displays plates with poor morphological characteristics.[2] However, disordered kaolinites have been found which comprise small, but well-formed hexagonal plates.[2,5]

For synthetic kaolinites no correlation has been observed between the internal structure and the macroscopic shape of the particles.[21]

1.6 The Surface of Kaolinite.

If a clay mineral is placed in an aqueous solution of a salt, it is found that cations which were originally bound to the surface of the clay particles may be exchanged for those in the solution. Thus clays are said to possess a cation exchange capacity.

Suggestions which have been made to explain the phenomenon of cation exchange of kaolinite[2] include:

(a) isomorphous replacement of trivalent ions, such as Al^{3+} or Fe^{3+}, for Si^{4+} in the tetrahedral layer and of divalent ions, such as Mg^{2+}, for Al^{3+} in the octahedral layer resulting in unbalanced charges within the structure, which are compensated by cations bound to the surface.

(b) ionisation of edge silanol groups.

However, recently, Ferris and Jepson[22] have shown, by careful measurements of the ion uptake of kaolinite, that there is no evidence for any definite cation exchange phenomena in pure kaolinite. Their observations were rationalised by suggesting the existence of an alumino-silicate gel coating on the kaolinite surface. The presence of an amorphous coating has been proposed by Van der Marel[23] to explain certain physical and chemical properties of kaolinite and evidence for such a layer has been provided independently by electron microscopic observations.[24]

In view of these considerations, in the present study reference will be made to adsorption of cations by kaolinite rather than cation exchange.

1.7 Thermal Transformations of Kaolinite.

Since the work reported in this thesis includes an account of the changes observed in the electron spin resonance spectra of kaolinites following thermal treatment, the structural changes of kaolinite on heating will be considered in this section.

The thermal reactions of kaolinite, which have been reviewed by Grim,[1] Holdridge and Vaughan,[25] Richardson,[26] and Brindley,[27] have been studied for at least a century and remain the subject of a considerable amount of research. Differential thermal analysis (D.T.A.) studies of kaolinites[26] show a number of characteristic reactions due to structural changes. Apart from a low temperature endothermic peak attributable to the removal of non-constitutional water, the D.T.A. curves of kaolinite exhibit:

(a) an intense endothermic peak at 773 to 873 K;
(b) an intense exothermic peak at 1123 to 1153 K;
(c) a weak exothermic peak at 1323 to 1523 K.

The endothermic reaction is due to dehydroxylation (i.e. the removal of structural hydroxyl groups as water) and results in the formation of metakaolinite. The small exothermic transformation has been attributed to the crystallisation of mullite and cristobalite on the basis of diffraction data. However, there is considerable controversy concerning the structure of metakaolinite and the origin of the main exothermic peak.

From single crystal X-ray studies, Brindley and Nakahira[28] showed the topotactic character of dehydroxylation. They suggested that water is lost more or less uniformly throughout the structure and that the metakaolinite formed retains a two-dimensionally ordered layer structure with disordered stacking of the layers along the c-axis. However, Taylor[29] proposed an alternative mechanism for the dehydroxylation of kaolinite in which no water is lost from regions where oriented conversion to a crystalline product occurs. According to this concept, the crystalline order in metakaolinite is dictated by the nature of the close packing of the oxygen atoms and Al^{3+} and Si^{4+} ions are distributed more or less randomly among the available tetrahedral interstices in the oxygen framework.

It is generally accepted, though, that the tetrahedral layer structure of kaolinite is retained in metakaolinite. Brindley and Gibbon[30] have suggested that the slight increase of the a and b parameters on dehydroxylation, as shown by electron diffraction patterns of single crystals, may be accounted for by a relaxation of the original twisted network. Various proposals have been made regarding the structure of the octahedral layer following dehydroxylation, but it is generally agreed that the Al^{3+} ions are in four-fold coordination. Brindley and Nakahira[28] suggested a sheet structure, but later investigations[30] favoured a chain-like or ribbon-like arrangement of the AlO_4 groups. Pampuch,[31] on the basis of infrared data, considered that about 12% of the hydroxyl groups are retained in metakaolinite and form part of a ribbon-like structure.

The exothermic transformation at about 1123 K has been interpreted both as recrystallisation of metakaolinite into γ-alumina and as nucleation of mullite.[2] Brindley and Nakahira[28] attribute the exothermic peak to crystallisation into an Al,Si spinel with Si^{4+} ions occupying octahedral sites. Nicholson and Fulrath[32] measured the exothermic heat of reaction and the value obtained was shown to correspond to the heat of crystallisation of amorphous silica into β-quartz. More recently Lemaitre et al[33] proposed that the exothermic effect had a double origin, namely simultaneous formation of (a) mullite and (b) spinel-type phase. Using specific mineralisers which promoted, selectively, formation of either (a) or (b), results had shown that the metakaolinite-mullite reaction could be represented by the following scheme:

$$\begin{tikzcd}
\text{METAKAOLINITE} \arrow[rr, "(a)"] \arrow[dr, "(b)"] & & \text{MULLITE} + x\ SiO_2 \\
& \text{SPINEL-TYPE PHASE} + SiO_2 \arrow[ur] &
\end{tikzcd}$$

(1.1)

In later studies,[34] they examined the influence of crystallinity of the original kaolinite on the reaction sequence and found that path (b) is the most probable reaction mechanism in disordered kaolinite while path (a) occurs readily in well-ordered kaolinites.

1.8 Previous Electron Spin Resonance Studies of Kaolinite.

Electron spin resonance (E.S.R.) spectroscopy was first reported in 1945, and has found diverse applications in many branches of science. This technique is applicable to atomic systems containing one or more electrons with unpaired spin and extensive discussions of the subject are available in published literature.[35,36,37,38]

The E.S.R. spectra of natural kaolinites in general contain two main features which consist of resonances centred at approximately $g = 2$ and $g = 4$ (see Fig. 1.4). Previous E.S.R studies[39] of natural kaolinites in this laboratory have shown that the apparent three-line spectrum in the region of $g = 4$, in fact, consists of four lines, two of which can be resolved only at 77 K. Theoretical considerations[40] indicated that the four lines were created by the superposition of two distinct sets of signals, which were attributed to iron (III) in different sites. It was proposed that one Fe^{3+} species (centre I) produced the single isotropic line at $g = 4.2$ while the other species (centre II) exhibited the three-line

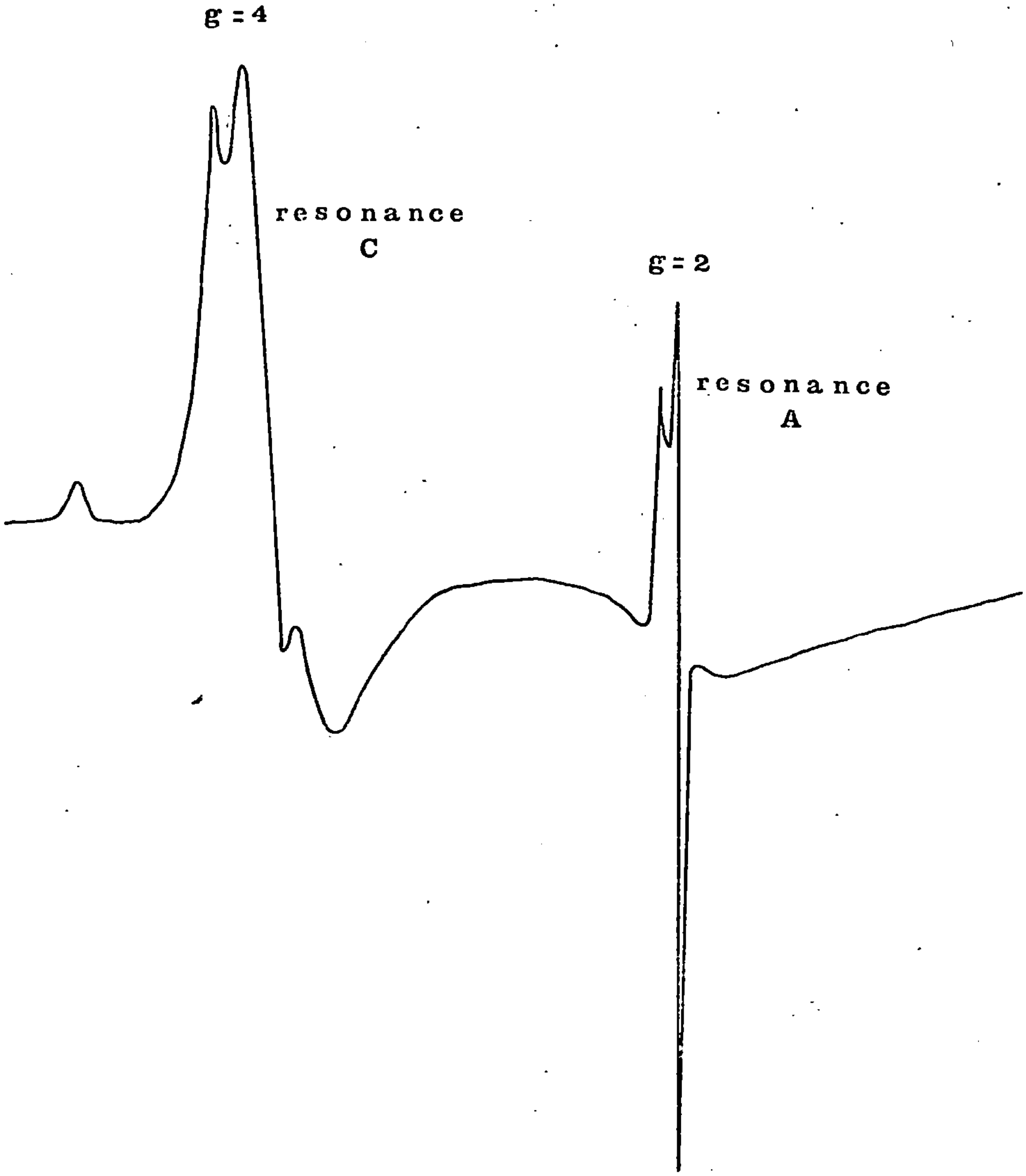

FIG. 1.4. E.S.R. spectrum of a typical natural kaolinite recorded at room temperature, full sweep.

spectrum with g-values of approximately 4.9, 3.7 and 3.5. These centres were interpreted as Fe^{3+} ions occupying sites of complete and partial orthorhombic symmetry respectively.[40] Angel and Hall[39] found that, following dehydroxylation, the resonance centred at $g = 4$ collapsed to a single isotropic line. From a consideration of the structure of metakaolinite[28,30] and of E.S.R. spectra of Fe^{3+} in silicate glasses,[41] they suggested that centres I and II might both be explained in terms of Fe^{3+} ions substituting for Si^{4+} in distorted tetrahedral sites.

Synthesis of an Fe^{3+}-doped kaolinite,[17] which exhibited an E.S.R. spectrum at $g = 4$ identical to spectra observed for natural samples, demonstrated unquestionably that Fe^{3+} ions were substituted in the kaolinite structure. In order to investigate the possible locations of the iron species, Jones et al[18] examined the effect of crystallinity on the E.S.R. line-shape parameter (namely the relative intensity of the two components of the resonance at $g = 4$) for a series of Fe^{3+}-doped synthetic kaolinites. They found a significant positive correlation between the two parameters and suggested that centre I was associated with layer stacking disorders and centre II with regions of regular stacking. Similar effects had been observed by Meads and Malden[42] for a series of naturally occurring kaolinites. However, the changes observed in the resonances at $g = 4$ for natural samples could have been due to varying amounts of micaceous impurities in the samples, as had previously been shown by Angel and Hall.[39] For this reason Jones et al[18] subjected samples of the same natural kaolinite to a range of pressures in order to produce a series of natural kaolinites with varying crystallinity indices, but identical impurities. The decrease in the E.S.R. lineshape parameter with decrease in crystallinity was explained by assuming that the symmetry of the environment of Fe^{3+} ions had been changed from that of centre II to centre I on increasing the structural disorder. Furthermore, from a consideration of the effect of pressure on the known structure of kaolinite, it was proposed that centres I and II occupied Al^{3+} sites in the octahedral layer. Further support for this hypothesis was provided by comparing E.S.R. spectra of kaolinites with those of gibbsite and of intercalation complexes of kaolinite.[18]

Herbillon and coworkers[19] subjected a number of kaolinites to treatment with hydrochloric acid which attacks the kaolinite by preferential dissolution of the octahedral layer.[2] It was found that for many of the samples the rate of dissolution of iron closely followed that of aluminium demonstrating that the iron was probably substituted in the octahedral layer. Furthermore the isotropic line at $g = 4.2$ decreased in intensity more quickly than the outer lines following increasing duration of the acid attack. This result would be expected if there were two distinct iron sites in the octahedral layer of kaolinites and one was less crystalline and more accessible to acid. For some of the kaolinites about 20% of the total iron content seemed to occupy sites which were more resistant to acid attack than the aluminium sites. It was, therefore, concluded that for these samples part of the iron was substituted either in the tetrahedral layer of kaolinite or in the mineralogical phases such as anatase, rutile and quartz, which are concentrated by the acid treatment.

The E.S.R. spectrum observed at $g = 2$ for kaolinite is shown on an expanded scale in Figure 1.5. It is clear that a number of weak lines (resonance B) are superimposed on the main two-line asymmetric signal (resonance A). Angel and Hall[39] found that preheating the clays for two hours at 573 K removed resonance B without causing any measurable changes in resonance A. Furthermore, X-irradiation of both untreated and heated kaolins reproduced and enhanced resonance B while resonance A was unaffected. From a consideration of its thermal stability, g-value and hyperfine splitting constant, it was concluded that resonance B could be attributed to either a trapped hole centre located on an Al-O bond following

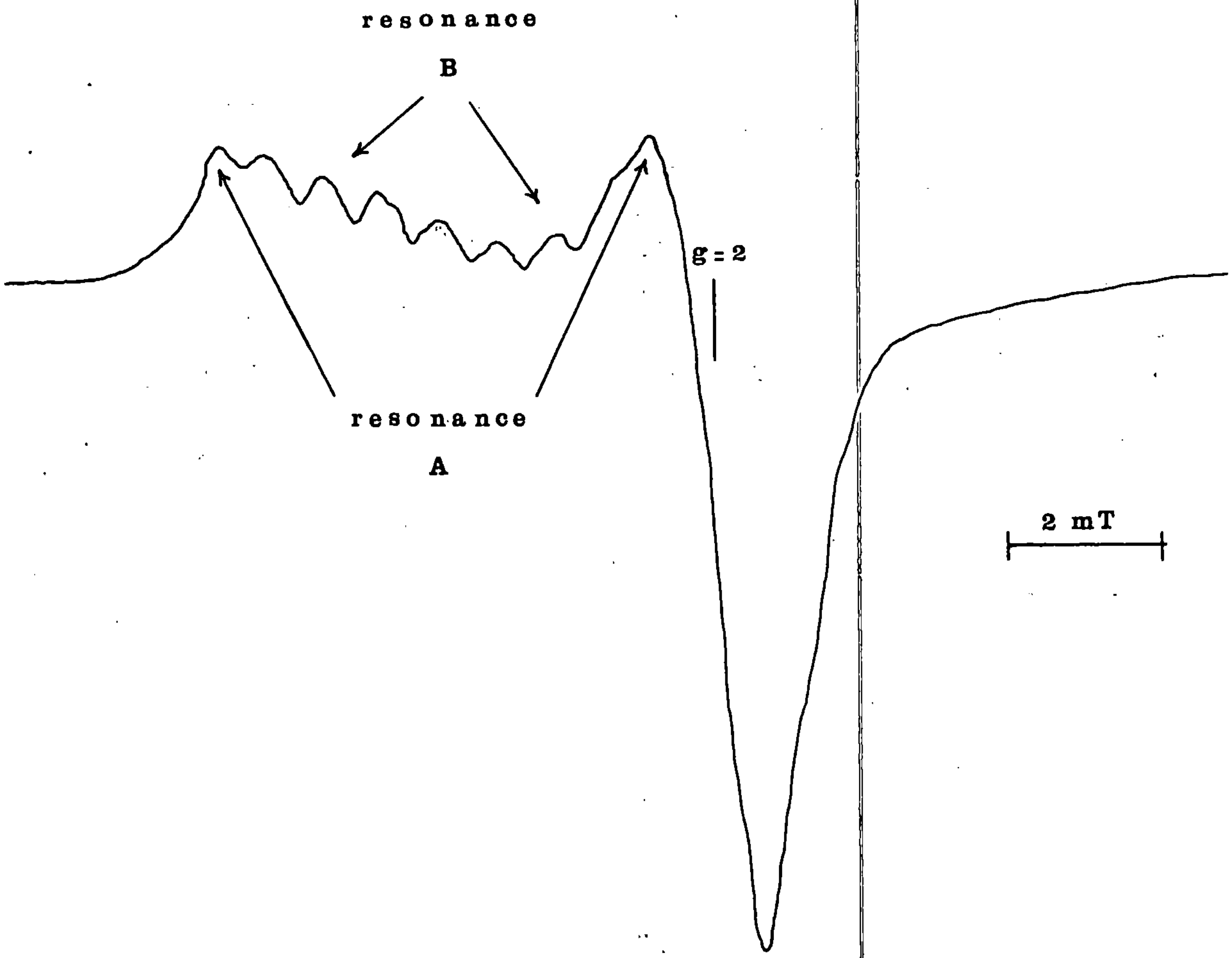

FIG. 1.5. E.S.R. spectrum of a typical natural kaolinite recorded at 77 K, from 0.32 Tesla.

substitution of Al^{3+} for Si^{4+} or an electron trapped at a hydroxyl vacancy in the octahedral layer.

In their study of natural kaolinites Angel and Hall,[39] on the basis of its high chemical and thermal stability, attributed resonance A to Fe^{3+} substituted in an axially distorted site. However, for synthetic kaolinites doped with Fe^{3+}, Angel et al[17] found no signal at $g = 2$. X-irradiation of both Fe^{3+} - doped and undoped synthetic kaolinites, while producing the B resonance, did not produce an asymmetric two-line resonance at $g = 2$ (resonance A) in natural kaolinites. These results indicated that resonance A was not attributable to Fe^{3+} nor was it merely an effect of irradiation on the intrinsic kaolinite structure.

Angel et al,[17] therefore, considered the possibility of substitution in the kaolinite structure of impurity ions which would require charge compensation and so might produce centres capable of trapping a hole following irradiation. It was considered that, for kaolinite, Mg^{2+} or Fe^{2+} substituting for Al^{3+} might provide the necessary precentre for the production of resonance A and, therefore, Mg^{2+} - doped kaolinites were synthesised. These samples did not exhibit E.S.R. signals, but following X-irradiation and annealing displayed a resonance at $g = 2$ identical to that found in natural kaolinites.

To summarise:

(a) The predominant asymmetric two-line resonance at $g = 2$ in natural kaolinites has been attributed to a defect centre (A-centre) stabilised by the presence of Mg^{2+} substituting for Al^{3+} in kaolinite. This defect is annealed only above 773 K, when dehydroxylation commences.

(b) Additional weak hyperfine signals at $g = 2$ can be attributed to other types of defect centres (B-centres) which can be destroyed and recreated by annealing below dehydroxylation temperature and X-irradiation respectively.

(c) The resonance at $g = 4$ consists of 2 components attributable to two substitutional Fe^{3+} centres (centres I and II) which are more probably located in the octahedral layer.

Angel and Hall[39] and Meads and Malden[42] also noted in the E.S.R. spectra of natural kaolinites weak broad resonances in the $g = 2$ region and also weak resonance lines centred at approximately $g = 2$ which were attributed to a vanadium impurity. However, these signals were not investigated in detail.

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CHAPTER 2.

AN ELECTRON SPIN RESONANCE STUDY OF VANADIUM IN NATURALLY OCCURRING KAOLINITES.

2.1 Introduction.

Vanadium is known to be an impurity in many clays.[1] Bundy et al[2] investigated the interdependence of various physical and chemical properties of a range of kaolinites from Georgia and found unexpectedly that an inverse relation existed between vanadium concentration and the magnitude of Hercules viscosity and crystallinity. They suggested that the relationships could be explained by assuming that vanadium occurred either as organic complexes or as adsorbed polyvalent anions.

Vanadium ions may exist in a number of different oxidation states, some of which are known to produce E.S.R. phenomena; this is discussed in more detail in section 2.3.2. Due to interaction of an unpaired 3d electron with the nuclear magnetic moment (nuclear spin of vanadium-51 = 7/2) the E.S.R. spectra often contain a distinct 8-line hyperfine pattern. Thus E.S.R. spectroscopy can provide a useful technique for the study of vanadium impurities associated with clays. Although a considerable amount of research has been carried out on the E.S.R. of vanadium in vanadyl porphyrins,[3,4,5] vanadyl phthalocyanine,[6,7] petroleum,[8-11] glasses[12-17] and single crystals of various materials,[18-22] there are few reports of E.S.R. of vanadium in clays. Hall and coworkers[23] have studied lignite and ball clay from South Devon using solvent fractionation techniques followed by E.S.R. They concluded that vanadium occurs as a heterogeneous mixture of vanadyl complexes in the organic matter associated with the samples. Hall[24] also observed a resonance in some kaolinites and dickites which could be assigned to vanadium impurities. Meads and Malden[25] noted a similar resonance in halloysite and a kaolin from Washington County, Georgia. The purpose of this work was to study vanadium in kaolinite in more detail.

2.2. Description of Samples.

Seventeen kaolinites from different mines were studied. Eleven were supplied by the Georgia Kaolin Company and contained one residual English kaolinite from St. Austell, Cornwall, and ten sedimentary kaolinites from Georgia, U.S.A. Two of the samples from Georgia known as Avant and Wrens, are of tertiary origin while the others (Chambers, Champion, Mines 11, 15, 24, 50 and 51) are cretaceous. For the English and cretaceous Georgia kaolinites coarse, medium and fine particle size fractions were provided. These fractions generally delineate the particle sizes used by the paper-coating industry, but were not obtainable for the tertiary kaolinites which have characteristically very fine particle size distribution. Chemical and particle size analyses were provided by the Georgia Kaolin Company for all the eleven samples.

An additional Georgia kaolinite, which will be referred to as GK, was obtained from English Clays, Lovering, Pochin and Company Limited (E.C.L.P.) together with a sample from which titanium oxides had been removed by froth flotation. The remaining five kaolinites were also supplied by E.C.L.P. and are described in more detail in chapter 5.

X.R.D. spectra of all the samples were recorded using a Hilger-Watts diffractometer and nickel-filtered Cu-K_α radiation. The only impurities detected in the English kaolinites were mica and smectite, while in the Georgia samples only anatase and rutile were observed. It should, however, be noted that the limit of detection of mineralogical impurities for this method was 5%.

2.3.1 Preliminary E.S.R. Study

E.S.R. spectra of the kaolinites described above were recorded at room temperature at X-band (9.3 GHz) using a Decca X1 spectrometer incorporating a Newport 7 inch magnet. The spectra exhibited 2 main features, called here resonances A and C, which were centred at approximately g = 2 and g = 4 respectively and have been considered in chapter 1.

In addition, all of the Georgia kaolinites exhibited a number of relatively weak lines centred at about g = 2 and will be referred to as resonance D (see Fig. 2.1(a)). However, this resonance was much less intense in the two

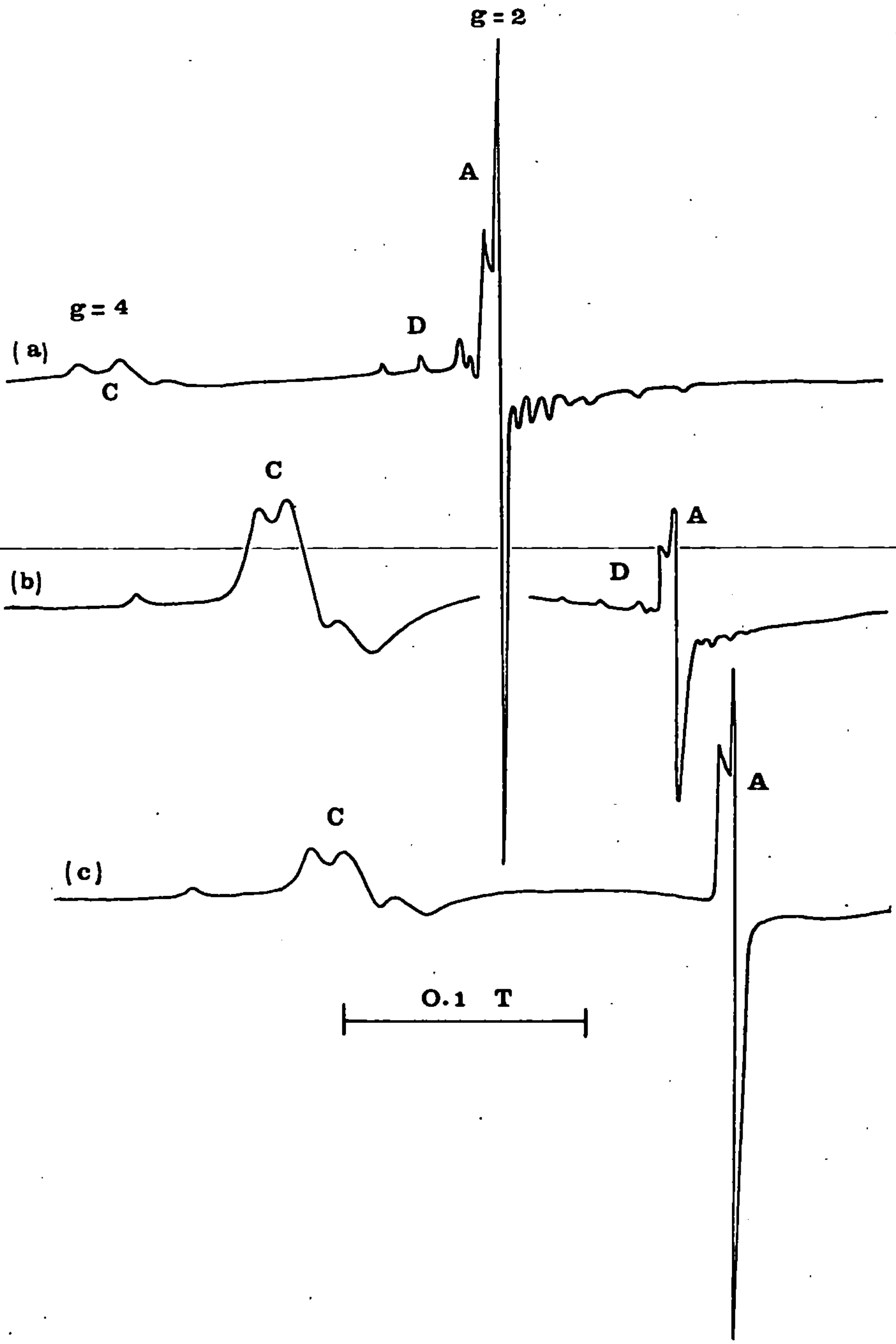

FIG. 2.1. E.S.R. spectra recorded at room temperature of
(a) Mine 24 kaolinite from Georgia, U.S.A.;
(b) Wrens kaolinite from Georgia, U.S.A.;
(c) Blackpool kaolinite from Cornwall, England.

tertiary kaolinites from Georgia (see Fig. 2.1(b)) and was not observed in any of the English samples (see Fig. 2.1(c)).

Resonance D consists essentially of overlapping sets of 8 peaks and 8 zero-crossings, which have different g-values and hyperfine splittings (see Fig. 2.2(a)). Such an asymmetric lineshape in polycrystalline samples is characteristic of a paramagnetic species in an approximately axially symmetric environment.[26] The vanadium-51 nucleus, which has nuclear spin of $I = 7/2$ and isotopic purity of 99.8%, is the only identifiable chemical impurity in the kaolinites which would give the observed hyperfine pattern of 8 lines. Therefore, resonance D can be attributed, with confidence, to a paramagnetic vanadium ion in an axially symmetric site. Spectra of this type may be fitted approximately to a spin Hamiltonian of the form:

$$\mathbf{H} = \beta\left[g_{\parallel} H_z S_z + g_{\perp}\left(H_x S_x + H_y S_y\right)\right] + A_{\parallel} I_z S_z + A_{\perp}\left(I_x S_x + I_y S_y\right) \qquad (2.1)$$

which gives rise to eight features associated with each of the two principal values of the g-tensor. Measurement of the parameters of the spin Hamiltonian (equation 2.1) was not attempted owing to the lack of intensity and resolution of resonance D combined with overlap with resonance A.

For a number of the Georgia kaolinites, E.S.R.

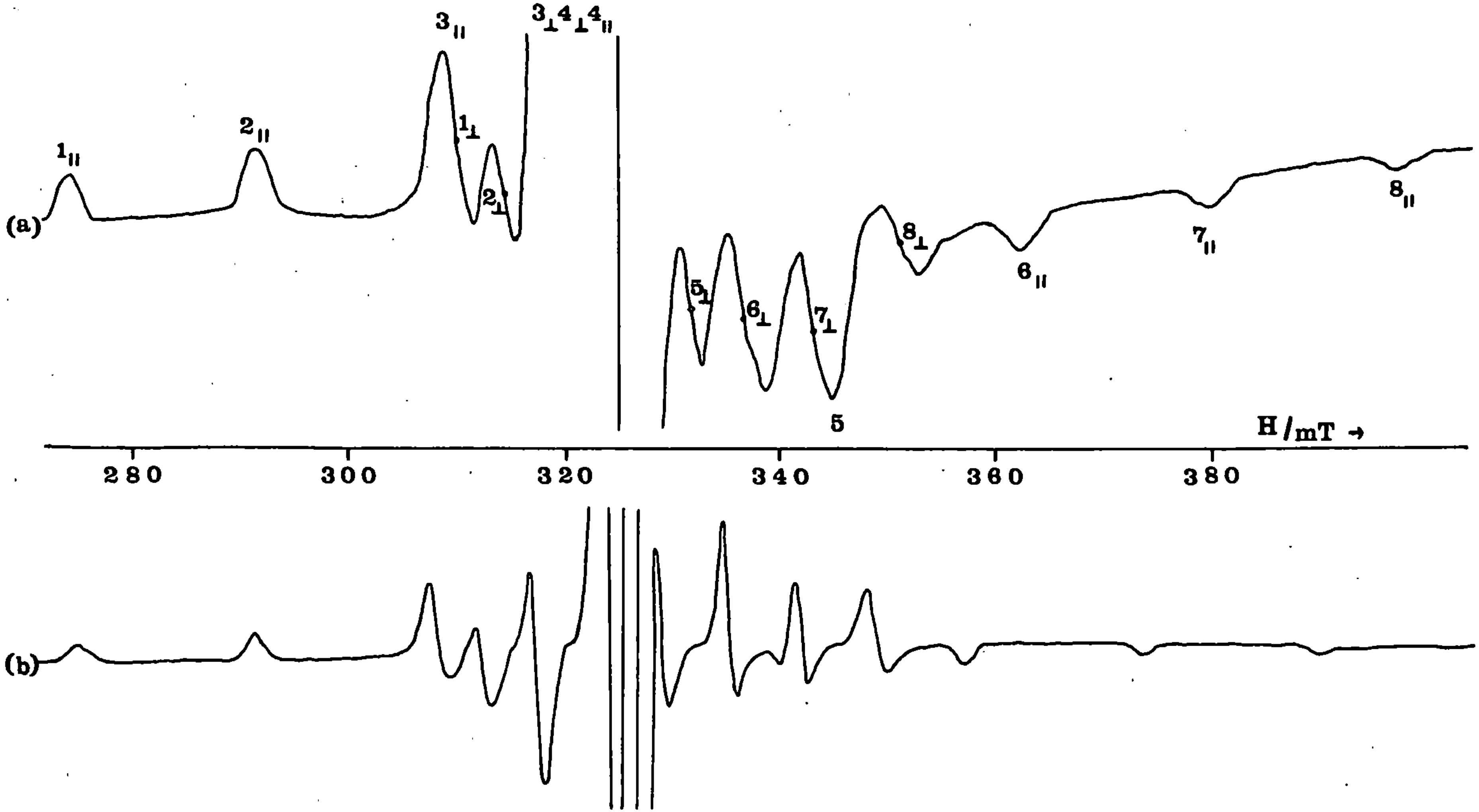

FIG. 2.2. E.S.R. spectra (recorded at room temperature) of:
(a) a typical Georgia kaolinite;
(b) Kuwait crude oil.

spectra were recorded at various temperatures from 77 K to 473 K. In all cases, similar spectra were obtained in which resonance D showed an increase in intensity with decreasing temperature.

Determination of the vanadium content of several kaolinites using flameless atomic absorption spectrophotometry was kindly carried out by A.J.Bale of the Institute of Marine Environmental Research (as part of his course at Plymouth Polytechnic leading to Licentiateship of the Royal Institute of Chemists). A Perkin Elmer 306 spectrophotometer with graphite atomiser unit HGA 72 was used and the untreated samples were injected as aqueous suspensions. The results are shown in Table 2.1. It can be seen that Wrens PD-1, in which resonance D is very weak, contains about 80 ppm vanadium whereas Mine 15 PD-1, which has a well-defined resonance, contains about 4 times as much vanadium. English PD-1 did not exhibit resonance D, but was found to contain a small amount of vanadium. This could be explained by one of the following postulations:

(a) the concentration of vanadium in English PD-1 is not sufficient to be observed by E.S.R.;

(b) the vanadium is not in a paramagnetic state;

(c) errors in the experimental determination may have resulted from the use of clay suspensions as opposed to true solutions.

SAMPLE		VANADIUM CONCENTRATION / p.p.m.
Mine 11	PD-1	209 ± 35
Mine 15	PD-1	303 ± 52
Mine 50	PD-1	163 ± 28
Wrens	PD-1	83 ± 14
Chambers	PD-1	149 ± 25
English	PD-1	21 ± 4

TABLE 2.1. Concentration of Vanadium in Various Naturally Occurring Kaolinites, as Determined by Flameless Atomic Absorption Spectrophotometry.

In flameless atomic absorption measurements, the influence of the matrix should be considered. In the above determinations, water was used as the blank, whereas it might have been better to have used a suspension of, say, a synthetic kaolinite known to be free from vanadium. Therefore, the concentrations of vanadium, quoted in table 2.1, should be considered as relative rather than absolute. Nevertheless, within the scope of the preliminary study, the vanadium analyses substantiated the assignment of resonance D to vanadium impurities.

2.3.2 Discussion of Results.

Of the 4 common oxidation states of vanadium which may be considered responsible for resonance D, vanadium (V) is eliminated as it has no 3d electrons and is diamagnetic. The spin states of V^{3+} and V^{2+} are S = 1 and S = 3/2 respectively. These ions have orbital singlet ground states in a crystal field of axial symmetry[27] and would, therefore, be recognised by the number of fine structure components (2S) in the spectra. In addition, liquid helium temperatures would be required to observe resonance for V^{3+} due to its very short spin-lattice relaxation time.[27] Thus, the observed resonance, which has only one fine structure component, can be logically attributed to tetravalent vanadium.

Vanadium (IV) may occur as the simple V^{4+} ion or as the vanadyl (IV) ion, $(VO)^{2+}$, which has a strong multiple covalent V-O bond. The hyperfine pattern found in the spectrum from Georgia kaolinites was found to be, similar to, but not directly superposable on that recorded for Kuwait crude oil (see Fig. 2.2(b)), which is known to contain vanadyl (IV) impurities.[28] However, it is clear from available literature[29] that studies of both the aqueous chemistry and the majority of the solid state chemistry of tetravalent vanadium involve $(VO)^{2+}$.

The possible location of vanadium in kaolinite samples will now be considered. Such an impurity may be:

(a) adsorbed on the surface of kaolinite and/or one of its ancillary minerals;

(b) associated with organic impurities;

(c) substituted in the kaolinite structure;

(d) substituted in the structure of one of its mineralogical impurities.

It has been shown recently that some cations are adsorbed on kaolinite as hydrated complexes.[30] It is probable, therefore, that the vanadium is present as the vanadyl (IV) ion, which is known to have well-characterised hydrated complexes.[29] Also, organic matter is known to contain vanadium as $(VO)^{2+}$ compounds.[31] Alternatively, if vanadium substitutes for aluminium in the octahedral layer or for silicon in the tetrahedral layer of kaolinite, on the basis of ionic size considerations, it would take the form of V^{4+} and not $(VO)^{2+}$. There is the possibility, though, that for V^{4+} substitution in either layer one V-O bond may possess more multiple bond character and so resemble the vanadyl (IV) ion coordinated with either 3 or 5 other oxygen atoms depending on its site in kaolinite. This is known to happen in vanadium (IV) oxide, where one bond is conspicuously shorter than the others in the VO_6 unit of its structure.[32] These possibilities would also apply to substitution in the ancillary minerals associated with kaolinite.

The preliminary work has shown that tetravalent vanadium is associated with Georgia kaolinites. Some vanadium could also have been present as V^{5+}, which is not observable by E.S.R. spectroscopy, or as V^{3+}, which would not have been detected at the temperatures used in this work. These possibilities will be discussed in chapter 6 with respect to later studies.

Following discussions with industrialists, it was clear that for practical applications a detailed knowledge of the situation of vanadium in the samples is more relevant than distinguishing between V^{4+}, $(VO)^{2+}$ or V^{4+} with some vanadyl character. This being so, various investigations were undertaken in an attempt to determine the location of vanadium in kaolinite.

2.4 The Effect of Particle Size on Resonance D.

It has been shown[2] that titanium oxides, mainly in the form of anatase, tend to be concentrated in fine particle size fractions of Georgia kaolins. For the samples studied in this work, with the exception of Gray, the TiO_2 content tended to increase with decreasing particle size, though, for some samples the relation was not clearly identified (see Fig. 2.3). In contrast, micaceous impurities tend to concentrate in coarse particle size fractions of kaolins. It has been found that there is a strong correlation between K_2O impurity determined chemically and the intensity of X.R.D. peaks of mica[2]. Indeed the mica content of kaolin is often deduced from a consideration of its X.R.D. spectrum together with its K_2O content.[33] On this basis, K_2O content was considered the only

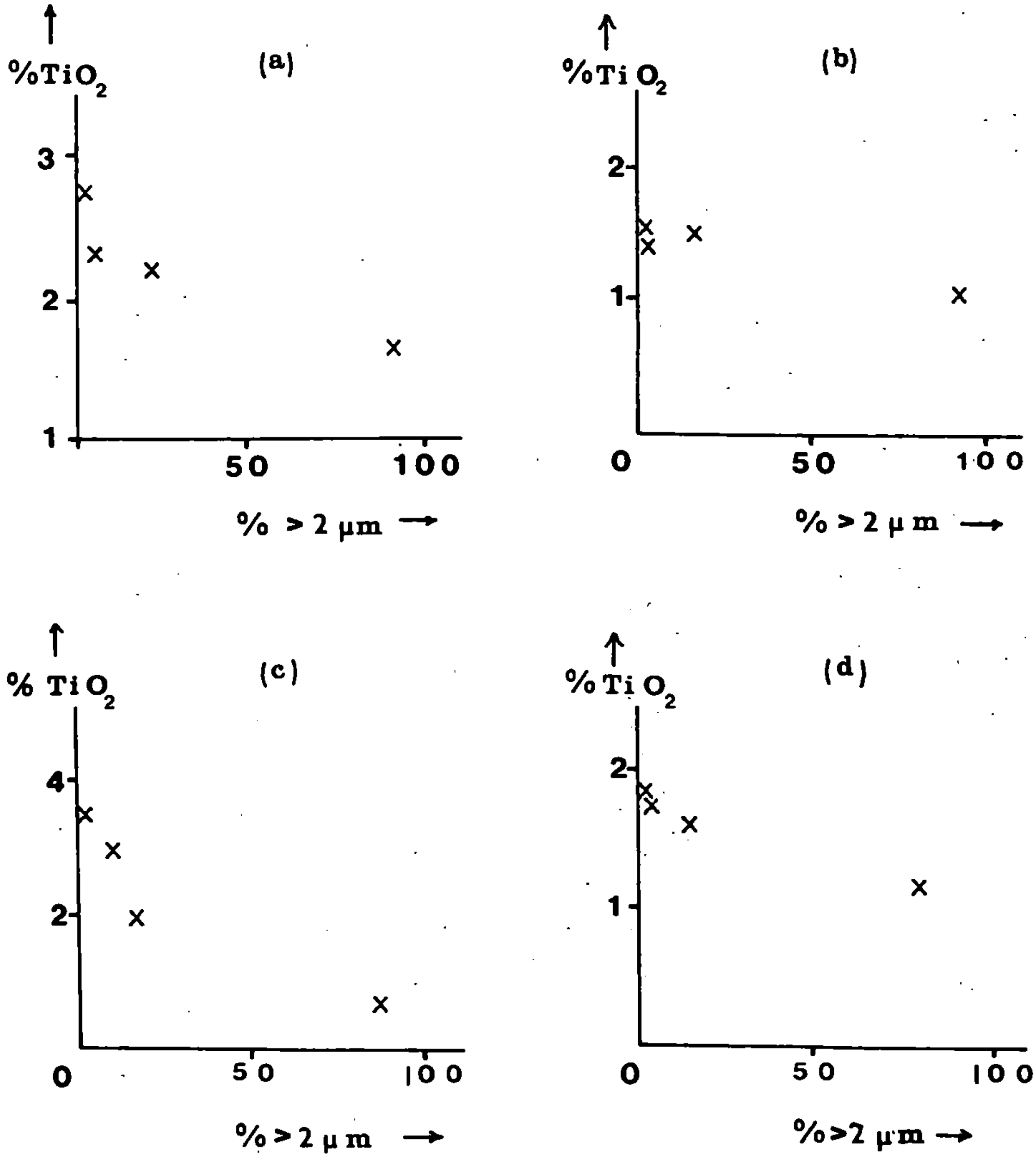

FIG. 2.3. Graphs of TiO_2 content versus particle size for various Georgia kaolinites.
(a) Chambers, (b) Mine 11,
(c) Mine 24, (d) Champion.

suitable parameter for comparing the variation of mica content with particle size in the samples under investigation. It was found that in all the samples K_2O content (and hence the inferred mica content) increased with increasing particle size (see Fig.2.4). It should be noted that the amount of K_2O in Georgia kaolinites is relatively small compared with the amount in English samples.

By comparing the concentration of vanadium in samples of varying particle size, it was anticipated that some evidence may be obtained to determine whether vanadium is associated with kaolinite or its micaceous or titaniferous impurities. At this stage of the work, the technique of flameless atomic absorption spectroscopy for determining the concentration of vanadium in kaolins was no longer available and alternative methods of analysis were considered.

Chemical analysis of kaolinites usually involves digestion in hydrofluoric acid or fusion with base to bring the clay into solution. Both these methods are time-consuming and sometimes hazardous. The elements in solution can then be determined by atomic absorption, gravimetric, volumetric, or spectrophotometric analyses. However, for the determination of vanadium levels in kaolins, which are of the order of 0.01%, it was established that these methods are subject to problems due to interference from the other elements of the clay or lack of sensitivity. Also it was found that X-ray fluorescence analysis was not suitable for estimating

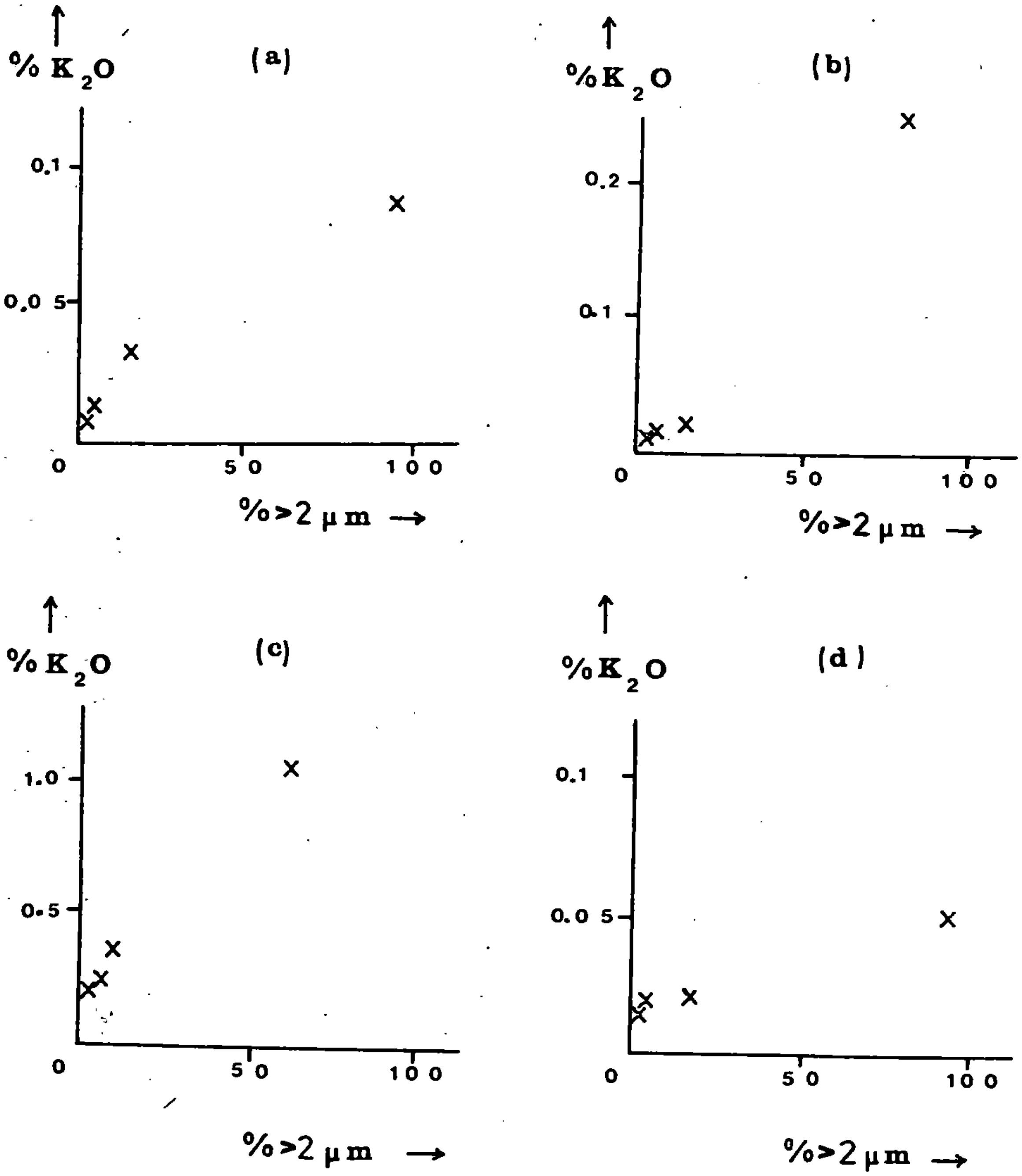

FIG. 2.4. Graphs of K_2O content versus particle size for various Georgia kaolinites.
(a) Champion, (b) Mine 50,
(c) Gray, (d) Mine 11.

vanadium in clays because of interference from chromium and titanium. (Confidential report supplied by the Institute of Marine and Environmental Research, Plymouth). A Hilger and Watts large quartz spectograph was the only apparatus available within the Polytechnic which might have provided a convenient method for a reliable determination of vanadium in kaolinites. However, even after considering the technique of spectrographic analysis in some detail[47,48] and following many repeated trials and discussions with experts at the British Ceramic Research Association, Stoke-on-Trent, no success was achieved.

Taking into consideration the limitations of the techniques described, E.S.R. spectroscopy was contemplated as a possible method for comparing the vanadium content of the kaolinite samples - at least, on a semi-quantitative basis. In fact, Saraceno et al[34] determined vanadium in petroleum quantitatively by E.S.R. and found close agreement with results from chemical analyses. More recently the vanadium content of protein solutions has been determined by E.S.R. to an acclaimed accuracy of ± 3%.[35] It must be emphasised that it is only the paramagnetic vanadium (and not necessarily total vanadium) that is detected by E.S.R.

For the E.S.R. technique the number of unpaired spins in a sample is proportional to the area under the absorption curve.[36] For vanadium spectra from kaolinites this area is difficult to measure, partly because of the large number of lines (which are recorded as first derivatives of the absorption curve) and partly owing to overlap with resonance A. However, for isotropic lines, the peak to peak amplitudes of the first derivative curves are proportional to the area under the absorption curves if the line shapes and linewidths remain constant.[36] In the present studies, it has been assumed that the same criteria may be applied for anisotropic lineshapes. Therefore, when considering the spectra of a series of samples from the same source differing only in particle size, it seems plausible to assume (as was done in this work) that the peak to peak height provides a reasonable measure of the relative concentrations of the paramagnetic vanadium.

Other factors which may affect the relative intensity of spectral lines, include:

(a) sample geometry,
(b) modulation amplitude,
(c) power level,
(d) degradation of Q-value of the cavity by the sample.

The sample geometry was kept constant by using identical fused quartz tubes of uniform diameter and approximately the same volume of substance for each determination. For each series of samples the microwave power level was adjusted to a constant level which prevented saturation. The modulation amplitude was also maintained at a constant level. Changes in Q-value of the cavity result from samples having different dielectric properties, but, as the samples were of the same origin in each set of experiments, and, as they were dried at 383 K prior to their E.S.R. study, no measurable changes of Q-value were detected.

As it has been assumed that the lineshape remains constant for spectra recorded for a set of samples differing only in particle size, it is reasonable to select one line of the hyperfine pattern as a measurable parameter to compare the relative concentrations of vanadium in the samples. In the determination of vanadium in petroleum, Saraceno and coworkers[34] chose the most intense central line, but this was not possible in the present work due to overlap with resonance A. The second line from the low field side of the spectrum was selected as this was found to be the most intense line free of overlap with other spectral lines.

For Georgia kaolinites, the results show that the relative concentration of vanadium appears to increase with decreasing particle size (see Fig. 2.5). The decrease suggests that vanadium is probably not associated with micaceous impurities, but may be associated with anatase or rutile and not the kaolinite. However, association of vanadium with the surface of kaolinite or inhibition of the crystal growth of kaolinite by vanadium are possible effects which might produce similar results.

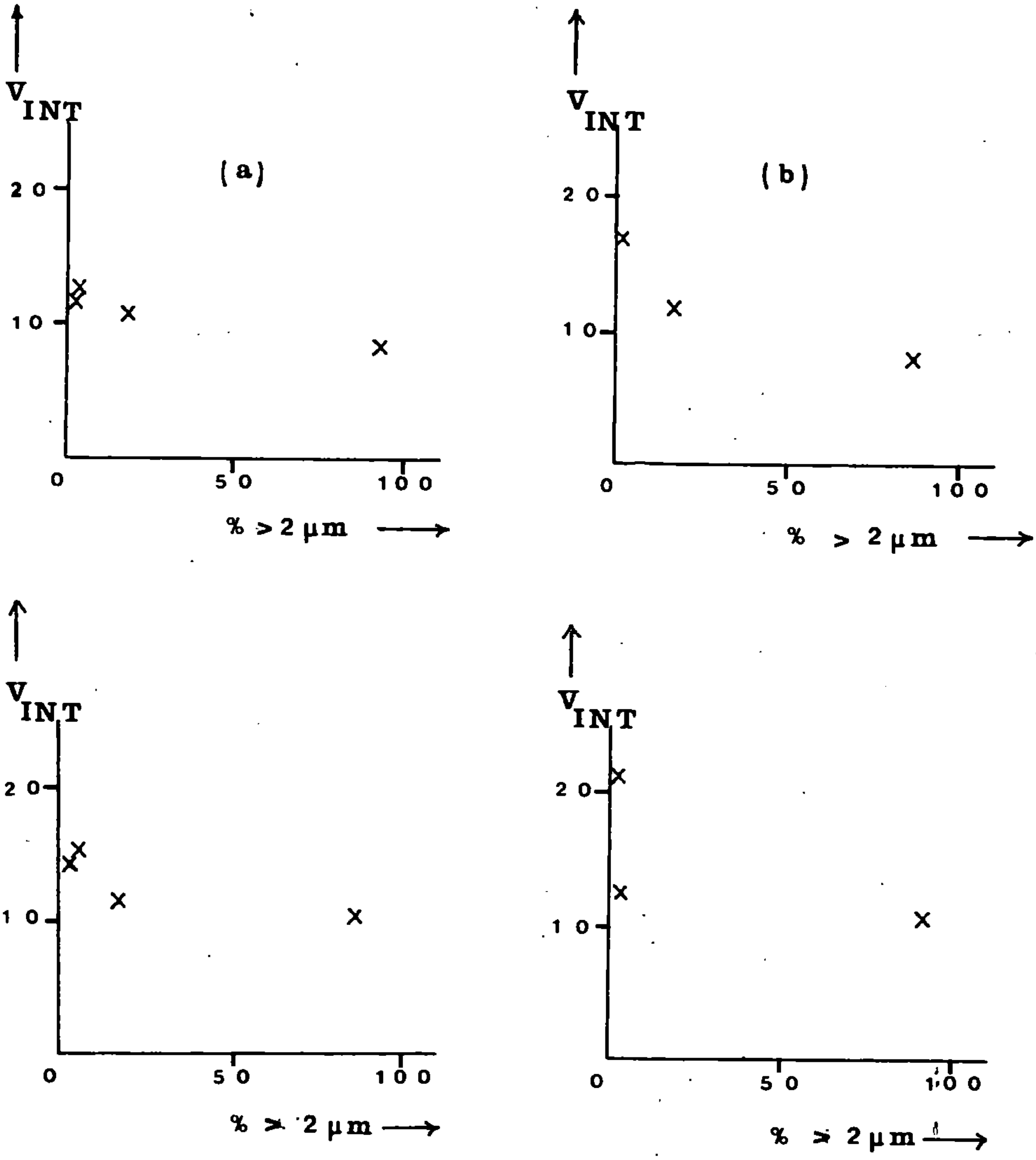

FIG.2.5. Graphs of the relative intensity of the vanadium resonance V_{INT}, versus particle size for various Georgia kaolinites.
(a) Champion, (b) Mine 15,
(c) Mine 24, (d) Mine 51.

2.5 The Effect of Magnetic Filtration on Resonance D.

The results of the previous section indicate that vanadium may be associated with titanium oxide impurities. Moreover, it is known that Georgia kaolinites contain appreciable amounts of such oxides (0.5 - 3%) and also have been found to exhibit vanadium resonances. In contrast, English kaolinites contain negligible quantities of titanium oxides and do not show vanadium spectra. For Georgia kaolins, Bundy and coworkers[2] found no correlation between vanadium and titanium contents obtained from chemical analysis, which suggests that vanadium is probably not associated with the titanium oxides.

In order to examine the possible association of vanadium with anatase or rutile a sample of kaolinite containing 1.5% titanium oxides was compared with a similar sample which had been refined by froth flotation to reduce the titanium impurity to about 0.2%. No change in the intensity of the vanadium signals for the two samples was noted thus providing further evidence that vanadium is not associated with titanium oxides.

Additional information was obtained by considering two samples which exhibited relatively intense vanadium resonances (Mine 24 and Mine 51) and had been magnetically refined. Magnetic separation techniques are used in the china-clay industry to increase the whiteness of kaolins by removing the weakly magnetic iron-stained titaniferous and micaceous impurities.[37, 38]

10 g of clay was deflocculated in 50 cm^3 of 0.03% aqueous dispex solution at pH 8. This suspension was allowed to pass slowly through the magnetic filtration apparatus shown in Fig. 2.6. with the magnet energised. The filter was rinsed with small volumes of dispex solution and the filtrate and washings were collected. The current supplied to the electro-magnet was then reduced and the residue was flushed into a separate container. After twice repeating the process, the filtrate and the combined residues were separately flocculated with hydrochloric acid and centrifuged. They were washed free of chloride and dried at 383 K for two hours.

E.S.R. and X.R.D. spectra were recorded for the filtrates, residues and unrefined samples. X.R.D. showed that the residues contained only small amounts of kaolinite mixed with anatase and rutile. These impurities could not be detected in the filtrates. However, for both the refined and unrefined kaolinite the E.S.R. signals due to vanadium were identical.

The results obtained from the magnetic separations supported those obtained from the previous experiments and again imply that vanadium is not associated with the titanium oxide impurities of kaolinite. Although micaceous impurities were not detected by X.R.D. in either the untreated sample or the residue, it is likely that mica was concentrated in the residue. The results

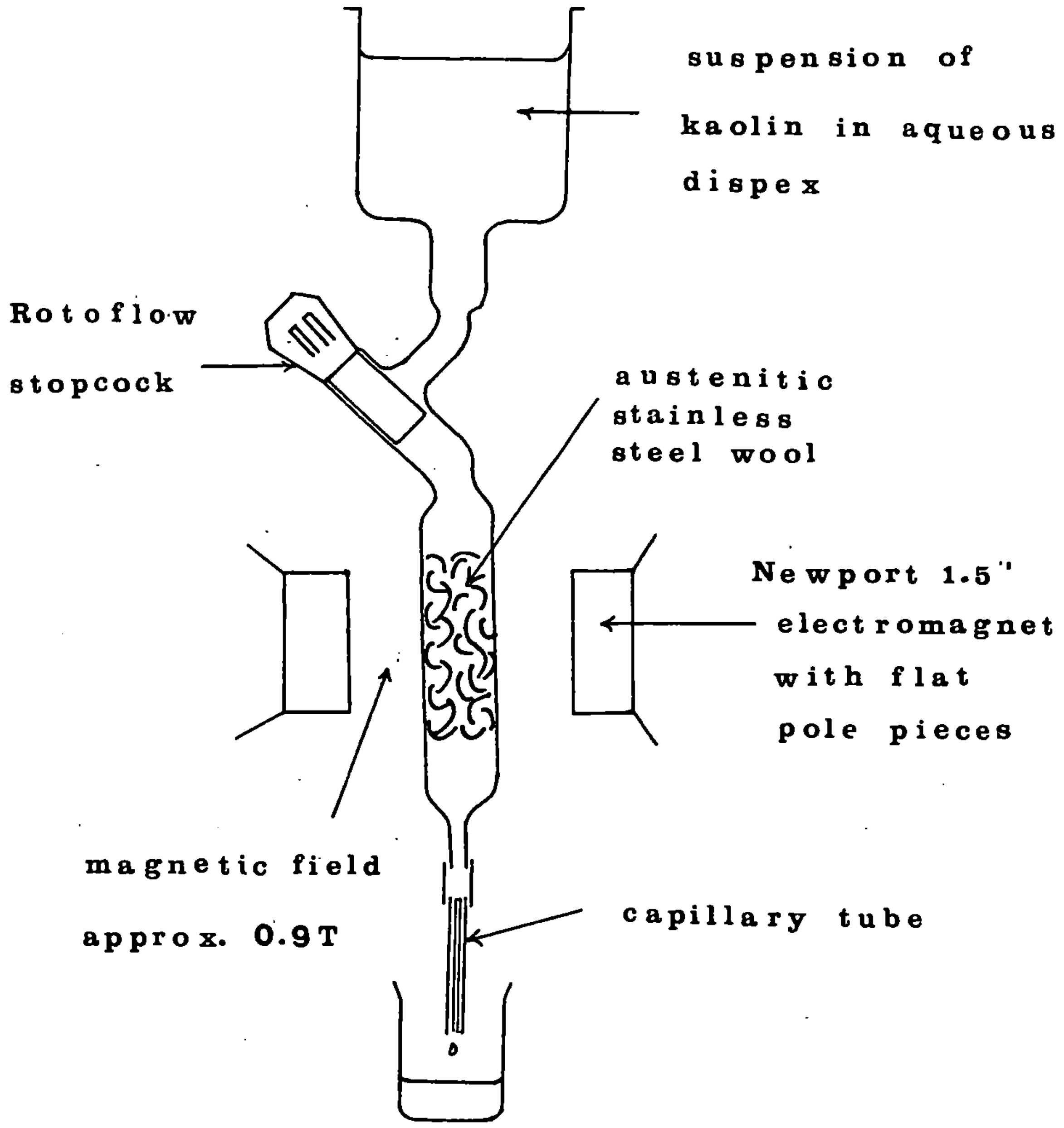

FIG. 2.6. Diagram of magnetic filtration apparatus.

of magnetic separation studies, therefore, show that vanadium is probably not associated with mica.

2.6 The Effect of Thermal Treatment on Resonance D.

Kaolinite is known to exhibit very distinct changes in crystalline phase on heating at elevated temperatures. The changes have been described in chapter 1. These thermal effects have provided valuable information in previous studies of resonances A and C in English kaolinites.[29] It was, therefore, anticipated that for kaolinites exhibiting vanadium resonances similar studies might prove useful. Samples from Mine 15 and Mine 24 were chosen as they both exhibit fairly intense vanadium signals. They were heated at various temperatures between 473 and 1473 K and at various times differing between 1 and 24 hours. E.S.R. and X.R.D. spectra were recorded for each sample.

It was found that both E.S.R. and X.R.D. spectra characteristic of unheated kaolinite remained unchanged up to preheating temperatures of 723 K (see Fig. 2.7 (a)). However, above this temperature, the intensity of the X-ray peaks began to decrease as a result of dehydroxylation and a decrease in the intensity of the vanadium resonance was observed (see Fig. 2.7 (b)). As the temperature or period of heating was increased, the X.R.D. pattern collapsed to the broad diffuse band characteristic of metakaolinite together with a weak peak with a d value of 3.52×10^{-10}m, which can be

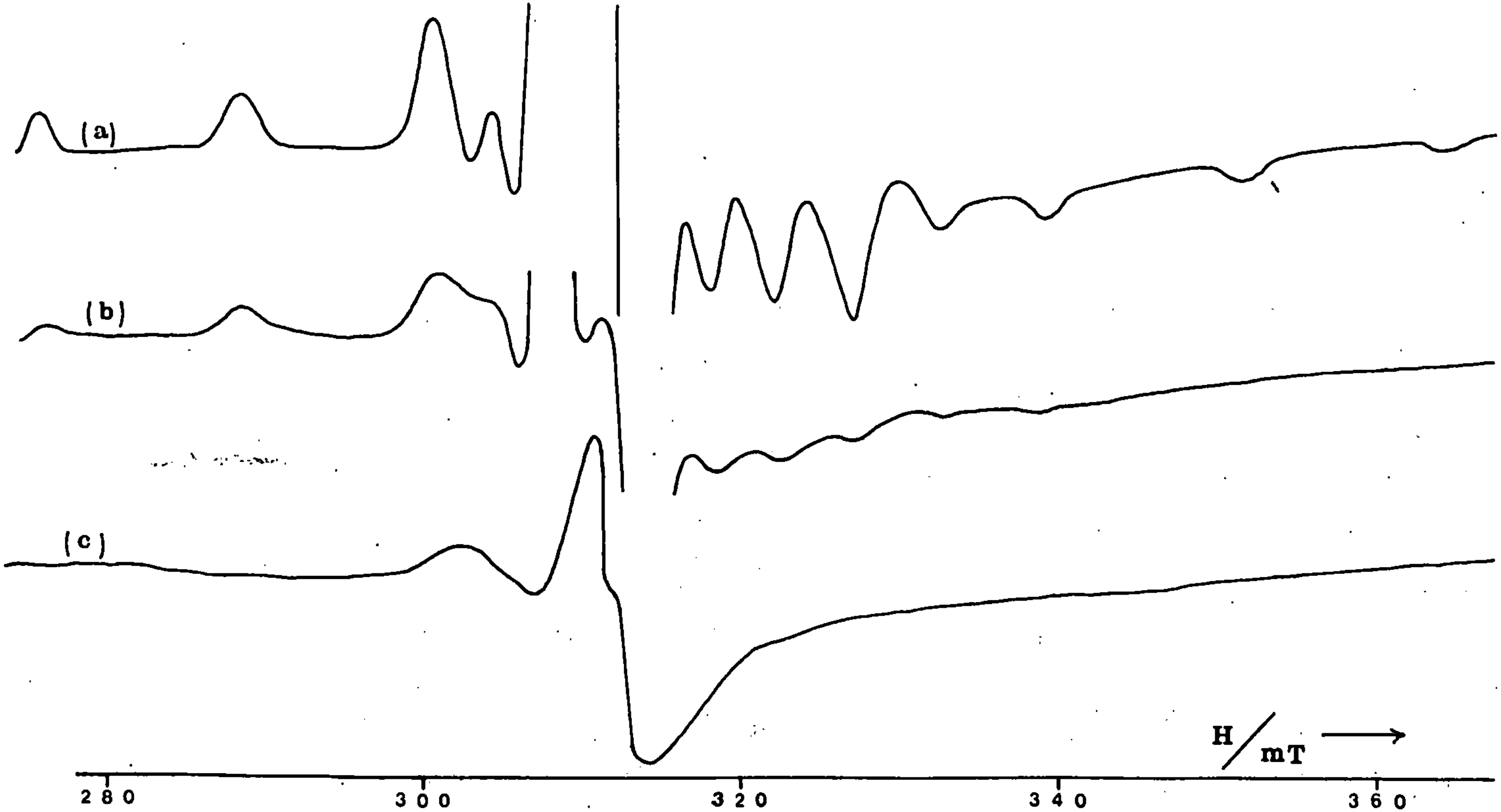

FIG. 2.7. E.S.R. spectra recorded at room temperature for Mine 15 kaolinite following heating at:
(a) 673 K for 24 hours, (b) 773 K for 1 hour, (c) 973 K for 1 hour.

attributed to anatase impurities. Also the vanadium signal collapsed to a very weak broad asymmetric 2-line resonance (see Fig. 2.7 (c)). Preheating samples at 1473 K for 2 hours led to the formation of mullite, which was identified by its X.R.D. spectrum, but there was no further change in the E.S.R. spectrum.

As dehydroxylation has a pronounced effect on the vanadium resonance, it seems feasible that vanadium is substituted within the kaolinite structure. If vanadium were associated with the surface of kaolinite, dehydroxylation would not be expected to have such an effect. At temperatures of 773 K, which were found to modify the vanadium resonance, one would not expect any structural change to occur in the anatase or rutile impurities.[45] In addition, it is known that in micas dehydroxylation occurs at higher temperatures.[40] However, some smectites[40] dehydroxylate at temperatures similar to those found for kaolinites and could, therefore, possibly be the source of the vanadium resonance.

The collapse of the vanadium signal will be discussed in detail in chapter 6.

2.7 The Effect of Chemical Treatment on Resonance D.

The location of vanadium within Georgia kaolinites was further investigated by chemical dissolution techniques combined with E.S.R. spectroscopy. First samples of Mine 15 PD-1 were boiled with a 1 : 1 mixture of concentrated sulphuric acid and concentrated nitric acid for periods varying between 1 and 6 hours.

Samples were then centrifuged, washed free of nitrate and dried at 383 K for 2 hours. Another sample was similarly treated with an aqueous solution of sodium hydroxide at a concentration of 0.5 mol dm^{-3}.

No changes in the X-ray spectra were observed for the samples subjected to alkaline attack, but the intensity of the basal reflections was considerably reduced following acid dissolution. However, for all these chemically treated samples no measurable changes in the vanadium resonance occurred.

The acid mixture used is a well known oxidising agent and, therefore, one would expect any organic matter associated with the kaolinites to have been removed when the samples were so treated. As there was no change in the vanadium resonance, it may be safely assumed that vanadium impurities in Georgia kaolinites do not occur as organic complexes. Confirmation of this supposition was achieved by warming a sample with 30% aqueous hydrogen peroxide solution for 3 days; its vanadium spectrum was identical to that of the untreated kaolin.

Alkaline dissolution is known to remove amorphous silica and alumina.[41] Therefore, one would expect this treatment to have a marked effect on the surface of kaolinite, which is thought to consist of an amorphous gel coating.[42,43] Moreover, deflocculation of samples in alkaline media followed by centrifugation has been found to remove smectite impurities.

It was thus concluded that vanadium is neither a surface contaminant of kaolinite nor associated with smectites.

Hydrochloric acid is known to dissolve clay minerals by preferential attack of the octahedral layer,[44] but anatase and rutile are resistant to acids.[46] Therefore, to investigate in more detail the possible influence of anatase or rutile on the clay system, samples were treated with hydrochloric acid. Kaolinites Mine 15 PD-1 and Mine 24 PD-1 were warmed at 353 K with hydrochloric acid at a concentration of 1 mol dm^{-3}. At intervals ranging from 1 hour to 7 days, samples were removed, centrifuged and washed free of chloride. They were then dried at 383 K for 2 hours prior to examination by E.S.R. and X.R.D.

The X.R.D. pattern of kaolinite persisted in all the treated samples. However, for those which had been subjected to acid attack for 7 days, the peaks were considerably reduced in intensity and broadened. There was little observable change in the vanadium resonance following acid dissolutions for up to 3 days. More prolonged treatment resulted in a decreased intensity and a corresponding reduction of resonances A and C was also noted.

Since the vanadium resonance decreased with increasing duration of the acid treatment, it was deduced that vanadium is not associated with titanium oxides, but may be substituted in the kaolinite structure, or possibly in the structure of micaceous or smectite impurities. Further, it seems probable that vanadium is present in the octahedral layer of these minerals. However, it has already been inferred that vanadium is not associated with smectites and micas.

2.8 Partial Orientation Studies of Resonance D.

Single crystals of kaolinite sufficiently large for orientation studies by E.S.R. do not exist. Nevertheless, it has been found that valuable information may be obtained by investigating bulk samples in which preferential orientation of the kaolinite particles has been deliberately induced by pressure.[39]

Samples of Georgia kaolinites were pressed into discs using a Research and Industrial Instruments Company 30 ton hydraulic press and evacuable 13 mm die. A narrow strip of the disc was placed vertically in a quartz sample tube and this was positioned in the cavity of the E.S.R. spectrometer. Spectra were recorded with the disc plane at various angles to the external magnetic field.

The vanadium resonance exhibited a definite orientation dependence. When the magnetic field was approximately perpendicular to the disc plane (corresponding to the kaolinite C-axis being aligned approximately parallel to the field), the component lines relating to $g_{\parallel}$ were enhanced (see Fig. 2.8(a)). When the plane of the disc was approximately parallel to the field (corresponding to the kaolinite c-axis

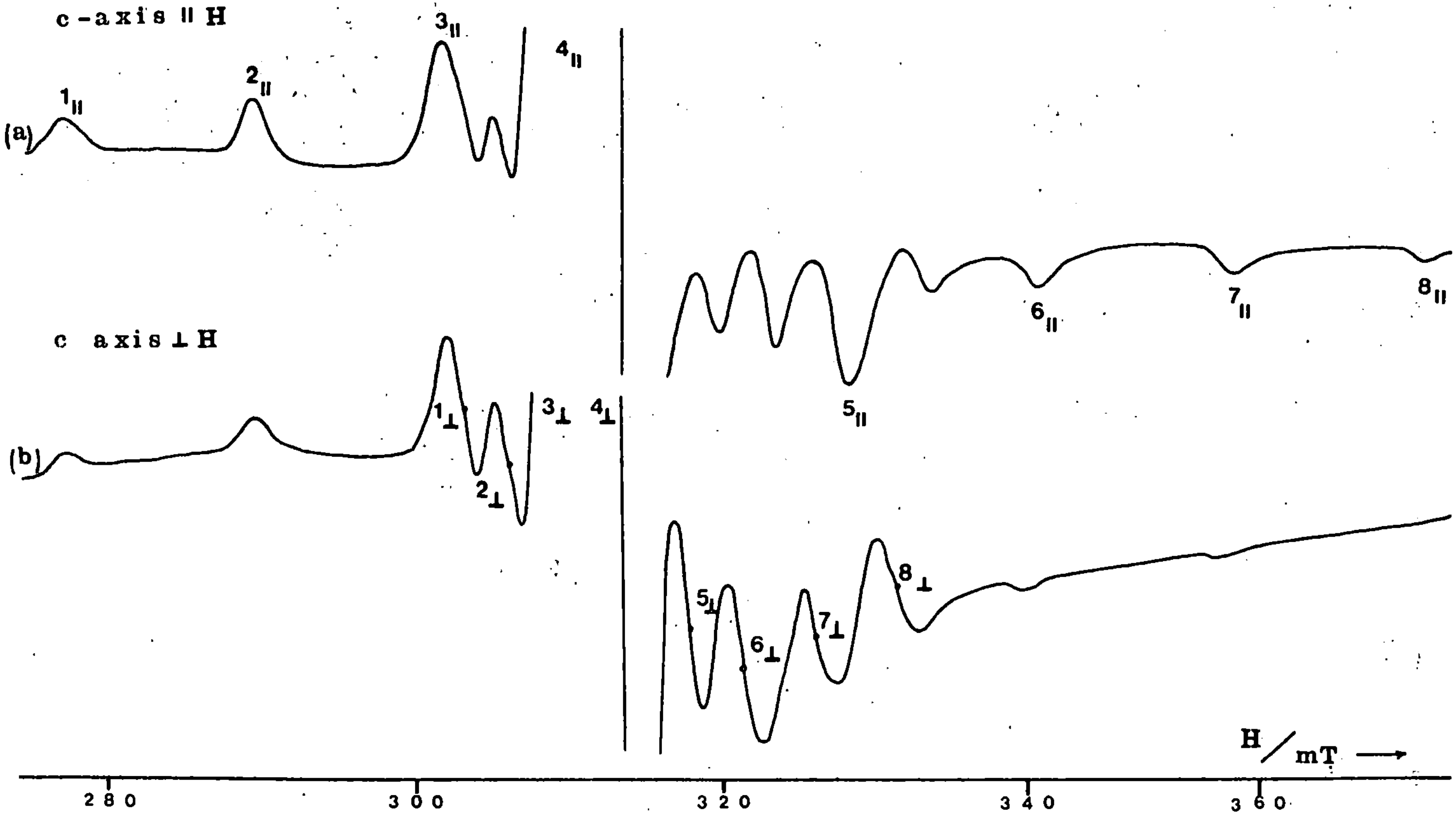

FIG.2.8. E.S.R. spectra of oriented samples of Mine 24 kaolinite recorded at room temperature.

being aligned approximately perpendicular to the field), the $g_{\perp}$ lines were enhanced (see Fig. 2.8 (b)). Measurements at intermediate angles showed progressively changing intensities.

The orientation effects show that the axis of symmetry of the vanadium centre resulting in resonance D lies close to the kaolinite c-axis. Therefore, vanadium may be substituted for either silicon or aluminium in the kaolinite structure or it may be adsorbed on the planar surfaces of kaolinite particles. However, these results do not exclude the possibility that vanadium is associated with smectites or micas, as these minerals also have a plate-like morphology and so tend to orientate with the basal planes of their particles predominantly in or near the disc plane. However, previous results have indicated that vanadium is probably not associated with these minerals.

2.9 The Effect of Relative Humidity on Resonance D.

In E.S.R. studies of paramagnetic species in solution, an isotropic spectrum is observed when the correlation time of the tumbling of the species is less than the E.S.R. time-scale of observation. McBride[30] found that kaolinites with Cu^{2+} or Mn^{2+} on the surface exhibited isotropic resonances when left in an atmosphere at 100% relative humidity, but at lower relative humidities anisotropic spectra were observed. These results were interpreted on the basis that, at high humidity, there are several layers of water molecules adsorbed on the kaolinite surface and so the cations have a higher degree of mobility. However, at low humidity, only a monolayer of water may be present resulting in a much lower mobility.

If vanadium is adsorbed on kaolinite (or one of its mineral impurities) a similar change in the nature of its E.S.R. signal would be expected at high relative humidity values. Therefore, samples of the Georgia kaolinites were kept in a water-vapour saturated container for 2 days to prepare fully hydrated clays. These were then quickly transferred to quartz E.S.R. tubes and sealed. E.S.R. spectra were recorded immediately.

In all samples, the vanadium resonances remained anisotropic regardless of the value of relative humidity. These results indicate clearly that vanadium is not located on the surface of these kaolinites.

2.10 Summary.

This E.S.R. study has shown that naturally occurring Georgia kaolinites possess a resonance centred at $g = 2$, which can be assigned to tetravalent vanadium. By combining E.S.R. spectroscopy with various techniques, it may be deduced that vanadium is substituted in the kaolinite structure, probably in the octahedral layer. Further studies of vanadium associated with synthetic kaolinites are presented in the next chapter.

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CHAPTER 3.

SYNTHESIS OF VANADIUM-DOPED KAOLINITES

3.1. Introduction.

A large volume of literature is available describing various syntheses of kaolinite which has been reviewed by Grim[1], and by Jones[2]. The methods reported generally fall into 3 categories:

(a) hydrothermal reaction of alumino-silicate gels or glasses at temperatures above 473 K;

(b) hydrothermal alteration of minerals, such as feldspars, at elevated temperatures;

(c) reactions at temperatures below 473 K.

However, not until 1974[3,4,5] were methods developed in this laboratory for the synthesis of selectively doped kaolinites. These samples have been used to provide an interpretation of E.S.R. spectra of kaolinites with respect to resonances A and C.

To support (and possibly extend) the conclusions drawn from the E.S.R. study of natural kaolinites with respect to the vanadium resonance, the synthesis of vanadium-doped kaolinites was attempted. So far as the author is aware, there have been no previous reports of the synthesis of kaolinite doped with vanadium.

3.2. Methods of Synthesis.

Vanadium-doped kaolinites were synthesised by hydrothermal reaction of alumino-silicate gels, which were prepared by hydrolysis of liquid A[5].

This liquid is formed when 1 mole of tetraethyl-silicate is refluxed with 1 mole of hot molten aluminium isopropoxide immediately following its vacuum distillation. The method had previously been developed in this laboratory and is described in detail elsewhere[5]. Hydrolysis of liquid A may be schematically represented by the following equation:

$$2\ \underset{\text{LIQUID A}}{\mathrm{Al(OC_3H_8),\ Si(OC_2H_5)_4}} + 7H_2O \longrightarrow \underset{\substack{\text{ALUMINO-SILICATE}\\ \text{GEL}}}{\mathrm{Al_2O_3,\ 2SiO_2}} + 8C_2H_5OH + 6C_3H_8OH \tag{3.1}$$

3.2.1. Synthesis via Vanadium-Doped Gels.

Various commercially available vanadium compounds were used as dopants. These were either dissolved in absolute ethanol and added to liquid A prior to hydrolysis or dissolved in the water used to hydrolyse liquid A. Liquid A was hydrolysed with excess deionised water over a period of about 6 weeks with occasional shaking and the resultant gel was dried at 383 K and then fired at 1273 K for 24 hours to remove any remaining organic matter.

The gels were reacted in stainless steel bombs similar to those designed by Tuttle[6]. A suspension of 0.4g of gel in 1.5cm^3 of water was placed in a polyfluoroethylene (P.T.F.E.) tube plugged with P.T.F.E. stoppers at each end ensuring that a 70% filling factor was obtained. The tube was placed in the pressure vessel and sufficient water was added so that the pressure of the contents and the surroundings of the tube would be equal during the reaction. The bomb was sealed and maintained at 553 ± 5 K for 7 days in a furnace controlled by a Eurotherm P.D.1 controller.

At the end of this period, the bomb was allowed to cool to room temperature. It was unsealed and the reaction product was washed from the P.T.F.E. tube and dried at 283 K. The synthetic kaolinites which were formed by this method (and which will be referred to as the VK-1 series), were then studied by X.R.D. and Electron Microscopy (E.M.). It was found that kaolinite was obtained with only 2 dopants: vanadium (III) chloride and vanadyl (IV) nitrate (see Fig. 3.1(a)). These synthetic kaolinites consisted of small (less than 0.5 μm) well-formed hexagonal plates (see Fig. 3.2). Using other dopants boehmite was formed as well as kaolinite (see Fig.3.1(b)).

Boehmite is recognised as being a co-product in the synthesis of kaolinite from alumino-silicate gels possessing an alumina content greater than 40%, which is the normal value found in kaolinites. In the extreme case where a gel containing 100% alumina was used, only boehmite was formed (see Fig.3.1(c)).

The formation of a mixture of kaolinite and boehmite from some of the doped gels would seem to indicate that hydrolysis of liquid A (which, in the absence of dopant, produces a gel containing 40% alumina) is affected by

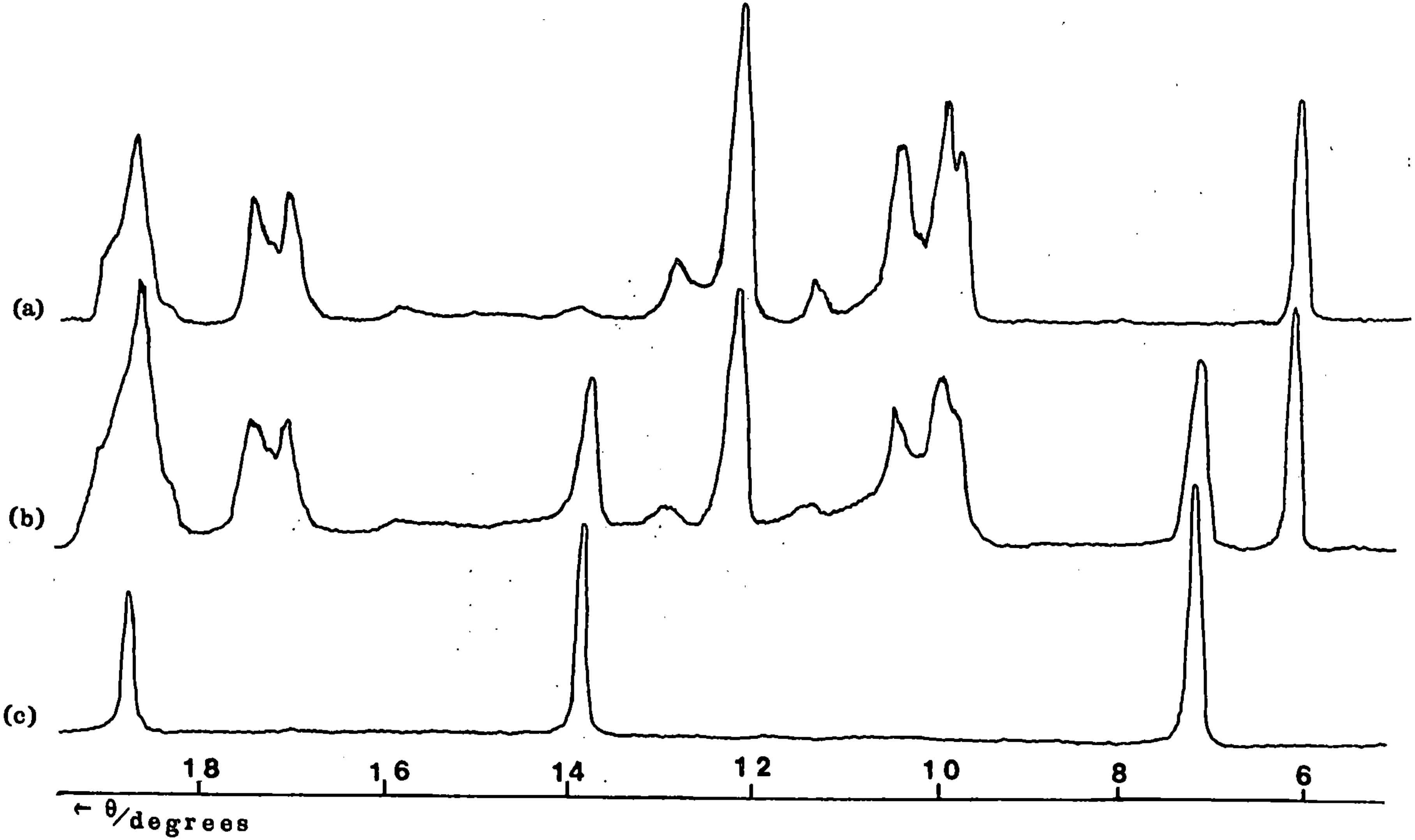
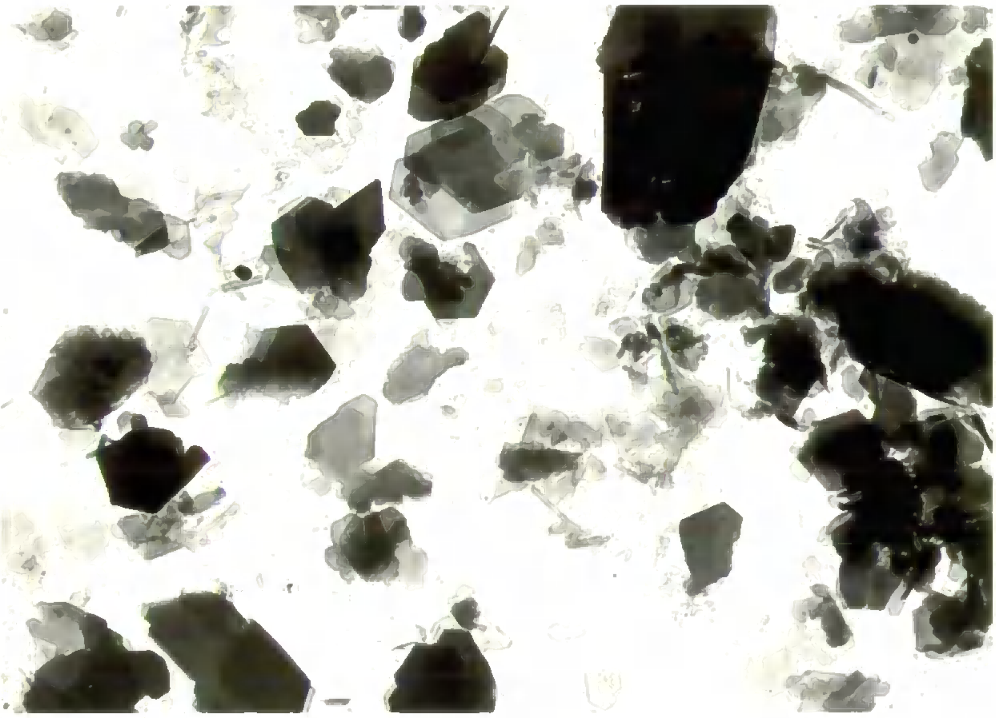


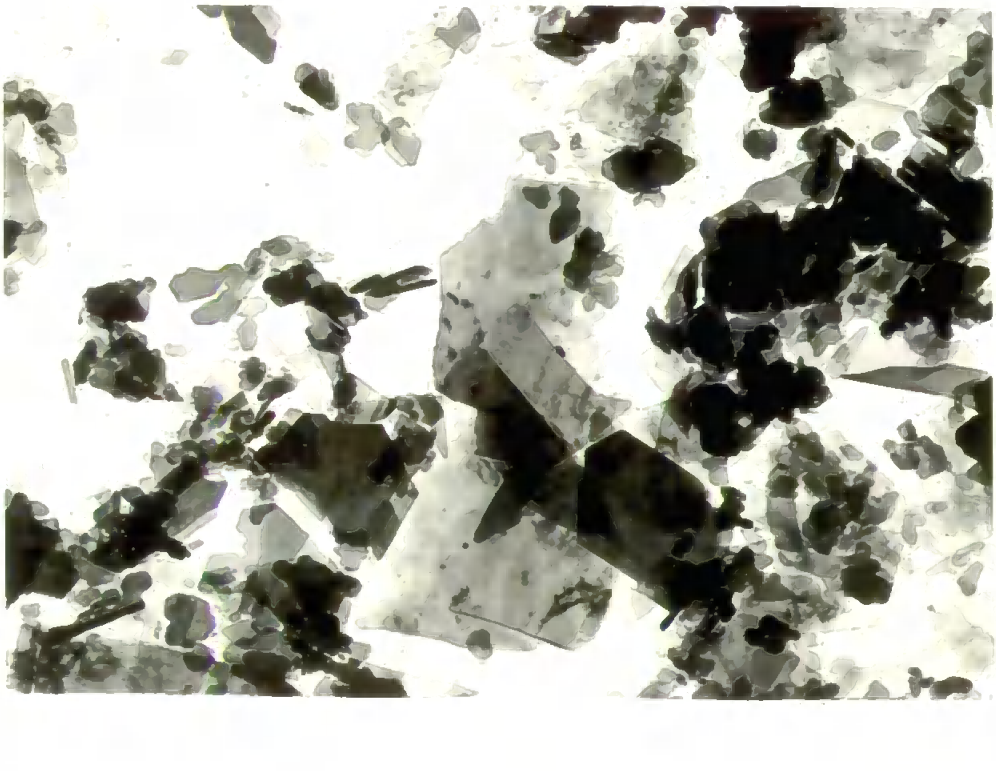
FIG. 3.1. X.R.D. spectra of:
(a) synthetic vanadium-doped kaolinite, series VK-1;
(b) synthetic vanadium-doped kaolinite and boehmite;
(c) synthetic boehmite.

Magnification: X 21,000

FIG. 3.2. Electron micrographs of synthetic vanadium-doped kaolinites of series VK-1.

Magnification: X 27,000





the presence of some vanadium salts. In fact, for reasons which are not understood, it would seem that these salts hinder the formation of silica from hydrolysis of the tetraethyl-silicate component of liquid A. Several vanadium-doped gels, which produced boehmite on reaction, were analysed gravimetrically for alumina[7] and were found to contain amounts exceeding 60%.

3.2.2 Synthesis via Undoped Gels.

In order to increase the number of samples available for study, an alternative method of doping synthetic kaolinite was developed using undoped gels reacted in an aqueous solution of vanadyl sulphate. Samples produced in this manner are referred to as the VK-2 series. X.R.D. spectra of the reaction products showed the presence of well-crystallised kaolinites.

3.3 E.S.R. Study of Vanadium-Doped Synthetic Kaolinites.

E.S.R. spectra were recorded for synthetic kaolinites containing different levels of dopants. They all exhibited resonances at approximately $g = 2$, which were directly superposable on similar resonances found in natural kaolinites (see Fig.3.3(a) to (c)). The alumino-silicate gels from which these kaolinites were made did not exhibit E.S.R. spectra (see Fig. 3.3(d)).

The relative intensity of the second low field spectral line was compared for kaolinites containing various concentrations of dopant. As these samples were prepared in a similar manner, the determination of

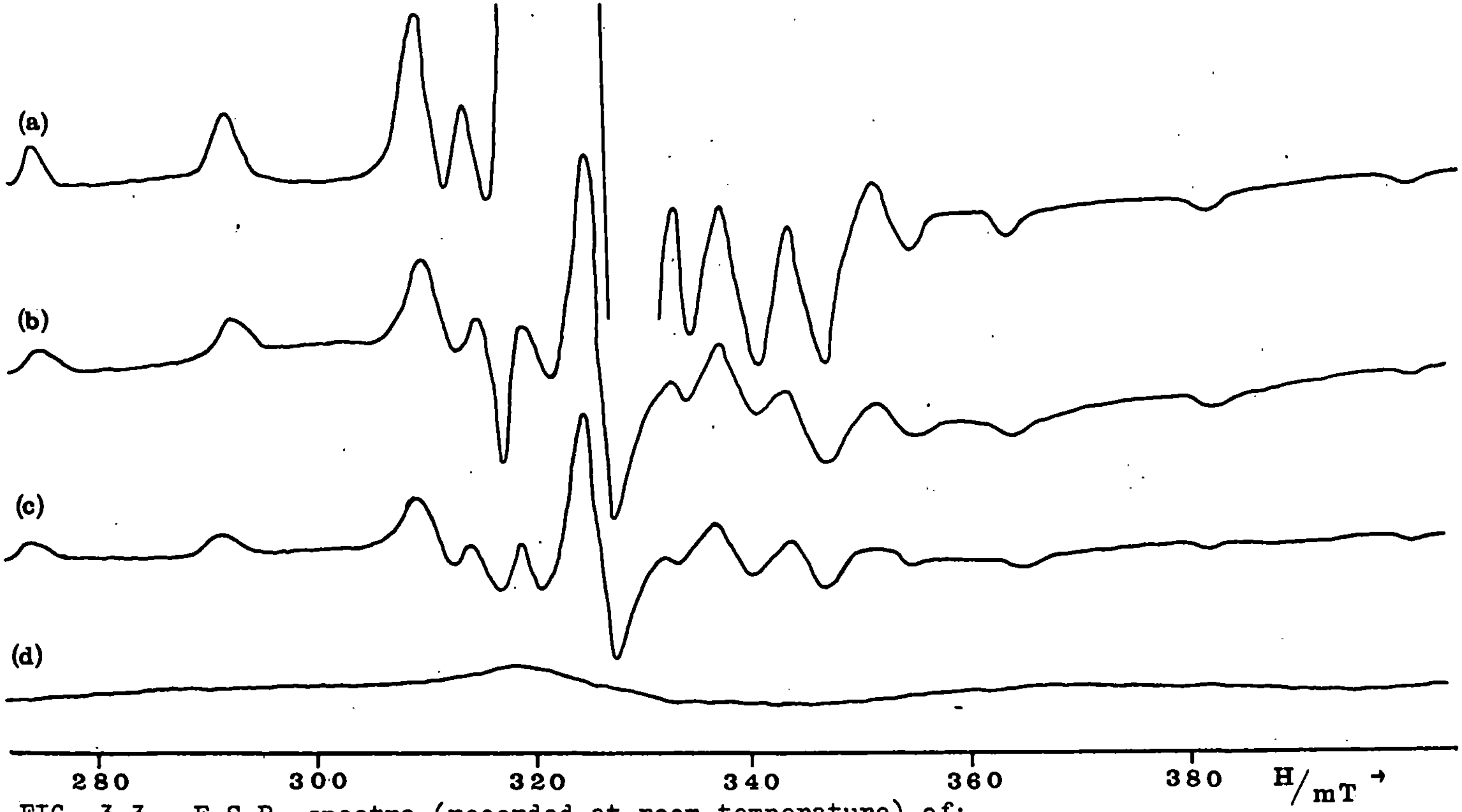


FIG. 3.3. E.S.R. spectra (recorded at room temperature) of:
(a) a typical natural Georgia kaolinite;
(b) a synthetic vanadium-doped kaolinite, series VK-1;
(c) a synthetic vanadium-doped kaolinite, series VK-2;
(d) a vanadium-doped alumino-silicate gel.

peak to peak height of signals for the semiquantitative analysis of paramagnetic vanadium is valid on the basis of considerations described previously in section 2.4.

It was found that the intensity of the vanadium resonance tended to increase as the concentration of dopant was increased until, at high levels of dopant, the intensity approached a constant value (see Fig.3.4.).

3.3.1. The Effect of Relative Humidity on the Vanadium Resonance

If vanadium were adsorbed on the surface of kaolinite, one would expect its E.S.R. spectrum to become isotropic at 100% relative humidity (see section 2.9). Therefore to determine whether the vanadium was substituted in the structure or adsorbed on the surface of the doped synthetic kaolinites, various samples were kept in water-vapour saturated containers for 2 days before their E.S.R. spectra were recorded.

In kaolinites of the VK-2 series, an 8-line isotropic spectrum was observed (see Fig.3.5(a)) and it was, therefore, deduced that vanadium was located on the surface. In contrast, E.S.R. spectra of the VK-1 series exhibited a number of additional lines superimposed on the original anisotropic vanadium(IV) resonance (see Fig.3.5(b)). It seemed probable that these extra lines could be attributed to an 8-line isotropic spectrum produced by vanadium adsorbed on

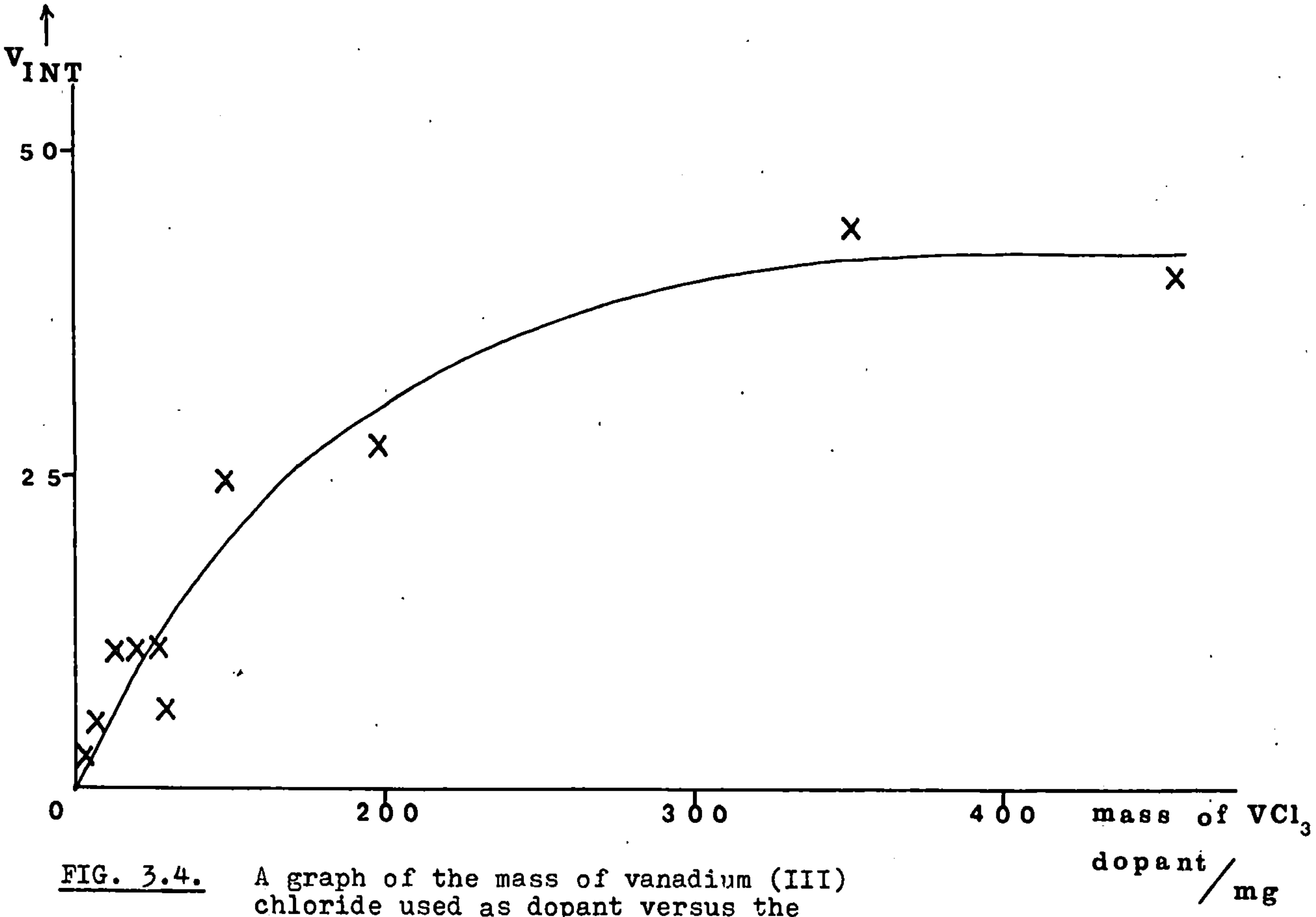


FIG. 3.4. A graph of the mass of vanadium (III) chloride used as dopant versus the relative intensity of the vanadium resonance, V_{INT}, for a series of vanadium-doped kaolinites.

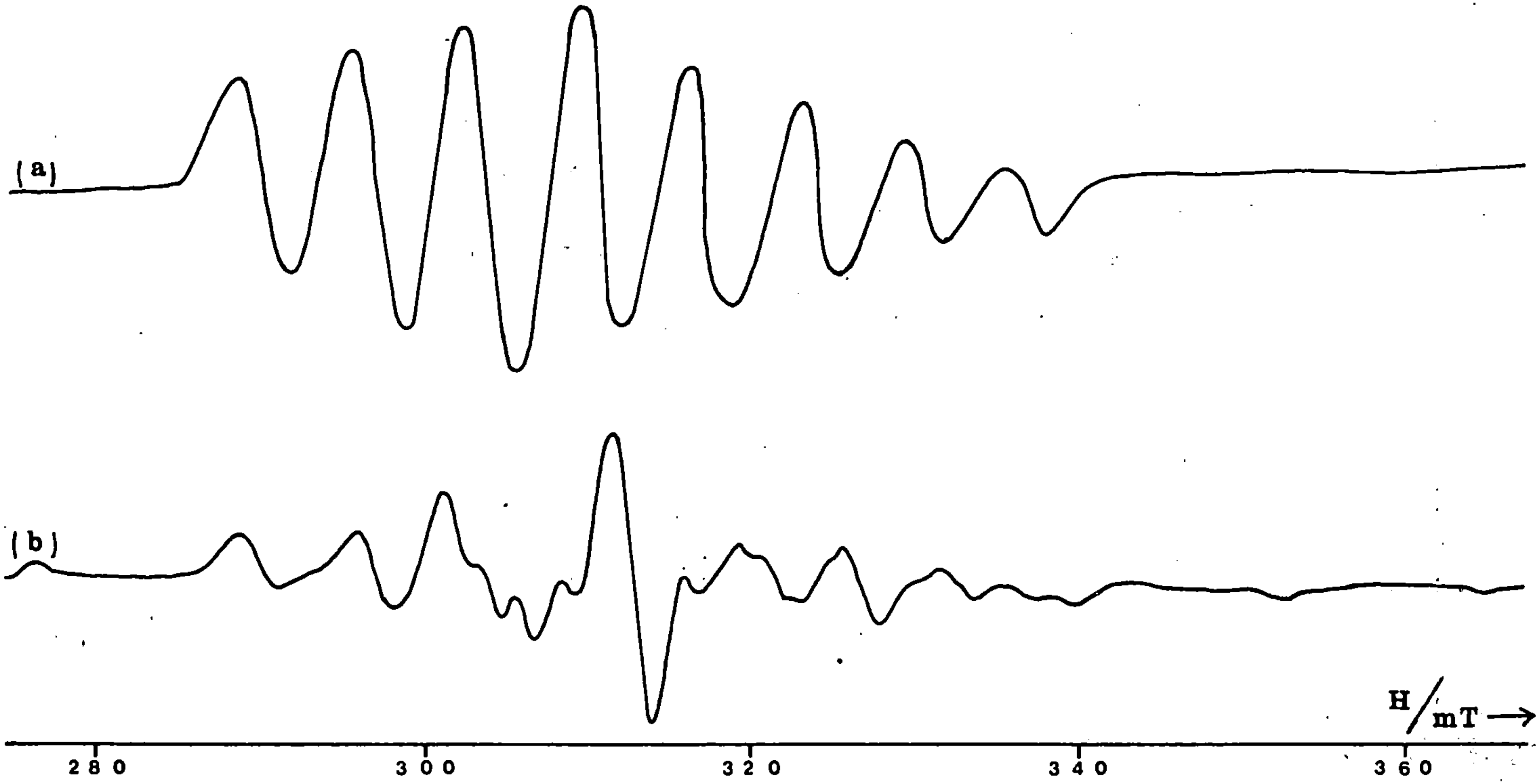


FIG. 3.5. E.S.R spectra recorded at room temperature and 100% relative humidity for synthetic vanadium-doped kaolinites of:
(a) the VK-2 series and (b) the VK-1 series.

the surface, but as the anisotropic spectrum was still discernible, it seemed plausible that vanadium was also present in the kaolinite structure.

To support these views, attempts were made to replace vanadium ions adsorbed on the surface of the synthetic kaolinites by hydrogen ions, which would not exhibit E.S.R. spectra. 1 g of kaolinite was stirred for two hours in 50cm^3 of hydrochloric acid (at a concentration of 0.1 mol dm^{-3}) and then centrifuged. The clay was stirred for 2 hours with another portion of hydrochloric acid; it was centrifuged, washed free of chloride and dried at 383 K. E.S.R. spectra were recorded for both dried samples and samples which had been left to equilibrate at 100% relative humidity. For both the VK-1 and VK-2 series of kaolinites, dried samples gave characteristic anisotropic vanadium (IV) spectra. Also fully hydrated kaolinites of the VK-1 series exhibited this anisotropic resonance. However, E.S.R. spectra of VK-2 kaolinites contained additional lines and were similar to spectra of hydrated VK-1 kaolinites prior to acid treatment. These extra lines were found to be removable by further treatments with hydrochloric acid.

It was concluded from the results that some vanadium is adsorbed on kaolinites of both the VK-1 and VK-2 series, though the latter possess a greater proportion as would be expected from a consideration of the method of synthesis used. The anisotropic vanadium (IV) resonance, which persisted after acid treatment of the samples, was attributed to vanadium substituted in the kaolinite structure.

3.3.2. The Effect of Thermal Treatment on the Vanadium Resonance.

The vanadium resonance in synthetic kaolinites was investigated as a function of preheating of the kaolinite. A number of the samples was heated at different temperatures between 473 and 1473 K for periods varying between 1 and 24 hours. Each treated sample was studied by E.S.R. and X.R.D.

On heating the samples at temperatures up to 723 K the E.S.R. and X-ray spectra resembled those of the untreated kaolinites. At higher temperatures the X.R.D. pattern collapsed to the broad band characteristic of metakaolinite, but the intensity of the E.S.R. spectrum remained essentially constant, though the lines appeared somewhat broader. At 1273 K the intensity of the vanadium resonance began to decrease and at 1473 K (when mullite was detected by X.R.D.) the E.S.R. signal was not observed.

Clearly the effect of thermal treatment on the vanadium resonance of synthetic kaolinite is very different to that encountered for natural samples. This dissimilarity might be accounted for by postulating that vanadium is located at different sites in the kaolinite structure for synthetic and natural kaolinites. In natural samples, the vanadium resonance collapses on dehydroxylation, when major alteration of the octahedral layer occurs[8]. However, in synthetic kaolinites, the vanadium resonance persists up to approximately 1273 K at which temperature metakaolinite is transferred into a spinel-type phase or mullite and the tetrahedral layer is altered[9]. Therefore, it seems feasible that vanadium may be substituted in the octahedral layer in natural kaolinites, but more probably in the tetrahedral layer for the vanadium-doped kaolinites synthesised in this work.

3.4. Thermal Analysis of Synthetic Vanadium-Doped Kaolinite.

It was not understood why vanadium should substitute in different layers for natural and synthetic kaolinites. However, it was feasible that the paramagnetic vanadium observed for synthetic products may have been present in the partially reacted alumino-silicate gel as opposed to the kaolinite formed. This being so, the determination of the relative amounts of kaolinite and possible unreacted gel in the synthetic products was attempted.

A method was devised which involved comparing the weight loss on dehydroxylation for synthetic kaolinites with that for natural samples. A number of synthetic kaolinites was subjected to simultaneous thermal gravimetric analysis (T.G.A.) and differential thermal analysis (D.T.A.) using a Stanton-Redcroft mass flow balance with calcined alumina as a reference. Each clay sample of about 100 mg was heated at a rate of 5 degrees per minute to 423 K and maintained at this temperature until constant weight was obtained, when it was assumed that all adsorbed water had been lost. Heating at the same rate was continued to 973 K and the sample was kept at this temperature until constant weight was attained. It was then assumed that all the structural water had been eliminated.

The D.T.A. curve exhibited an endothermic peak at about 793 ± 10 K which corresponds to dehydroxylation (see Fig. 3.6(a)) and was accompanied by a weight loss on the T.G.A. curve. After correcting the T.G.A. results for buoyancy effects, the percentage weight loss on dehydroxylation was evaluated (see Fig. 3.6 (b)).

Several natural kaolinites were analysed and were found to give weight losses of 13.5 ± 0.4%. The percentage of kaolinite in the synthetic samples was estimated by comparing the actual weight loss with the average weight loss in natural kaolinites. On this basis it was found that the majority of the synthetic kaolinites contained 85 ± 5% kaolinite. As a control, unreacted alumino-silicate gel was also subjected to thermal analysis, but neither D.T.A. peaks nor weight losses were observed.

Experiments were also undertaken to compare the

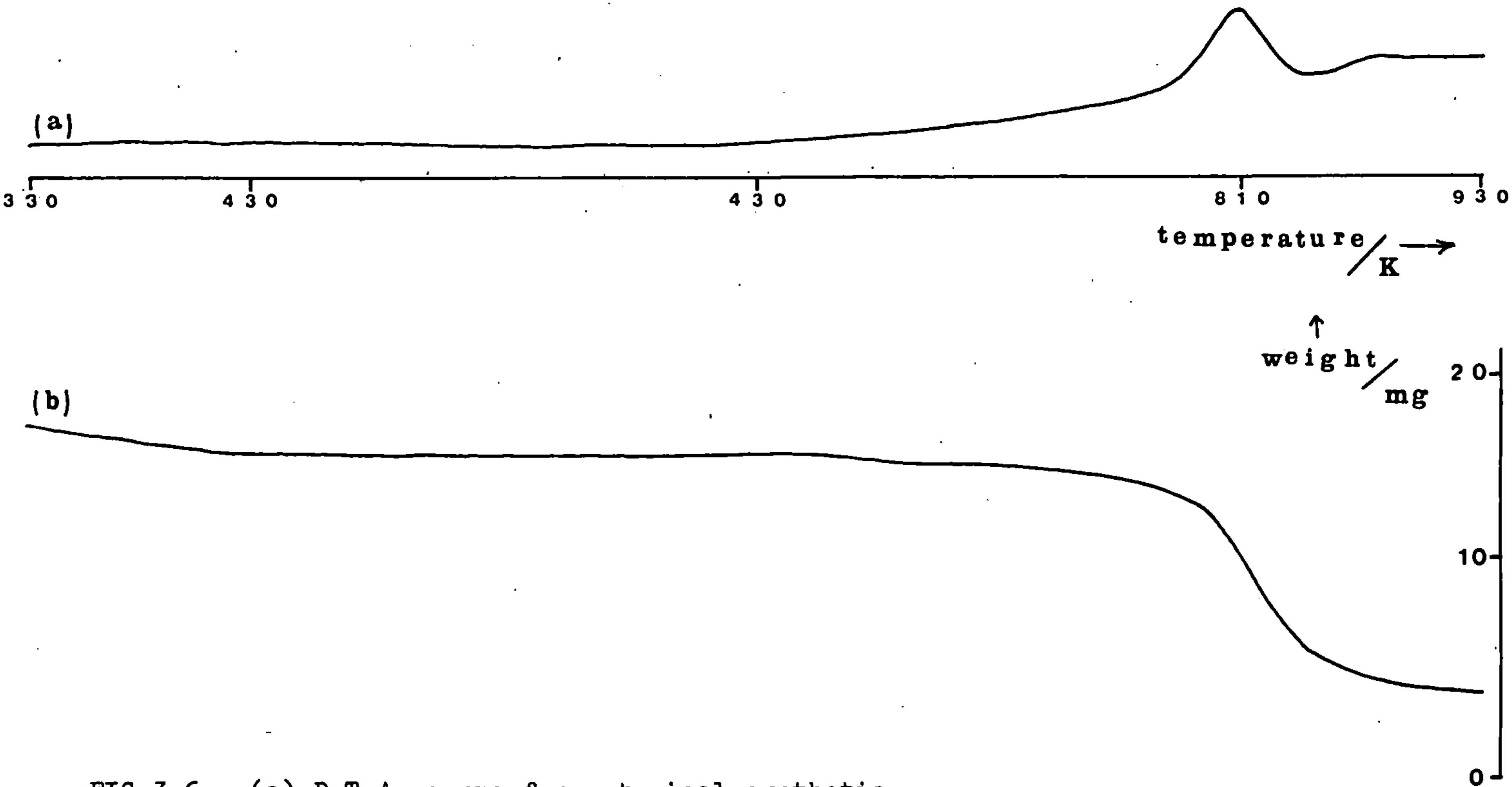


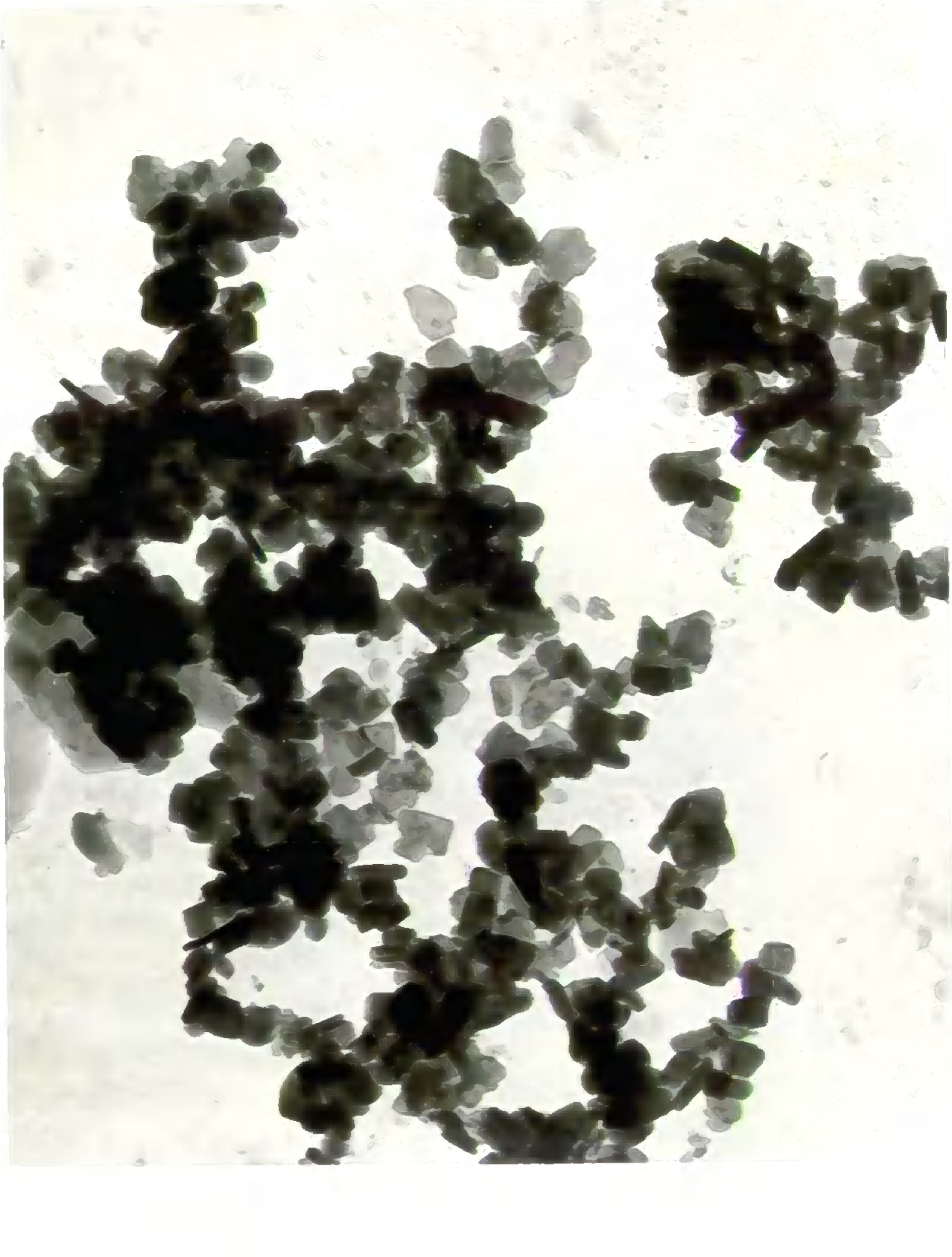
FIG.3.6. (a) D.T.A. curve for a typical synthetic vanadium-doped kaolinite,
(b) T.G.A. curve, corrected for buoyancy.

percentage of kaolinite with the relative intensity of the vanadium E.S.R. signal for a series of synthetic samples. This series of kaolinites was synthesised using the same vanadium-doped alumino-silicate gel, but different times of reaction were used to produce a range of samples with increasing kaolinite content. Other conditions were reproduced as closely as possible by using P.T.F.E. liners and plugs of equal lengths, by keeping filling factors constant and by reacting the samples in the same Tuttle bomb. It was found that the intensity of the vanadium resonance increased as the percentage of kaolinite in the sample increased. It was concluded, therefore, that vanadium was incorporated in the synthetic kaolinite and not in some other phase, which may have been precipitated during the formation of kaolinite but was not detected by X.R.D. It is improbable that another phase would be formed at the same rate as kaolinite.

3.5 E.S.R. Study of Vanadium-Doped Synthetic Boehmite.

To support the hypothesis that vanadium in natural kaolinites is substituted in the octahedral layer, the synthesis of vanadium-doped boehmite was attempted as this mineral has a structure similar to that of the octahedral layer of kaolinite. A vanadium-doped alumina gel was prepared by reacting a solution of aluminium chloride (which contained a small amount of vanadium (III) chloride) with dilute ammonia solution. This was maintained at a temperature of approximately

FIG. 3.7. Electron micrograph of vanadium-doped synthetic boehmite.
(magnification: X 55,500).



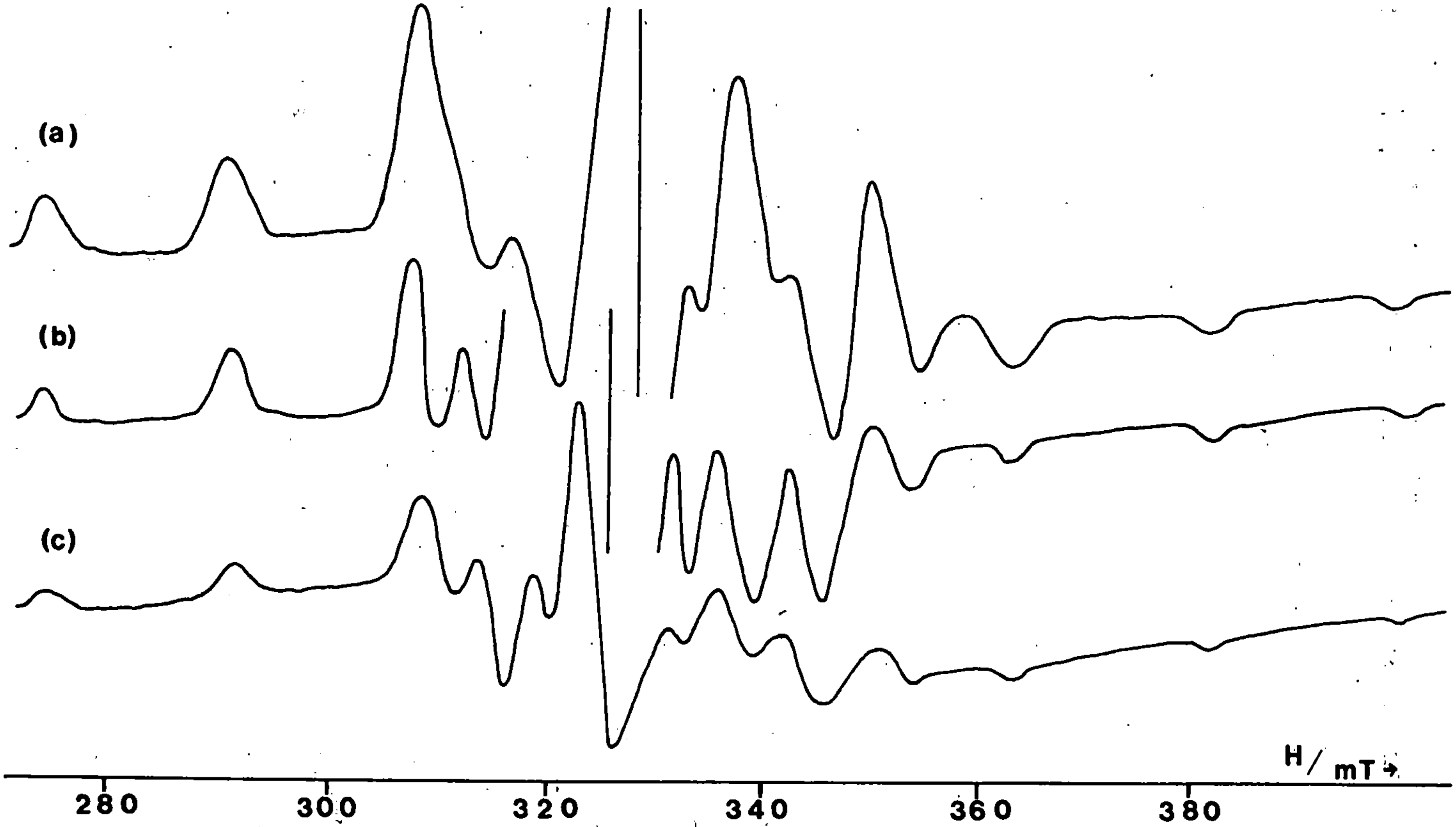


FIG. 3.8. E.S.R. spectra (recorded at room temperature) of:
(a) synthetic vanadium-doped boehmite,
(b) a typical natural Georgia kaolinite,
(c) synthetic vanadium-doped kaolinite.

323 K for one week and stirred intermittently. It was then dried at 383 K and fired at 773 K for 24 hours. The reactions may be represented by the following equations:

$$\begin{array}{l} 2\,\mathrm{AlCl_3} + 6\,\mathrm{NH_4OH} \longrightarrow 2\,\mathrm{Al(OH)_3} + 6\,\mathrm{NH_4Cl} \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow 773\ \mathrm{K} \qquad (3.2) \\ \qquad\qquad\qquad \mathrm{Al_2O_3} + 3\,\mathrm{H_2O}\uparrow + 6\,\mathrm{NH_3}\uparrow + 6\,\mathrm{HCl}\uparrow \end{array}$$

The gel was reacted hydrothermally, as previously described for the synthesis of kaolinite.

The synthetic boehmite produced was identified by X.R.D. and was found to consist of small characteristic rhombohedral plates (see Fig. 3.7). The sample exhibited E.S.R. signals characteristic of vanadium (IV) and exactly superposable on those obtained from natural and synthetic kaolinites (see Fig. 3.8). This resonance was studied as a function of thermal treatment of the boehmite. For preheating temperatures of up to 773 K there was no observable change in the E.S.R. signal or the X-ray spectrum. However, as the temperature was further increased, the intensity of both the vanadium resonance and the X-ray reflections decreased. Since the behaviour of the vanadium signal with respect to thermal treatment was found to be similar in synthetic boehmite and natural kaolinites, it seems reasonable to conclude that vanadium substitutes in the octahedral layer of natural kaolinite.

The synthesis of a vanadium-doped silica mineral was attempted to support the theory that, in the vanadium-doped synthetic kaolinites produced in this work, vanadium is substituted in the tetrahedral layer. A vanadium-doped silica gel was produced by adding a solution of vanadium (III) chloride to tetraethylsilicate and hydrolysing this mixture with dilute ammonia solution. This gel was hydrothermally reacted as before. However, the product exhibited neither an E.S.R. spectrum nor an X.R.D. pattern.

3.6 Adsorption of Vanadium by Synthetic and Natural Kaolinites.

In addition to exhibiting E.S.R. signals which have been assigned to substituted vanadium, synthetic vanadium-doped kaolinites also gave resonances attributable to vanadium ions adsorbed on the surface. Therefore, the effect of washing natural and undoped synthetic kaolinites with vanadyl (IV) sulphate solutions was investigated.

1 g of kaolinite was stirred for 2 hours with 50 cm^3 of aqueous vanadyl (IV) sulphate solution at a concentration of 2.5×10^{-2} mol dm^{-3}. The suspension was centrifuged and the clay was treated similarly with 2 further 50 cm^3 portions of vanadyl (IV) solution. It was then washed with deionised water until free of sulphate and dried at 383 K. E.S.R. spectra were recorded for the dried samples and for samples which had been maintained at 100% relative humidity for 2 days.

Dried samples of vanadyl-washed undoped synthetic and natural English kaolinites gave spectra similar to those of vanadium-doped synthetic and Georgia natural kaolinites respectively (see Fig. 3.9(a) and (b)). However, fully hydrated samples exhibited 8-line isotropic resonances characteristic of surface vanadium (see Fig. 3.9(c)). E.S.R. spectra of dried vanadyl-washed Georgia kaolinites were similar to those of the untreated samples, but at 100% relative humidity 8-line isotropic resonances were observed at g = 2. These isotropic signals, which are attributable to adsorbed vanadium ions, could be removed by washing the samples with 3 successive 50 cm^3 aliquots of 1 mol dm^{-3} hydrochloric acid.

The results show that vanadium ions are readily adsorbed by natural and synthetic kaolinites.

3. 7 Summary.

E.S.R. studies of natural and synthetic vanadium-doped kaolinites have shown that vanadium may be substituted in both the octahedral and the tetrahedral layers of kaolinite. However, for the suite of natural kaolinites from Georgia which were investigated vanadium was present only in the octahedral layer.

Also it has been shown that vanadium may be adsorbed on the surface of kaolinite. It was found that it was very simple to distinguish between surface and substituted vanadium by comparing E.S.R. spectra of samples recorded at low and high values of relative humidity.

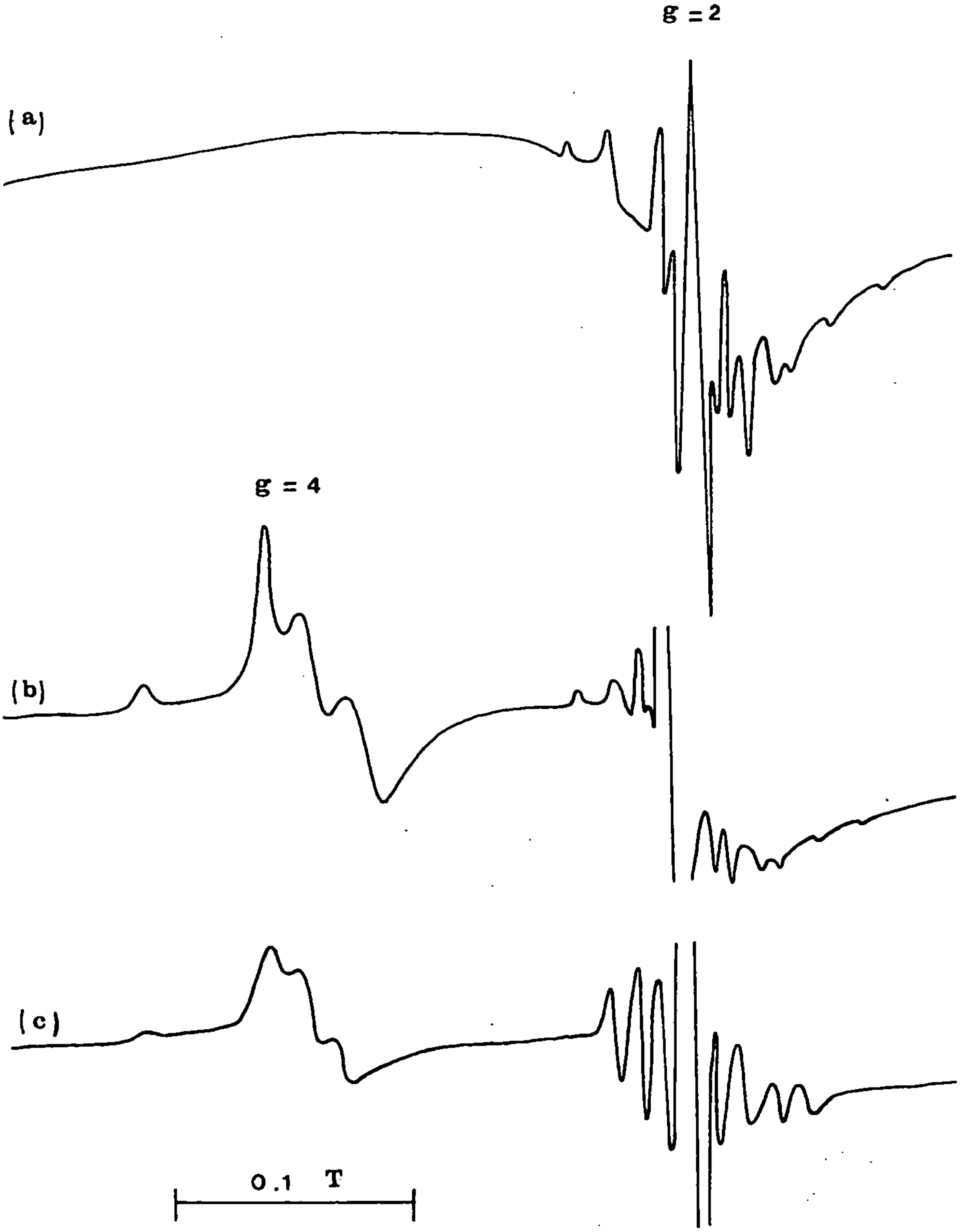


FIG.3.9. E.S.R spectra recorded at room temperature for samples of vanadyl (IV)-washed:
(a) undoped synthetic kaolinite, dried at 383 K,
(b) Blackpool kaolinite, dried at 383 K,
(c) Blackpool kaolinite, at 100% relative humidity.

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CHAPTER 4.

SYNTHESIS OF IRON (II) - DOPED KAOLINITE.

4.1 Introduction.

Previous work in this laboratory[1,2,3] has shown that synthetic magnesium-doped kaolinites, following X-irradiation and annealing, exhibit an asymmetric two-line E.S.R. signal centred at $g = 2$, which is identical to resonance A observed in natural kaolinites. It was concluded that this resonance can be attributed to a hole trapped by substitution of Mg^{2+} for Al^{3+} in the octahedral layer. As Fe^{2+} has the same charge as Mg^{2+} and a similar ionic radius, it might be possible that Fe^{2+} can perform the same function as Mg^{2+}. However, attempts to produce synthetic kaolinite doped with Fe^{2+} had previously been unsuccessful[1].

In this work preparation of a synthetic Fe^{2+} -doped kaolinite was discovered accidentally when the synthesis of an $^{57}Fe^{3+}$-doped kaolinite had been undertaken to provide a sample suitable for study of the location of substituted Fe^{3+} by Mössbauer spectroscopy. This technique detects only the iron-57 isotope, which is 2.24% abundant. In natural kaolinites the total iron impurity is usually less than 2% and consequently the ^{57}Fe content is less that 0.04%. Due to the low concentration of ^{57}Fe, poor counting statistics have been inevitable in past Mössbauer studies of natural kaolinites and have resulted in difficulties in interpreting the spectra[4]. For this reason the synthesis of ^{57}Fe-doped kaolinite was attempted. It should be noted that with the Mössbauer technique it is possible to detect and distinguish Fe^{2+} and Fe^{3+} at room temperature.

4.2 Synthesis of ^{57}Fe-Doped kaolinite.

Previous syntheses[1,2,3] of iron-doped kaolinites had involved preparation of iron (III) benzoate from commercially available iron (III) chloride. The benzoate was then dissolved in dimethyl-formamide (D.M.F.) and added to liquid A prior to hydrolysis. Hydrothermal reaction of the alumino-silicate gels so formed produced Fe^{3+}-doped kaolinites with resonances at g = 4 similar to those found in natural kaolinites.

Iron-57 can be obtained commercially only in the form of metallic filings or chips and is very expensive (approximately £3,000 per gram). Due to the high cost, a reliable method had to be devised to prepare iron (III) benzoate from 10mg of metallic iron-57, which was the maximum amount available in this work.

Initially, a method was developed using natural iron. 10mg of iron filings were dissolved in 0.5 cm^3 hydrochloric acid by heating over a water bath and then the pH was adjusted to 5 by addition of an aqueous solution of sodium acetate at a concentration of 10 mol dm^{-3}. An aqueous solution of ammonium benzoate (0.4 mol dm^{-3}) was added dropwise with stirring until precipitation of iron (III) benzoate was complete.

This brown precipitate was filtered on a small Gooch crucible of porosity 4 and rinsed with sodium acetate solution and finally deionised water. It was then dried at 323 K.

The dried iron (III) benzoate was dissolved in 1 cm^3 of D.M.F. and the solution was mixed thoroughly with 5 cm^3 of liquid A. This was hydrolysed with excess water to produce an iron-doped alumino-silicate gel. The gel was hydrothermally reacted in a manner similar to that described in section 3.2 for the synthesis of vanadium-doped kaolinites.

The iron-doped kaolinites formed using this method were well-crystallised and exhibited resonances at g = 4 characteristic of Fe^{3+} in kaolinite. However, these signals were significantly less intense than those of kaolinites which had been synthesised using iron (III) benzoate prepared from commercially available iron (III) chloride. Nevertheless, the method was considered to be sufficiently reproducible to initiate the experiments from which an ^{57}Fe-doped kaolinite was synthesised.

4.3 E.S.R and Mössbauer Study of Synthetic ^{57}Fe-Doped Kaolinite

Although the ^{57}Fe-doped kaolinite exhibited a fairly weak, but clearly defined, resonance at g = 4 attributable to Fe^{3+} (see Fig. 4.1), the Mössbauer spectrum (see Fig. 4.2) gave values of 1.14 mm s^{-1} and 2.53 mm s^{-1} for the isomer shift and quadrupole

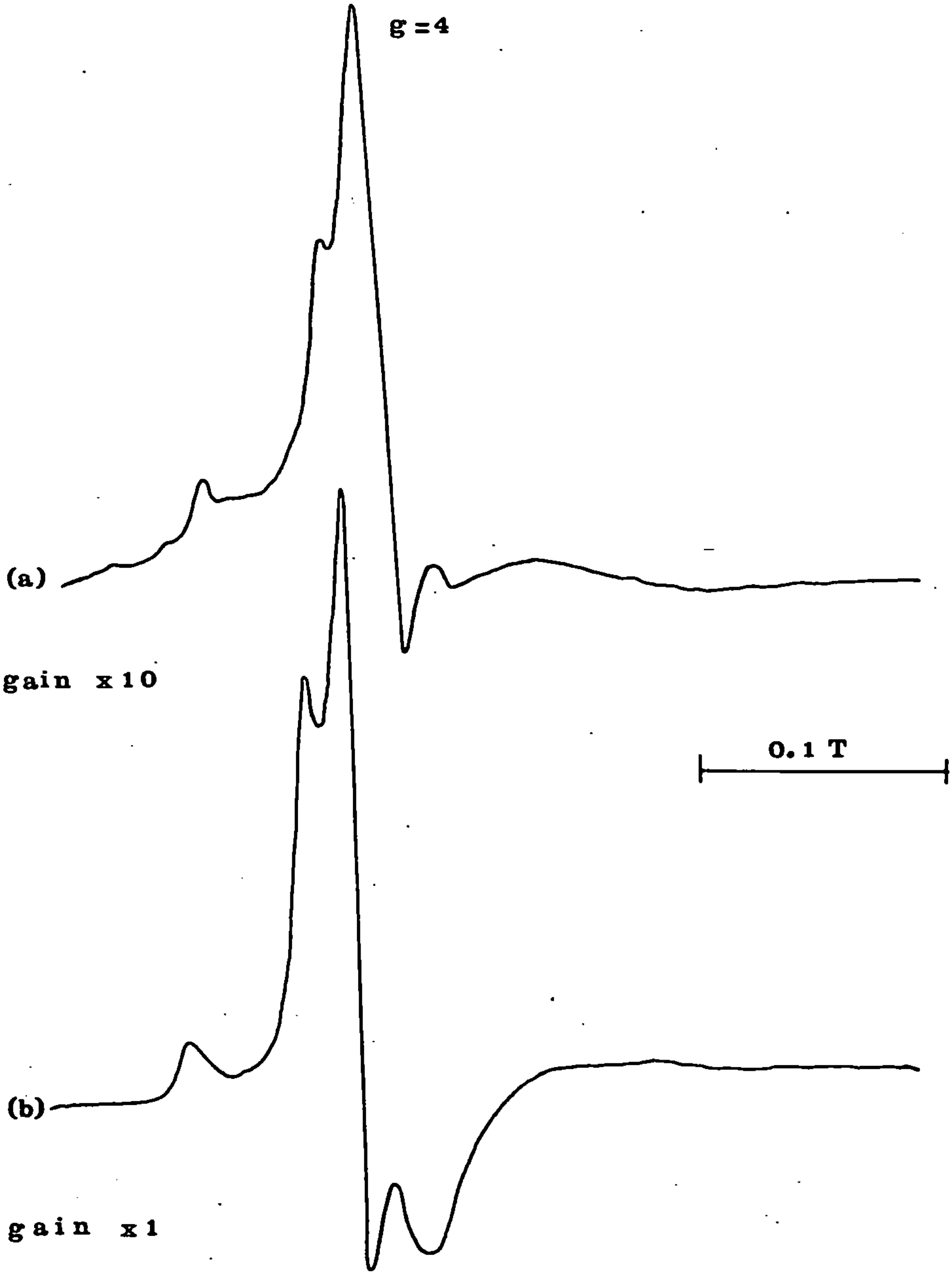

FIG. 4.1. E.S.R. spectra recorded at room temperature of:
(a) synthetic ^{57}Fe-doped kaolinite;
(b) synthetic ^{56}Fe^{3+}-doped kaolinite.

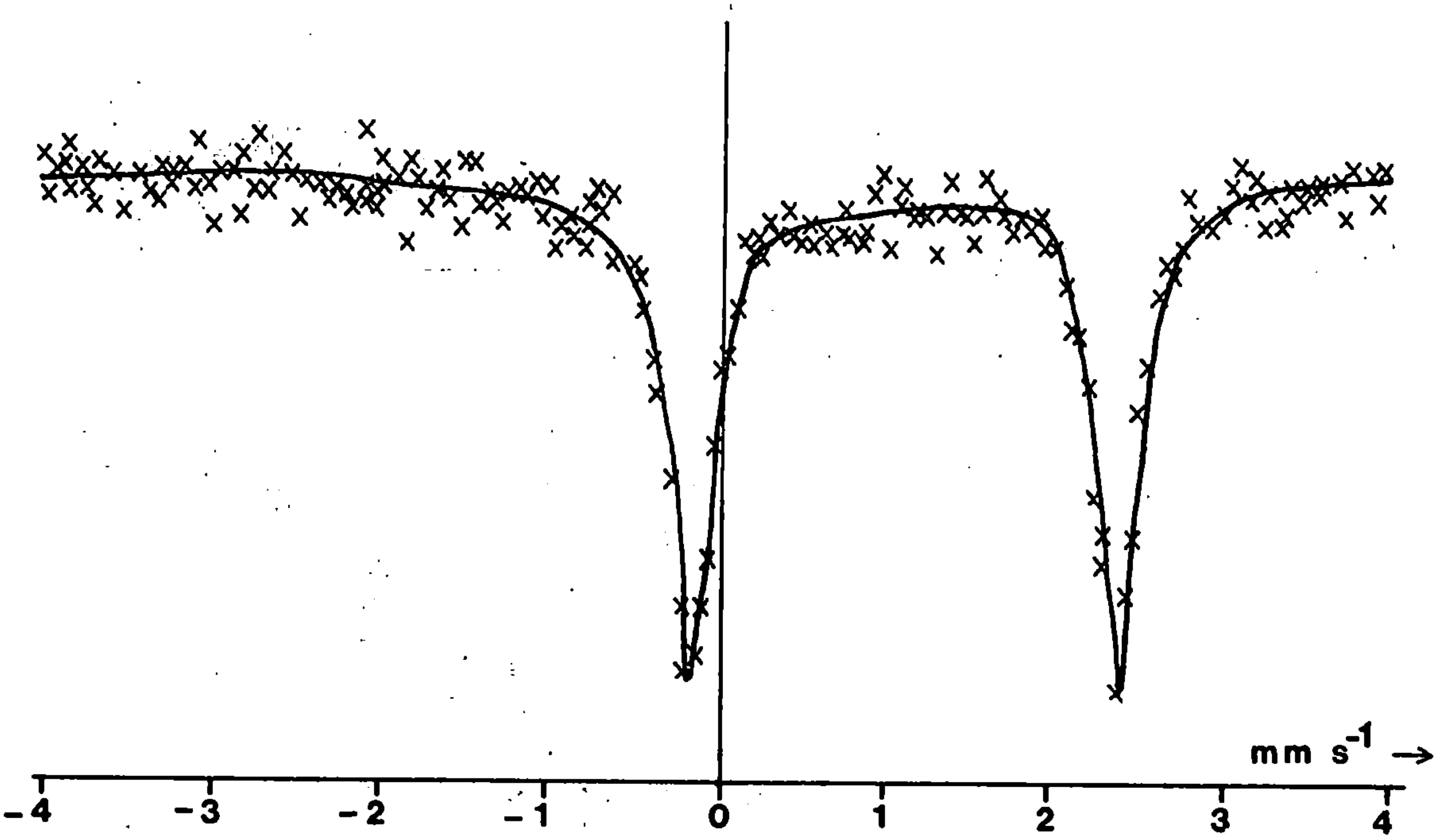

FIG. 4.2. Mössbauer spectrum of $^{57}Fe^{2+}$-doped synthetic kaolinite at room temperature.

splitting respectively, indicating, most unexpectedly, that the majority of the iron was substituted in the kaolinite structure at Fe^{2+} and not Fe^{3+}. Consultation with a number of experts confirmed that it is difficult to determine the limit of detection of Fe^{3+} by Mössbauer spectroscopy. However, for the iron-doped kaolinite, it was generally agreed that the E.S.R. technique is probably more sensitive than Mössbauer by at least one, if not two, orders of magnitude. Such a large difference in sensitivity would easily account for the observation by E.S.R. of the weak signal at $g = 4$ due to Fe^{3+}, which was not detected by the Mössbauer technique. (The values of isomer shift and quadrupole splitting of Fe^{3+} in kaolinite are 0.48 mm s^{-1} and 0.52 mm s^{-1}, respectively [4]).

Although these results were most unexpected and very difficult to explain, the samples produced provided a unique means of validating the hypothesis that Fe^{2+} may stabilise a defect and produce an asymmetric two-line resonance at $g = 2$. Accordingly the $^{57}Fe^{2+}$-doped kaolinite was X-irradiated with a dose of approximately 1 MRad and then annealed for 2 hours at 473 K. It was found to exhibit a resonance at $g = 2$ identical to that observed in natural kaolinites (see Fig. 4.3). A synthetic kaolinite had been produced, doped with iron, but which exhibited both the groups of signals at $g = 2$ and $g = 4$ common to natural

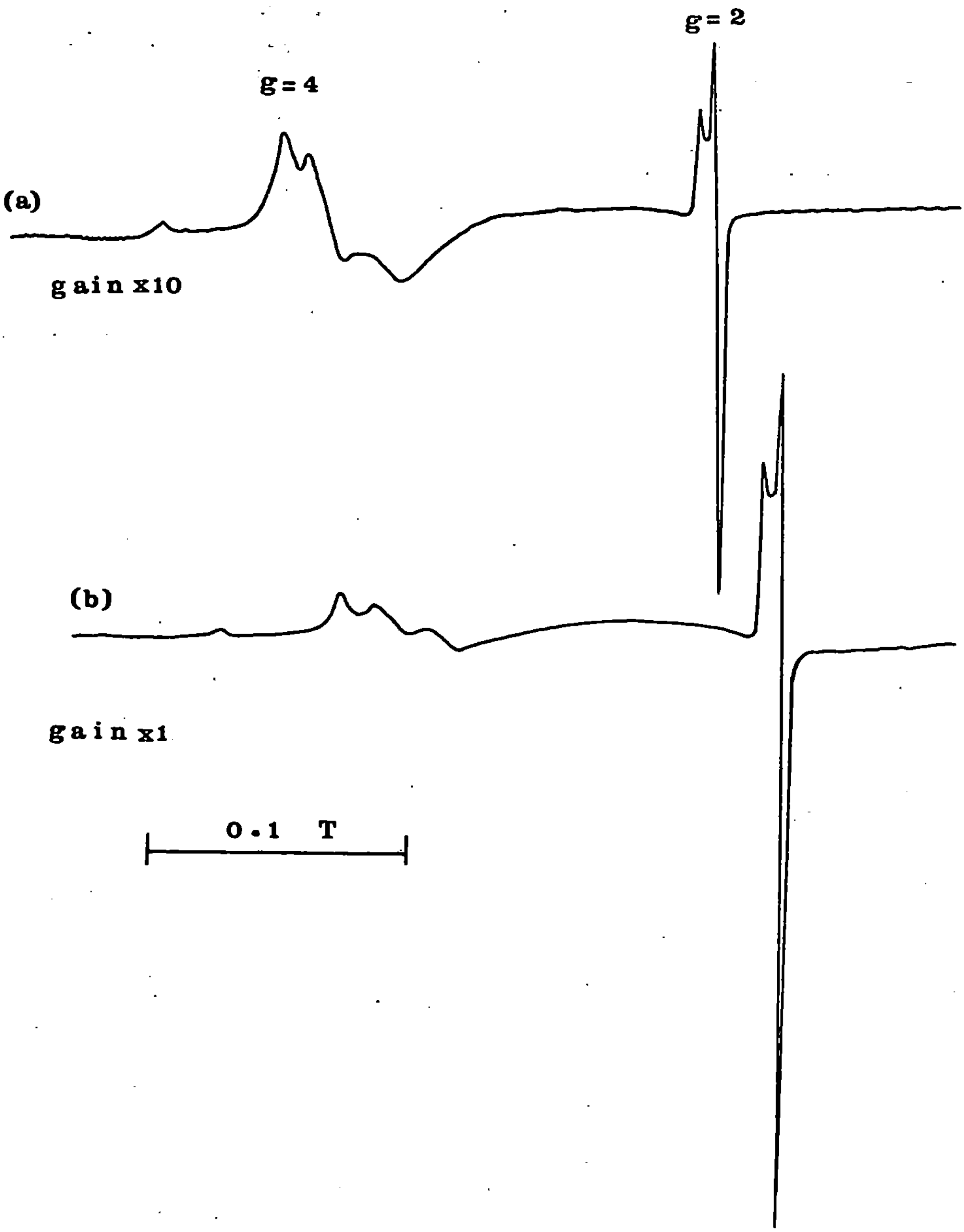

FIG. 4.3. E.S.R. spectra recorded at room temperature of:
(a) synthetic ^{57}Fe-doped kaolinite, X-irradiated and annealed;
(b) a typical natural kaolinite.

samples.

It must be emphasised that for the resonance at g = 2 substituted Fe^{2+} does not in itself produce the signal, but acts as a precentre which traps a paramagnetic defect which is formed on irradiation. It is known that Fe^{2+} would not be detected directly by E.S.R. at room temperature because of its extremely short relaxation time.[5]

4.4 Further Studies of the Synthesis of ^{57}Fe-Doped Kaolinite.

Although the experiments described above had produced both interesting and significant results, the reason for iron substituting preferentially as Fe^{2+} was not clear. Therefore, the method of synthesis of the ^{57}Fe-doped kaolinite was investigated in more detail.

Kaolinites which had been synthesised using iron (III) benzoate prepared from commercially available iron (III) chloride as dopant did not produce resonances at g = 2 following X-irradiation and annealing.[1] It was also found that these kaolinites exhibited Mössbauer spectra which indicated that the majority of the iron was in the Fe^{3+} state. The only difference between this method of synthesis and the method used for the ^{57}Fe-doped kaolinite was that in the latter the $^{57}Fe^{3+}$ solution had been prepared by dissolving metallic iron in acid while in the former the $^{56}Fe^{3+}$ solution had been prepared by dissolving commercially available iron (III) chloride in water.

When iron dissolves in hydrochloric acid, formation of both Fe^{3+} and Fe^{2+} ions would be expected. However, it is known that oxygen from the air can convert Fe^{2+} to Fe^{3+} in solution.[6] This oxidation process occurs in acid solution, but is more rapid as the pH is increased. It had been anticipated in the preparation of ^{57}Fe-doped kaolinite that any Fe^{2+} ions remaining in solution at pH 5 would have been oxidised in subsequent stages of the gel production and final synthesis. The results obtained clearly contradict the anticipated effects.

In order to ensure complete oxidation of the iron, experiments with natural iron were made to find an oxidising agent which, when added to the iron solution, would convert all the iron ions to Fe^{3+}. It was found, by testing with conventional methods for Fe^{2+} and Fe^{3+} in solution, that nitric acid was a suitable oxidising agent and that the most convenient method was to dissolve iron in aqua regia. Solutions prepared in this way gave negative results for Fe^{2+} when tested with potassium ferricyanide solution.

An alumino-silicate gel was, therefore, prepared by dissolving 10 mg of ^{57}Fe in 0.5 cm^3 of aqua regia and the pH of the solution was adjusted to 5 by addition of sodium acetate solution. Then the method was continued as before. However, the kaolinite formed produced a g = 2 signal following irradiation and annealing and the Mössbauer spectrum revealed that the majority of the iron had substituted at Fe^{2+}. It would seem that, at some stage during the gel formation, Fe^{3+} had been reduced to Fe^{2+}. However, it was not immediately apparent why this should have occurred in the synthesis using metallic iron but not in the preparation using iron (III) chloride.

It is known that aluminium isopropoxide can act as a reducing agent when catalysed by mineral acids.[7] It was possible that iron (III) benzoate prepared from iron dissolved in aqua regia may have still contained traces of acid after washing with water. Therefore, when the benzoate in D.M.F. solution was added to liquid A, the acid would have catalysed the reduction of Fe^{3+} by aluminium isopropoxide. In the preparation of iron (III) benzoate from iron (III) chloride no acid was involved and so Fe^{3+} would not be reduced by aluminium isopropoxide.

In order to investigate the possible effects of mineral acids, an alternative method of preparation of iron (III) benzoate was developed which procluded acid. The method involved production of iron (III) chloride by direct chlorination of 10 mg of iron metal at 673 K. The iron (III) chloride was then dissolved in the minimum quantity of deionised water and iron (III) benzoate was precipitated by addition of a solution of ammonium benzoate. The kaolinite formed from a gel doped with iron (III) benzoate prepared by this method still produced a resonance at g = 2 after irradiation and annealing. However, Mössbauer results indicated that there had been a reduction in the ratio of Fe^{2+} to Fe^{3+} (see Fig. 4.4). These results were puzzling, as it was difficult to understand how, in the methods used, appreciable quantities of substituted Fe^{2+} had appeared in the final products.

When organic matter is decomposed at elevated temperatures, it is known that finely divided carbon black is often formed which is an effective reducing agent. It was possible that firing of the alumino-silicate gels at 1273 K to remove remaining organic material had resulted in the formation of carbon, which may have reduced Fe^{3+} to Fe^{2+}. However, this effect would also have been expected in kaolinites where the iron (III) benzoate had been prepared from commercial iron (III) chloride and these samples were found to contain negligible quantities of Fe^{2+}.

Nevertheless, it was considered worthwhile to study the possible effects of carbon formation. An alumino-silicate gel doped with iron (III) benzoate prepared from iron metal was subjected to rotary evaporation at reduced pressure to remove organic contaminants. However, the kaolinite produced on subsequent hydrothermal reaction was found to contain a similar quantity of Fe^{2+} to that obtained from a gel which had been fired at 1273 K.

In a further attempt to produce an ^{57}Fe-doped

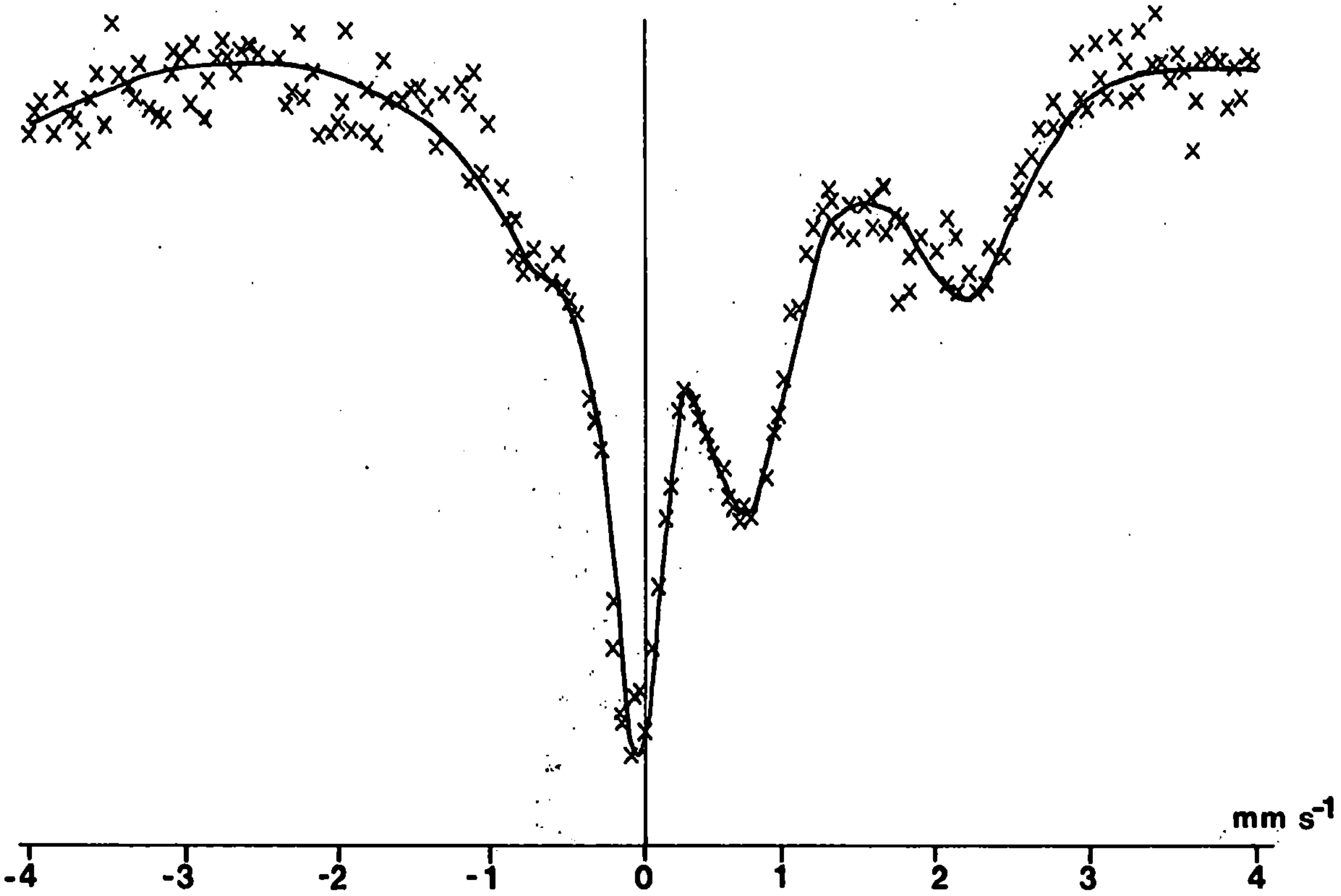

FIG. 4.4. Mössbauer spectrum of $^{57}Fe^{2+}$- and $^{57}Fe^{3+}$- doped synthetic kaolinite at room temperature.

kaolinite in which iron was substituted as Fe^{3+}, a portion of ^{57}Fe-doped alumino-silicate gel was heated in oxygen at 1673 K for 2 hours when it was anticipated that any Fe^{2+} present in the gel would be oxidised to Fe^{3+}. However, the kaolinite produced on hydrothermal reaction was found to contain a similar quantity of Fe^{2+} to that obtained from a gel which had not been heated in oxygen.

To find that Fe^{2+} had not been oxidised under such extreme conditions was a most unexpected result. Discussions with a number of experts in the field of mineral synthesis led to the conclusion that Fe^{2+} must be very closely associated with, or bound within, the gel. An alternative explanation is that iron may be present as Fe^{3+} in the alumino-silicate gel, but is reduced by the hydrothermal reaction used to synthesise the kaolinite. This seems improbable, though, as hydrothermal reaction of gels doped with iron (III) benzoate prepared from commercially available iron (III) chloride produced kaolinites in which virtually all the iron was substituted as Fe^{3+}.

To date no satisfactory reason has been found to explain why an Fe^{2+}-doped gel is formed when iron (III) benzoate, which has been prepared from metallic iron, is used as dopant whereas an Fe^{3+}-doped kaolinite is produced when iron (III) benzoate prepared from commercially available iron (III) chloride is used. Later in this thesis, a detailed discussion on some of the properties of the oxides of iron is presented, which demonstrates the complicated chemistry which might be involved in reactions including iron.

Prior to the experiments described above, it was generally accepted that it was difficult to attribute an asymmetric 2-line resonance at g = 2 in kaolinite to iron. Although it was not possible, after considerable efforts, to explain the chemistry of the reactions which produced Fe^{2+}-doped kaolinites, the results were thought to be sufficiently important to warrant publication. They form the basis of a paper which is bound at the end of this thesis.

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CHAPTER 5.

ELECTRON SPIN RESONANCE STUDY OF IRON OXIDE PHASES ASSOCIATED WITH KAOLINITE.

5.1 Introduction.

Previous E.S.R. studies in this laboratory[1,2,3] and work undertaken as part of this thesis (see chapter 4) have shown that kaolinite contains iron substituted in its structure. Other research[4,5,6] has established that some iron is present in the structure of ancillary minerals such as anatase, rutile, quartz and micas. Also iron is known to occur with kaolinite in the form of iron oxides and hydroxides,[7,8,9] either as distinct particles or as coatings bound on the surfaces of kaolinite or its mineralogical impurities.

These so-called free iron oxides have been considered mainly as impurities which reduce the whiteness of kaolinite and are, therefore, detrimental in the application of the material in the paper industry. Considerable research efforts have been made to study the removal of these oxides and the various methods of removal have been reviewed by several authors.[9,10,11,12,13] Additional work has been directed to the interaction of iron oxides with with kaolinite surfaces. In general the methods used have taken the form of precipitating iron oxides and hydroxides on kaolinite in conjunction with E.M., X-ray and chemical analyses.[7,13,14,15,16]

There has been more research, however, on the nature[17,18] and adsorption characteristics[19,20,21] of iron oxides occurring in soils. In addition, studies of iron oxides and hydroxides in the absence of clay have been extensive. These have been aimed at identifying, characterising and studying the interrelationships of the various precipitation products from iron (II) and iron (III) salts in solution.[22-30]

The object of this work was to study the iron oxides and hydroxides associated with kaolinite in greater depth using E.S.R. methods. Previous E.S.R. studies of iron oxides in synthetic zeolites [31,32,33]and lunar samples[34-42] have demonstrated the potential of this technique.

5.2. Description of Samples.

This study was carried out using 16 distinct kaolinites. 11 of these (Avant, Chambers, Champion, Gray, English, Wrens and Mines 11,15,24,50 and 51) were supplied by the U.S. Georgia Kaolin Company and have been described in chapter 2. These samples had been washed, flocculated with sulphuric acid and rewashed.

The remaining 5 kaolinites were obtained from English Clays, Lovering, Pochin and Company Limited. Four of the clays, referred to as Blackpool, Cholwich Town, Dubbers and Lee Moor, had only been worked and filter pressed and had not been treated chemically. The fifth sample was a commercially available clay known as Supreme, which had probably been magnetically refined and bleached (private communication). Chemical and particle size analyses were available for these samples.

5.3 Preliminary Studies.

5.3.1 Crystallinity Measurements.

X.R.D. spectra were recorded for all the samples using a Hilger and Watts diffractometer and nickel-filtered Cu K_α radiation. Crystallinity indices were measured using Hinckley's method.[43]

5.3.2 Preliminary E.S.R. Study.

The E.S.R. spectra of the 16 kaolinites described above were recorded at X-band (9.3 GHz) at room temperature using a Decca X1 spectrometer. All of the spectra exhibited two resonances, A and C, which were centred at about $g = 2$ and $g = 4$ respectively and which have been discussed previously. In addition, the spectra contained a broad resonance, F1, of variable intensity and of linewidth of the order of 0.1 tesla, centred at approximately $g = 2$ (see Fig. 5.1). Resonances of this type are characteristic of ferromagnetic materials and, in kaolinites have been attributed to strong coupling of two $S = 5/2$ ions in adjacent sites either within the kaolinite structure or within the structure of associated iron oxides.[5,44,45] No changes were observed in resonance F1 when the temperature was

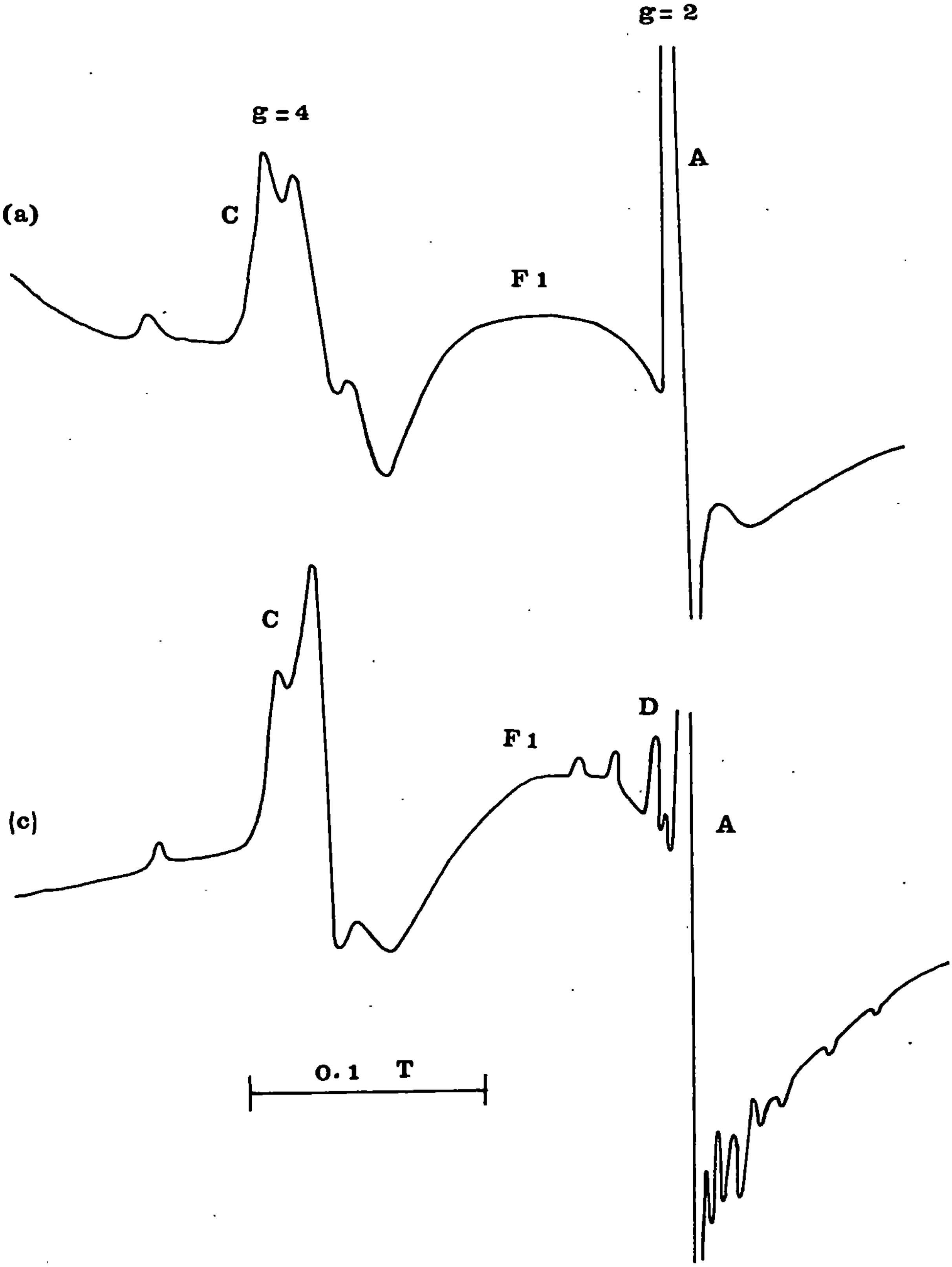

FIG. 5.1. E.S.R spectra recorded at room temperature of:
(a) a typical English kaolinite,
(b) a typical Georgia kaolinite.

reduced to 77 K.

5.3.3 Brightness Measurements.

As iron oxides form one of the major non-white components in kaolinites, brightness measurements were taken for the kaolinites under study. The brightness was measured using a system which was built from equipment available in the laboratory and has been described in detail by Richards.[46] Light of wavelength 458 nm was used and the percentage of light reflected from a pressed disc of kaolinite was compared with barium sulphate as the standard. The values of brightness for the samples were found to lie in the range 75 to 90% with the processed English kaolinite, Supreme, having the highest value and Dubbers and the two American tertiary kaolinites the lowest.

5.4. The Effect of Particle Size on Resonance F1.

As coarse, medium and fine particle size fractions were available for many of the kaolinites, the possible effect of particle size on the resonance F1 and on brightness was studied. Taking account of previous considerations (see section 2.4) the peak to peak height of the broad resonance was taken as a measure of its intensity in samples from the same source, but differing in particle size.

However, no simple relationship between the intensity of resonance F1 and particle size was found.

In Gray, Mines 11, 15 and 50 the intensity tended to increase as particle size increased, whereas in English and Mine 24 the reverse was noted. In Champion, Mine 51 and Chambers no correlation was found. Therefore, no general relationship between titanium or mica content (which have previously been shown to be related to particle size) and resonance F1 could be deduced from these results. However, the intensity of the resonance was found to have a positive, though sometimes poor, correlation with the total iron oxide content.

In all the samples, brightness increased with decreasing particle size. The effect may be attributed to decreased mica content or possibly increased scattering effects.

5.5 The Effect of Thermal Treatment.

The effect of preheating on the broad resonance of kaolinite was investigated for samples Mine 15, Mine 24, Avant and Blackpool. These were chosen as being fairly representative of the suite of kaolinites under study. A small quantity of each sample was heated at various temperatures between 473 and 1473 K for lengths of time varying from 1 to 24 hours. Then E.S.R., X.R.D. and brightness measurements were recorded for each treated sample.

For all of the samples brightness was found to decrease initially on heating and then eventually to rise above the original value. After heating at 673 K for one hour the minimum value was obtained and heating at 773 K for 24 hours was required before the brightness started to increase. On heating at above 1273 K, a maximum value of brightness was reached.

In samples Mine 15 and Avant there was no apparent change in resonance F1 on heating at temperatures up to 973 K. Above this temperature, the resonance began to decrease but did not collapse completely. However, in Mine 24 and Blackpool preheating at 473 K resulted in the formation of another fairly intense broad resonance, which will be referred to as F2. Resonance F2 was on the low field side of the original broad resonance (F1), and superposed on it. F2 increased in intensity on heating at higher temperatures, but reached a maximum after one hour at 673 K (see Fig. 5.2(a) and (c)). This resonance persisted up to 973 K but collapsed on heating at this temperature for 24 hours. In the Blackpool sample resonance F1 remained after preheating at 1473 K, but in Mine 24 PD-1 it decreased considerably above 1173 K.

Heating the samples at 673 K for one hour had no effect on the X.R.D. pattern. However, prolonged heating above 723 K caused the peaks to decrease in intensity and above 823 K, the spectrum collapsed to a broad diffuse band characteristic of metakaolinite. The presence of mullite was noted at 1473 K.

At this stage of the work, taking into account all

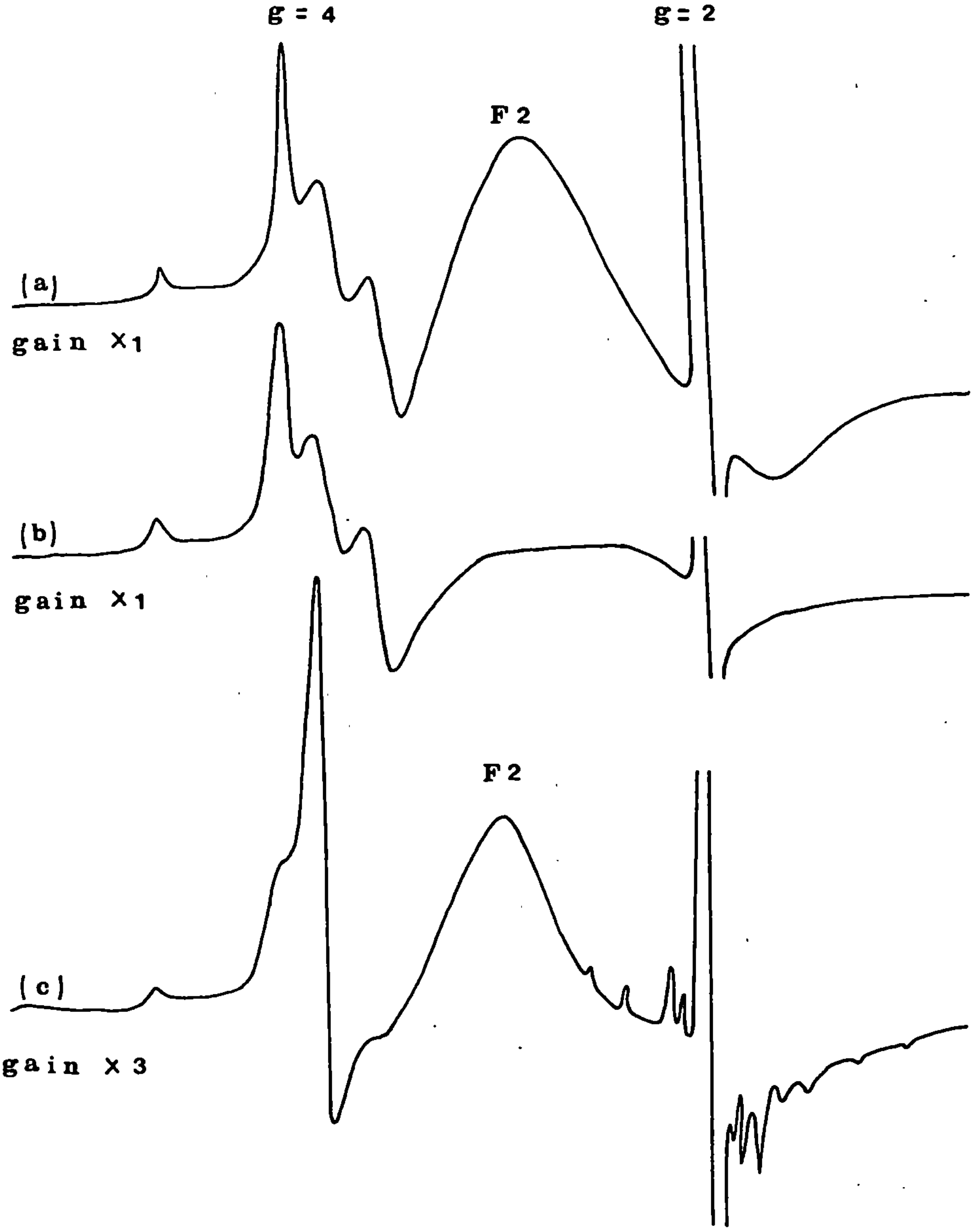

FIG.5.2. E.S.R. spectra recorded at room temperature for:
(a) Blackpool kaolinite heated at 673 K in air for 1 hour.
(b) Blackpool kaolinite heated at 673 K, then deferrified.
(c) Mine 24 kaolinite heated at 673 K in air for 1 hour.

the data available on the samples, it was not clear why two of the kaolinites had produced resonance F2 on heating and two had not. To investigate the effect of thermal treatment more fully, samples of the remaining 12 kaolinites were heated at 673 K for one hour and their E.S.R. spectra were recorded. This treatment was chosen as it involved the shortest period of time and the correspondingly lowest temperature for full development of F2 in Blackpool and Mine 24. It was found that all English kaolinites (i.e. Blackpool, Cholwich Town, Dubbers, Lee Moor, Supreme and English) produced the intense broad resonance F2, but, in contrast, only two of the eleven American kaolinites (Mine 24 and Champion) exhibited the resonance and on a much weaker scale. In these two American samples, no relationship between the intensity of F2 and particle size was found, but for the English sample the intensity increased as the particle size decreased. These results suggest that, in English kaolinites, resonance F2 is not related to mica content, which has been found to concentrate in large particle size fractions (see section 2.4). An alternative explanation is that the resonance is associated with the clay surface.

Production of resonance F2 was not related to crystallinity of the sample. Therefore, it is improbable that the resonance is due to disorder in the kaolinite structure.

E.S.R. spectra were recorded at various temperatures between 77 and 473 K for English samples which had been heated at 673 K for 1 hour. In all cases, as the temperature was decreased, there was a decrease in the peak to peak height of resonance F2, which was accompanied by an increase in the line-width; the g-value was also found to increase (see Fig.5.3). This behaviour is characteristic of ferromagnetic or ferrimagnetic materials.[34]

In addition to differences between English and Georgia kaolinites with respect to resonance F2, it was noted that on heating the samples at 673 K for one hour, the isotropic line of the g = 4 signal had increased in intensity in all the American samples, while there was no such change in intensity in the English kaolinites. This effect will be discussed in chapter 6.

In all the samples the brightness was found to decrease appreciably (4 - 12%) on heating at 673 K for one hour. To the author's knowledge, no similar results have been reported in the literature and, therefore, an explanation of this effect was sought. It did not seem likely that it was due to changes in the broad resonance or g = 4 signal, as these were not observed for all the samples. It was thought that organic matter associated with the kaolinites might be responsible, as organic material is known to produce finely divided carbon black on partial oxidation. At elevated temperature the carbon would be oxidised

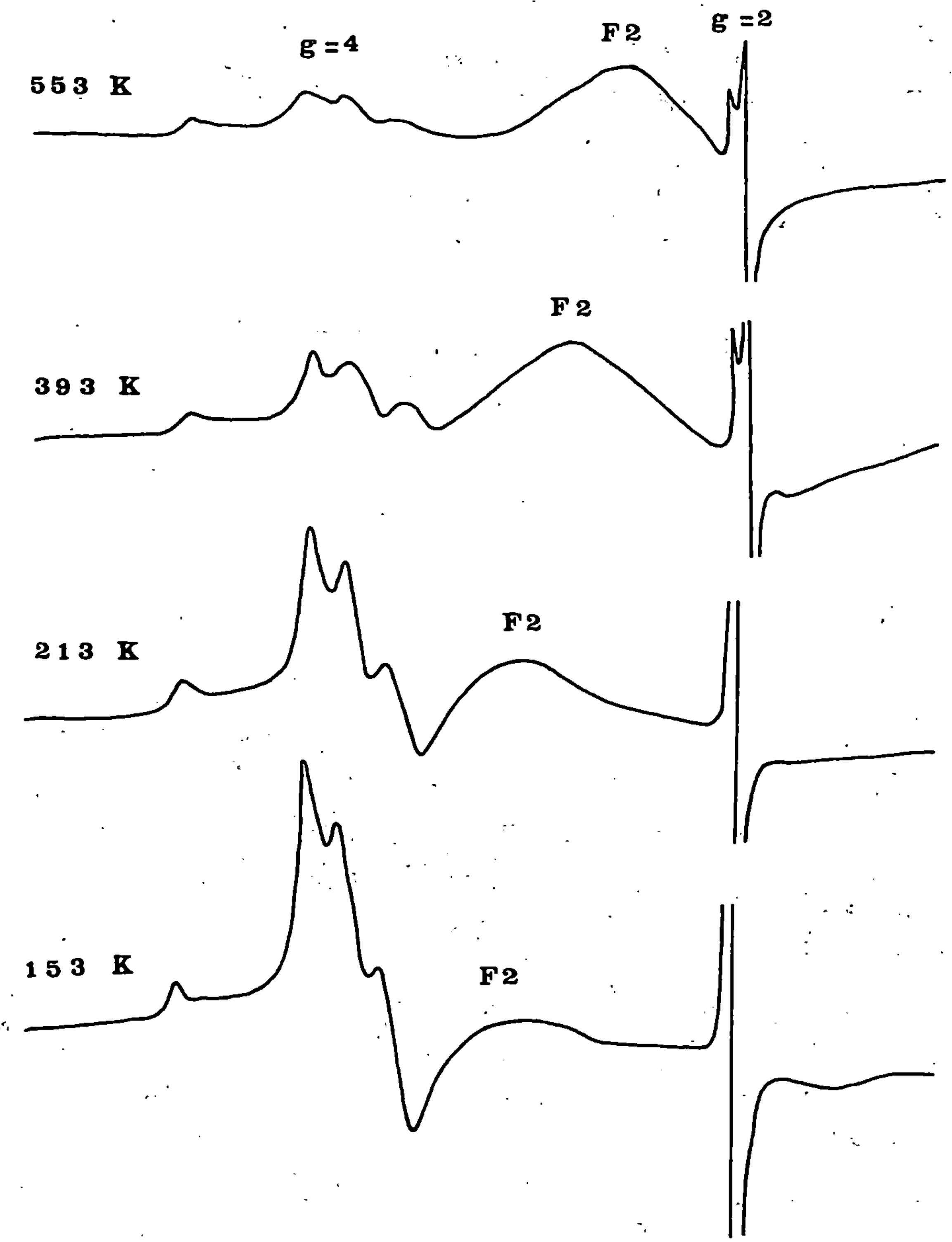

FIG. 5.3. E.S.R. spectra of Blackpool kaolinite heated at 673 K for 1 hour, recorded at various temperatures.

to carbon dioxide and this could account for the observed increase in brightness of the kaolin.

In order to remove organic matter samples of the kaolinites were warmed gently with 30% w/v hydrogen peroxide solution for several days, a treatment which is known to completely oxidise organic matter associated with kaolins.[47] The samples were then washed thoroughly with deionised water and dried at 383 K for two hours. Brightness was determined before and after heating at 673 K for one hour and compared with the values for the untreated kaolinites. It was found that no change in brightness resulted from treating with hydrogen peroxide. However, the heated sample was found to have a significantly lower brightness value when it had been previously warmed with hydrogen peroxide. It must be concluded from these results that the presence of organic matter cannot account for the decrease in brightness values on heating. Moreover, the pronounced reduction in brightness which occurred when heating was preceded by the peroxide treatment was a most unexpected result.

In all the kaolinites the B centre resonance (which consists of hyperfine lines superimposed on the main two line signal, centre A, at g = 2 and which was discussed in chapter 1) was removed by heating at 673 K for one hour. This result agreed with previous studies.[44,48] It was conceivable, therefore, that the decrease in brightness on heating is related to the annealing of the B centres. Hall[48] found that for heated samples on subsequent X-irradiation the B centre signals reappeared. Therefore, several preheated samples were irradiated with doses of approximately 1 MRad and their brightness values re-determined. However, no significant change in brightness was observed following the X-irradiation.

Another possibility was that the iron oxides associated with kaolinites changed on heating so as to cause a decrease in brightness. This will be considered in more detail in the next section.

5.6 The Effect of Chemical Treatment on Resonances F1 and F2.

If broad resonances F1 and F2 are due to iron oxides and hydroxides associated with kaolinite, it should be possible to remove them by subjecting the kaolinite to a number of different chemical treatments. Herbillon et al[5], in their E.S.R. study of kaolinites from tropical soils observed a broad resonance at approximately g = 2. They found that de Endredy's treatment[12] was more successful in reducing this broad resonance than the dithionite-citrate-bicarbonate method of Mehra and Jackson.[11] Therefore, the former procedure was adopted for removing iron impurities from the kaolinites under study. For the sake of conciseness, the de Endredy treatment will be referred to as deferrification throughout the remainder of this thesis.

A suspension of 2 g of sample in 100 cm^3 of

Tamm's solution (0.1 mol dm^{-3} with respect to oxalic acid and 0.175 mol dm^{-3} with respect to ammonium oxalate) was exposed to ultraviolet (U.V.) radiation from the near U.V. region using a Mineralight medium pressure mercury lamp; it was stirred magnetically. An exposure time of two hours was chosen as it was known[5] that use of longer times resulted in precipitation of iron (II) oxalate. The suspension was centrifuged and the supernatant tested for iron using the ammonium thioglycollate test.[49] The residue was washed twice with deionised water and the procedure repeated until no iron was found in the supernatant. The residue was then washed free of oxalate and was dried at 383 K for two hours. Brightness measurements and E.S.R. and X.R.D. spectra were recorded.

The X.R.D. patterns were found to be similar to those of untreated samples indicating that the above treatment had a negligible effect on the structure of kaolinite. In the American samples the treatment appeared to have no effect on the resonance F1 and no significant change in brightness was noted. The intensity of F1 in English kaolinites decreased following deferrification but it was not completely removed (see Fig. 5.4(a)). Also there were marked improvements in the brightness values of Cholwich Town, Dubbers and Lee Moor samples. The increase may be attributed to removal of discolouring iron oxides and

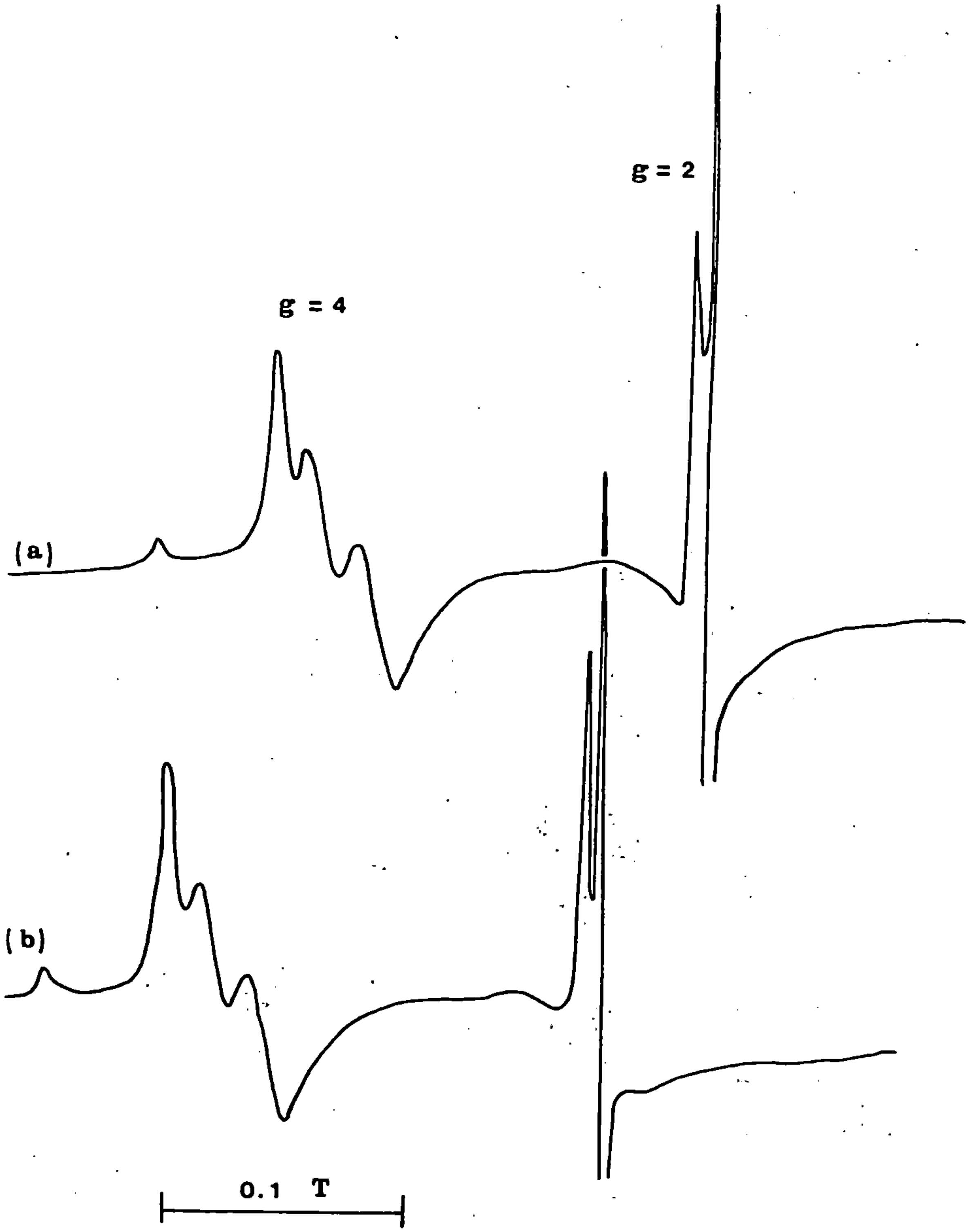

FIG.5.4. E.S.R. spectra recorded at room temperature for Blackpool kaolinite:
(a) deferrified,
(b) deferrified, then heated at 673 K for 1 hour in air.

hydroxides.

It was noted that, in general, more extraction steps were required to remove available iron from American kaolinites than from English samples. This result gave the first indication that the former probably contain iron in a less readily soluble phase.

The treated samples were then heated at 673 K for one hour. Mine 24, Champion and the English kaolinite did not produce resonance F2 (see Fig. 5.4(b)), and no change was noted in the E.S.R. spectra of the other samples. However, there was a distinct drop in brightness for all the kaolinites and the brightness values were between 3 and 20% lower than those found when heating had not been preceded by deferrification. If the lowering of the brightness of kaolinite on heating were attributable to free iron oxides, one would expect samples, which had been deferrified and then heated at 673 K, to possess higher brightness values than untreated kaolinites. Therefore, the results obtained show that the effect of heating at 673 K, which reduces the brightness of kaolinite, cannot be explained by the presence of iron oxides.

English samples, which had been treated at 673 K for one hour, were deferrified. It was found that the resonance F2 was removed (see Fig. 5.2 (c)) and there was also an increase in brightness, though the brightness value was significantly lower than that of the original kaolinite.

For English kaolinites, resonance F2 was removed by deferrification and was not produced on heating at 673 K for samples which had been thus treated. It was, therefore, deduced that resonance F2 was caused by free iron oxides which are removed on deferrification. However, deferrification had little, or no effect on resonance F1. Therefore, it was concluded that this resonance was not wholly attributable to the iron oxides.

5.7. The Effect of Magnetic Separation.

Micaceous and titaniferous impurities of kaolins are known to be iron-stained.[4,6] Therefore, resonances F1 and F2 may be attributable to these minerals and not to the kaolinite. For this reason, samples were magnetically refined, as described in section 2.5.

E.S.R. spectra were recorded for the residues and filtrates obtained from the magnetic separation of the kaolins and the effects of deferrification and preheating at 673 K for one hour were studied. The results are summarised in Table 5.1. X-ray spectra showed that the residues obtained from English kaolins consisted of micas together with small amounts of kaolinite, while those from Georgia kaolins consisted of anatase and rutile in addition to some kaolinite.

Since the resonances F1 and F2 are observed in magnetically refined English kaolinites, they cannot

TABLE 5.1. Broad Resonances Observed in Magnetically Refined Samples of Kaolins and Their Residues.

Treatment / Sample	English Kaolins	Mine 24, Champion	Other Georgia Kaolins
Filtrate from magnetic separation	F1 (m.) (see Fig.5.5(a))	F1 (w.)	F1 (m.)
Filtrate heated at 673 K for 1 hour	F2 (s.) (see Fig.5.5(b))	F1 (w.)	F1 (m.)
Filtrate deferrified then heated at 673 K for 1 hour	F1 (m.)	F1 (w.)	F1 (m.)
Residue from magnetic separation	F1 (s.) (see Fig.5.5(c))	F1 (s.)	F1 (s.)
Residue heated at 673 K for 1 hour	F2 (v.s.) (see Fig.5.5(d))	F2 (v.s.)	F1 (s.)
Residue deferrified, then heated at 673 K for 1 hour	F1 (s.)	F1 (s.)	F1 (s.)

Key: v.s. - very intense; s. - intense; m. - medium; w - weak.

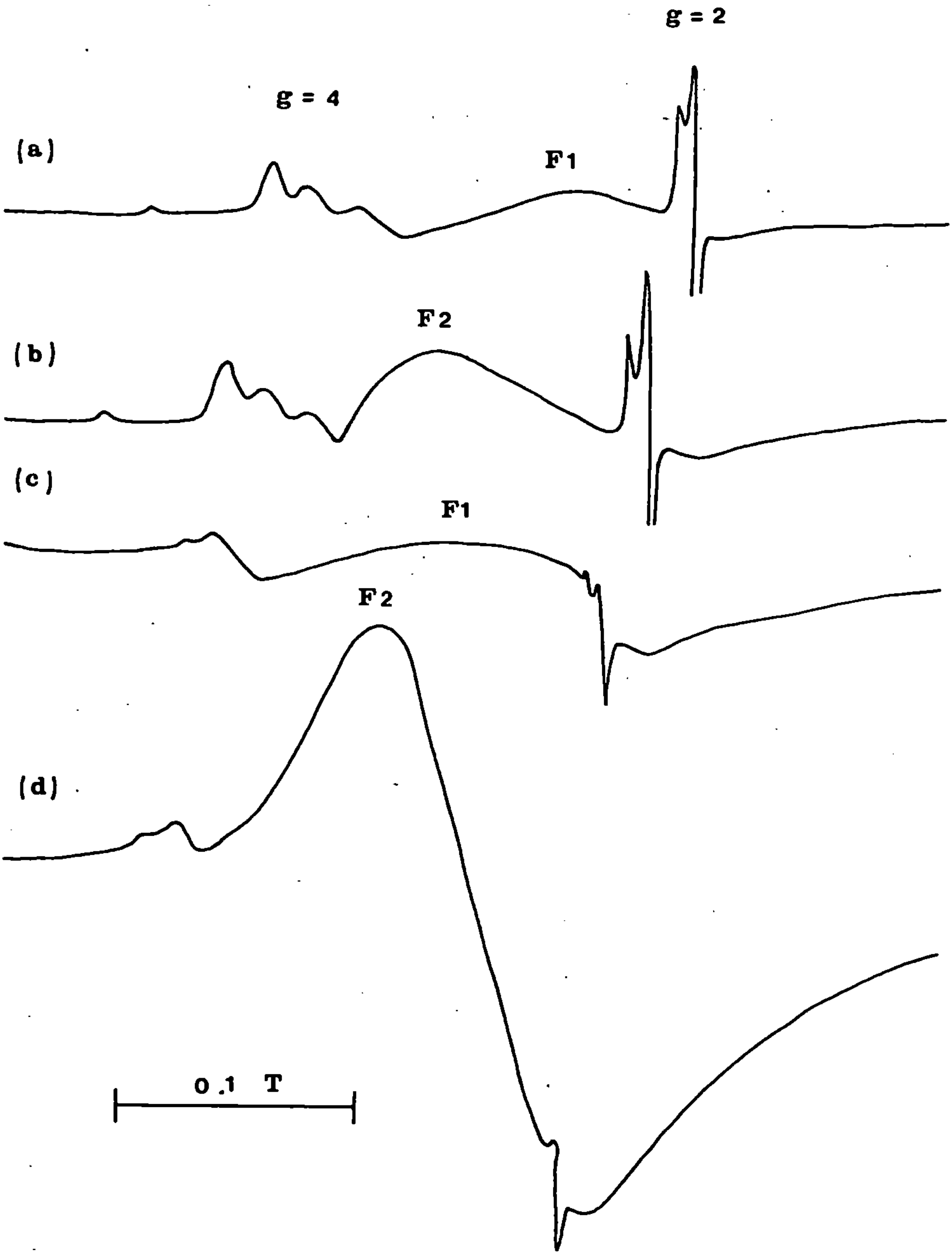

FIG.5.5. E.S.R. spectra recorded at room temperature for Blackpool kaolinite:
(a) filtrate from magnetic separation,
(b) filtrate, heated at 673 K for 1 hour in air,
(c) residue from magnetic separation,
(d) residue heated at 673 K for 1 hour in air.

be attributed solely to micaceous impurities. However, only the residues obtained from magnetic separation of samples Mine 24 and Champion exhibit F2 and so this resonance may be assigned to iron oxides associated with titaniferous impurities. These results provided an explanation for the differences observed in the E.S.R. spectra of Mine 24 and Champion compared with the remaining Georgia kaolinites after preheating. It was now clear that thermal treatment in air at 673 K had a markedly different effect on English and Georgia kaolinites, which could not be explained by the presence, or absence, of micaceous or titaniferous impurities.

To summarise: all the kaolinites exhibit resonance F1 to varying extents, but it is only the English kaolinites which produce resonance F2 on heating at 673 K for one hour in air. The species responsible for resonance F2 is an iron oxide which may be removed by deferrification. The small component of F2, which is shown by two of the American samples, is not associated with the kaolinite fraction.

5.8 The Effect of Thermal Treatment in Atmospheres of Hydrogen, Oxygen and Nitrogen.

In their study of the source of ferromagnetism in zircon, Lewis and Senftle[50] heated zircon specimens in reducing and in oxidising atmospheres at 723 K and followed the reactions by magnetisation measurements. They interpreted the results in terms of an iron oxide coating which consisted mainly of hematite together with some maghemite and/or magnetite.

The effect of similar treatments on natural kaolinites was examined with the intention of identifying the surface oxides. Several samples were heated in hydrogen for one hour at temperatures ranging from 473 to 873 K. For the English kaolinites, resonance F2 developed at temperatures below 673 K (see Fig.5.6 (a)), but, at this temperature, a much more intense resonance (which will be referred to as F3) was observed centred at about g = 2.4. The intensity of resonance F3 reached a maximum value following heating in hydrogen at 723 K (see Fig.5.6.(b)) and then remained constant up to temperatures of 873 K. Georgia kaolinites also exhibited a similar intense resonance on heating in hydrogen (see Fig.5.7 (a)), though the signal did not develop below 773 K for some of the samples (see Fig.5.7 (b) and (c)).

It was found that resonance F3 was readily removed from both English and American kaolinites by warming the samples in hydrochloric acid for two minutes, centrifuging and washing until chloride free (see Fig. 5.6 (c) and Fig. 5.7 (d)). Kaolinites, from which free iron oxides had been removed by deferrification were heated at 723 K for 1 hour. It was found that resonance F3 did not develop in English kaolinites, but was produced by the Georgia samples, even after magnetic refining. The very different behaviours of English

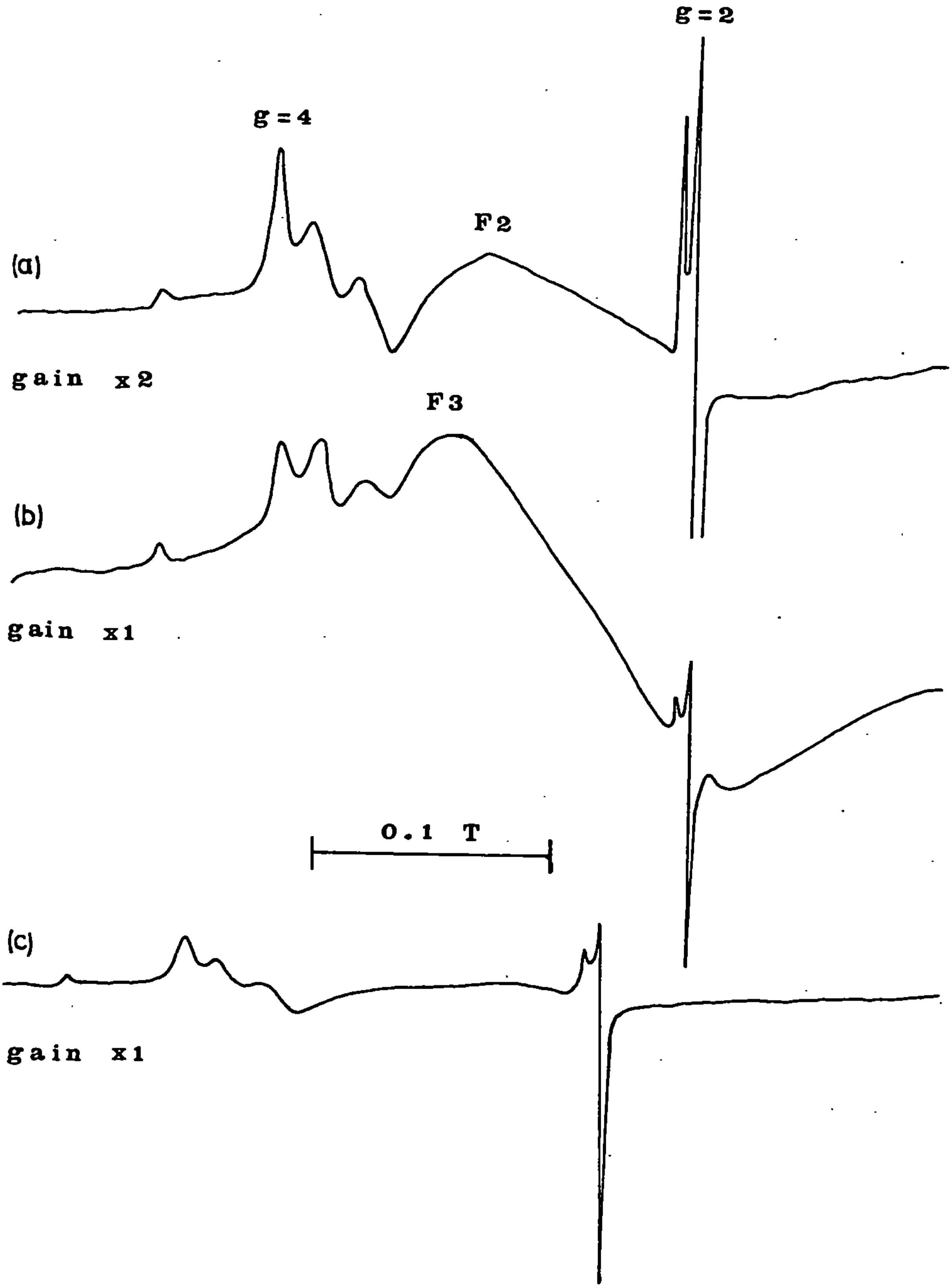

FIG. 5.6. E.S.R. spectra recorded at room temperature of Blackpool kaolinite heated in hydrogen:
(a) for 1 hour at 623 K,
(b) for 1 hour at 673 K,
(c) for 1 hour at 673 K, then treated with hydrochloric acid.

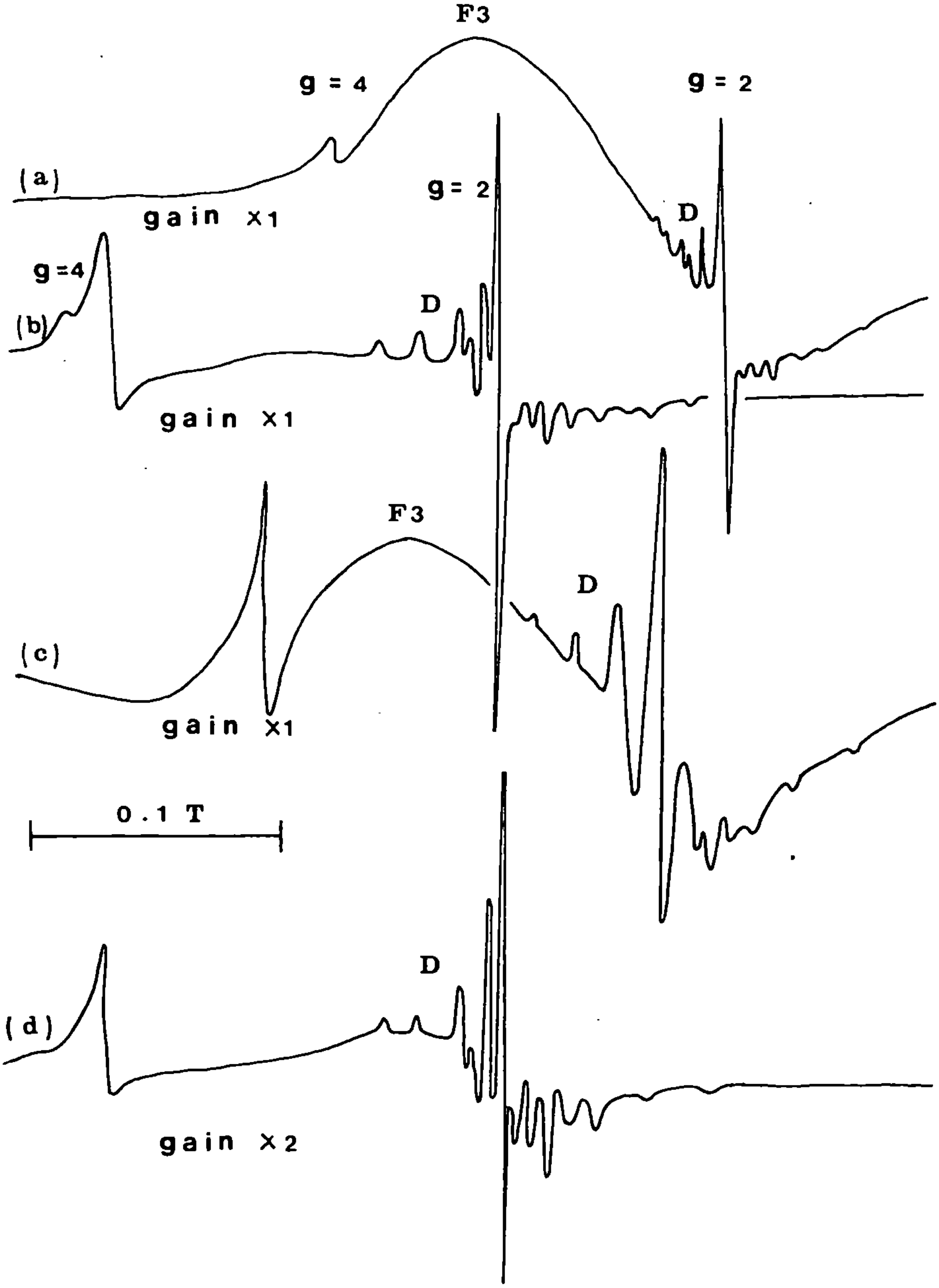

FIG.5.7. E.S.R. spectra recorded at room temperature for:
(a) Mine 11 kaolinite heated at 723 K for 1 hour in hydrogen,
(b) Mine 15 kaolinite heated at 723 K for 1 hour in hydrogen,
(c) Mine 15 kaolinite heated at 773 K for 1 hour in hydrogen,
(d) Mine 11 kaolinite heated at 723 K in hydrogen, then treated with hydrochloric acid.

and American kaolinites following hydrogen treatment at 723 K combined with removal of iron oxides by deferrification provides more evidence that there is a marked difference between the iron oxide impurities associated with the two groups of kaolinites. These results will be discussed at the end of the section.

It was noted that for all of the Georgia kaolinites, which had been heated for 1 hour at 723 K in hydrogen, resonance A had decreased in intensity, while resonance D and the isotropic line of resonance C had increased in intensity. No reduction of resonance A was noted in English kaolinites which had been treated similarly, though further heating at 723 K under hydrogen resulted in a decrease in resonance A with resonance C remaining unaltered. These effects (except for the change in resonance C in Georgia kaolinites) were not observed in the samples when they were heated at similar temperatures in air. As it is known that dehydroxylation at 823 K causes the collapse of resonance A,[44] it was tempting to conclude that hydrogen had catalysed dehydroxylation at a lower temperature. However, this seemed improbable as X-ray spectra of samples heated in hydrogen were similar to those of untreated samples and resonance C in English samples was unaffected. Therefore, an alternative explanation was sought.

Resonance A has been attributed to a defect trapped by a precentre on irradiation and this precentre has been shown to take the form of a foreign ion substituting within the kaolinite structure.[1,2,3,48] It is known that U.V.-radiation, in contrast to X-irradiation, does not produce A centres in kaolinite. Therefore, on the basis of the calculation of the recoil energy of a proton, one possible mechanism of defect formation is that X-irradiation removes a proton or a hydrogen atom. In this work, by heating kaolinite in hydrogen at 723 K, it might be possible that the hydrogen atom was replaced, thus accounting for the removal of resonance A at temperatures below 823 K.

If this hypothesis is valid, one would expect that resonance A would be regrown in hydrogen-treated kaolinite following X-irradiation and annealing. However, no resonance was observed when such a sample had been X-irradiated with a dose of 1 MRad and then annealed at 473 K for two hours. It was suspected, though, that the sample might have occluded hydrogen, which would prevent reformation of resonance A. Therefore, the hydrogen-treated kaolinite was evacuated at 10^{-6} Torr for 24 hours prior to X-irradiation and annealing. This sample was found to exhibit the asymmetric 2-line resonance centred at approximately $g = 2$ which is characteristic of untreated kaolinites. These results show that the collapse of the defect resonance A in samples heated in hydrogen may be explained by assuming that the initial removal of a hydrogen atom is necessary for the formation of resonance A.

The observed increase in the vanadium resonance on heating Georgia kaolinites in hydrogen would be expected if these samples contained vanadium (V) as well as vanadium (IV), which is responsible for the resonance in untreated samples. Vanadium (V) is diamagnetic and so would not be detected by E.S.R. However, it may readily be reduced to vanadium (IV)[52] and so samples, which had been hydrogen treated, would contain more vanadium (IV) and exhibit a more intense vanadium resonance.

Samples of English and Georgia kaolinites heated for one hour in oxygen or nitrogen at 723 K, produced similar results to those obtained for samples heated in air (see section 5.5).

These results with respect to resonances F2 and F3 can be explained by assuming that the iron oxide phase on the surface of English kaolinites differs from that on Georgia kaolinites. On heating in air, oxygen or nitrogen at 723 K, the oxides characteristic of English samples are transformed to a ferromagnetic phase (which is responsible for resonance F2) while those associated with Georgia kaolinites are unaffected. However, heating in hydrogen at this temperature converts both forms of iron oxide into another ferromagnetic phase (which produces F3). English kaolinites, which have been deferrified do not exhibit the resonances F2 and F3 whereas Georgia kaolinites produce F3 both before and after such treatment. Therefore, the English oxides are thought to be removed by deferrification while the oxides on the Georgia kaolinite seem to be less readily soluble.

5.9 Precipitation of Iron Hydroxides on Kaolinite Surfaces.

With a view to identifying the different iron phases present on English and Georgia kaolinites, various kaolinite-iron hydroxide complexes were synthesised. Samples of English kaolinite from Blackpool pit, St. Austell, were deferrified to remove free iron oxides. The samples were then coated with different iron hydroxides using 3 methods described by Greenland and Oades.[14] These methods involved:

(a) precipitation of goethite at pH 8;

(b) precipitation of lepidocrocite at pH 3;

(c) precipitation of amorphous hydroxides at pH = 3,5 and 7.

The kaolinite-hydroxide complexes so formed were studied by E.S.R. and X.R.D. before and after heating at 673 K for 1 hour in air and at 723 K for 1 hour in hydrogen. X-ray spectra were obtained using iron-filtered Co K_α radiation and an A.E.I. diffractometer. The results are summarised in Table 5.2.

Unfortunately the iron hydroxide coatings were not identifiable by X.R.D. However it was noted from the E.S.R. results that kaolinites coated with

TABLE 5.2. Relative Intensities of Broad Resonances at About $g = 2$ Observed for Iron Hydroxides Precipitated on Blackpool Kaolinite.

Coating / Treatment	Goethite	Lepidocrocite	Amorphous Hydroxides		
			pH 3	pH 5	pH 7
Untreated	weak^{+} (Fig.5.8(a))	medium^{+} Fig.5.8(b))	medium^{+}	weak^{+}	weak^{+}
673 K 1 hour	weak^{+} (Fig.5.8(c))	very intense^{+} (Fig.5.8(d))	intense^{+}	medium^{+}	weak^{+}
723 K 1 hour in hydrogen	very intense*	very intense* (Fig.5.8(e))	very intense*	-	-

Key: + :- kaolinite only detected by X.R.D.

* :- in addition to kaolinite, hematite and magnetite detected by X.R.D.

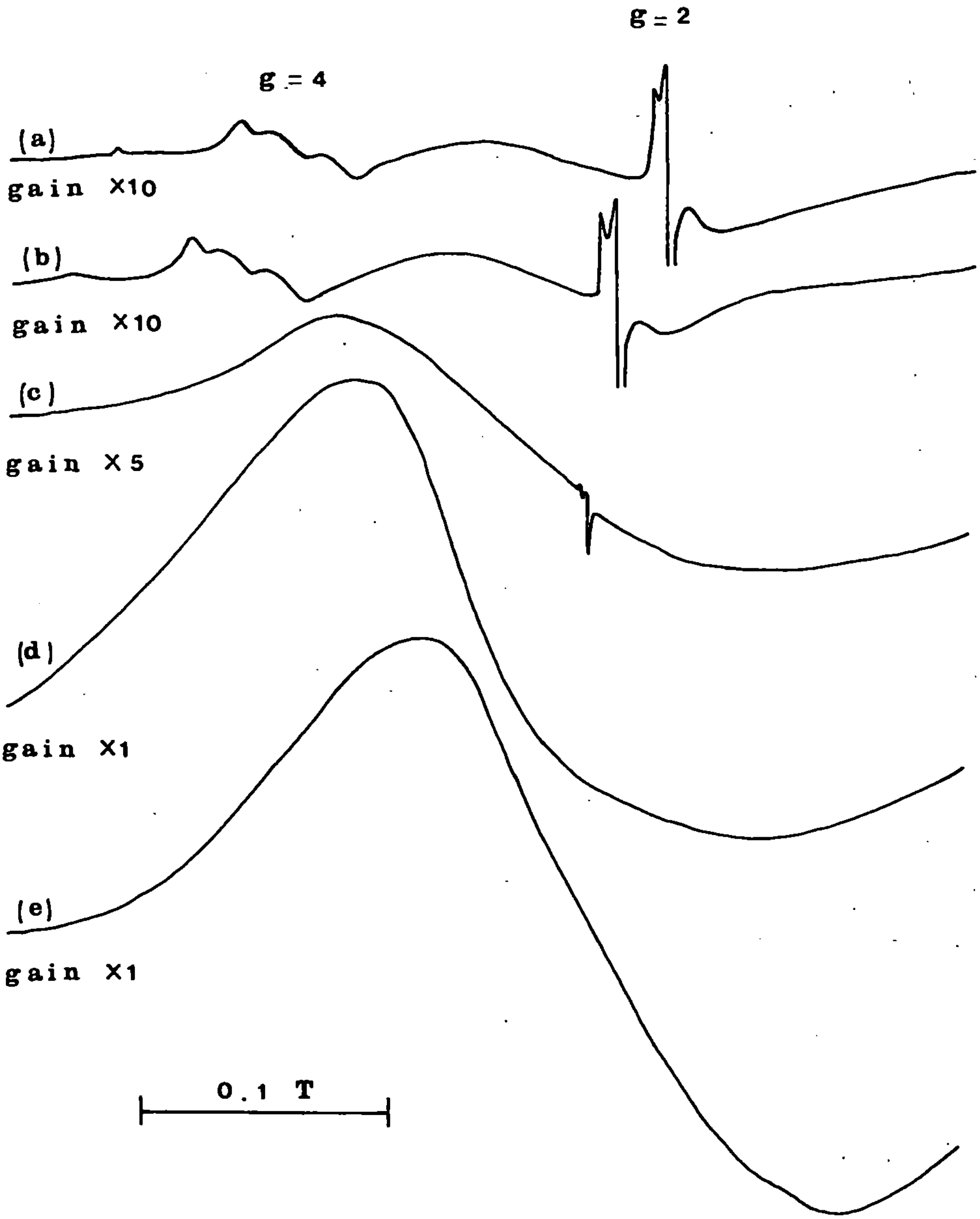

FIG.5.8. E.S.R. spectra recorded at room temperature of deferrified Blackpool kaolinite coated with:
(a) goethite, (b) goethite and heated at 673 K for 1 hour in air,
(c) lepidocrocite,
(d) lepidocrocite and heated at 673 K for 1 hour in air,
(e) lepidocrocite and heated at 723 K for 1 hour in hydrogen.

hydroxides precipitated at low pH resembled natural English kaolinites. In contrast, kaolinites coated with hydroxides precipitated at higher pH produced results similar to those obtained from natural Georgia kaolinites.

5.10 E.S.R. Study of Naturally Occurring Iron Oxides and Hydroxides.

To obtain more information on the different iron phases responsible for the broad resonances exhibited by kaolinites, the magnetic properties of naturally occurring iron oxides and hydroxides were considered. These are summarised in Table 5.3. where it can be seen that species detectable by E.S.R. at room temperature are amorphous oxides, maghemite, lepidocrocite, magnetite and possibly hematite.

Resonance F2 was observed to be ferromagnetic (or ferrimagnetic) in nature and, since its linewidth increased with decreasing temperature, it may be assigned to only maghemite or hematite. This type of resonance is produced when English kaolinites are heated at 673 K in air and maghemite is known to be transformed into hematite at this temperature.[56] It seems reasonable, therefore, to attribute resonance F2 to hematite. However, there is a divergence of opinion in the literature[37,38] as to whether hematite would be detectable at room temperature by E.S.R.

To clarify the situation a study was made of some available iron oxides and hydroxides. Samples of

TABLE 5.3. Magnetic Properties of Naturally Occurring Iron Oxides and Hydroxides.

Name	Formula	Magnetic Properties
Amorphous Oxides	-	Paramagnetic.[22]
Hematite	α -Fe_2O_3	Weakly ferromagnetic above 263 K.[50] (Controversy in literature regarding observance by E.S.R. at X-band at room temperature.[37,38])
Goethite	α -FeOOH	Antiferromagnetic with Neel temperature of 393 K.[37]
Akaganite	β -FeOOH	Antiferromagnetic with Neel temperature of 293 K.[54]
Maghemite	γ -Fe_2O_3	Ferrimagnetic.[53]
Lepidocrocite	γ -FeOOH	Antiferromagnetic with Neel temperature of 73 K.[54]
Magnetite	Fe_3O_4	Ferrimagnetic.[53] E.S.R. linewidth decreases with decreasing temperature to 103 K.[55]

naturally occurring magnetite and hematite (which were obtained from the Department of Geology, Plymouth Polytechnic) and synthetic goethite and lepidocrocite (which were kindly donated by Professor U.Schwertmann of Technische Hochschule, Munich) were heated in air at 673 K and in hydrogen at 723 K for one hour. They were then examined by E.S.R. and X.R.D. The results are shown in Table 5.4.

It was found that hematite exhibited a broad resonance, but it was not of sufficient intensity to account for resonance F2 of kaolinites. However, lepidocrocite produced an intense broad resonance on heating both in air and in hydrogen, a behaviour pattern which is similar to that observed in the English kaolinites. In contrast, the E.S.R. spectra of both goethite and hematite were unaffected by heating in air at 673 K, but an intense broad resonance developed on heating in hydrogen; this behaviour resembles that of Georgia kaolinites. Therefore, it may be reasonable to infer that English kaolinites are associated with a lepidocrocite-like phase while Georgia kaolinites are associated with a geothite- or hematite-like phase. These results will be discussed more fully in chapter 6.

TABLE 5.4. Relative Intensities of Broad Resonances at About g = 2 Observed for Iron Oxides and Hydroxides

Sample / Treatment	Goethite	Lepidocrocite	Hematite	Magnetite
Untreated	weak (see Fig.5.9(a))	medium (see Fig.5.10(a)	medium	intense
673 K 1 hour	weak^{h} (see Fig.5.9(b))	intense (see Fig.5.10(b))	medium^{h}	intense^{h+a}
723 K 1 hour	intense^{h,a,f} (see Fig.5.9(c))	intense^{h+a+f} (see Fig.5.10(c))	intense^{h+a+f}	intense^{h+a+f}

Key:- a - magnetite; b - maghemite

f - iron ; h - hematite

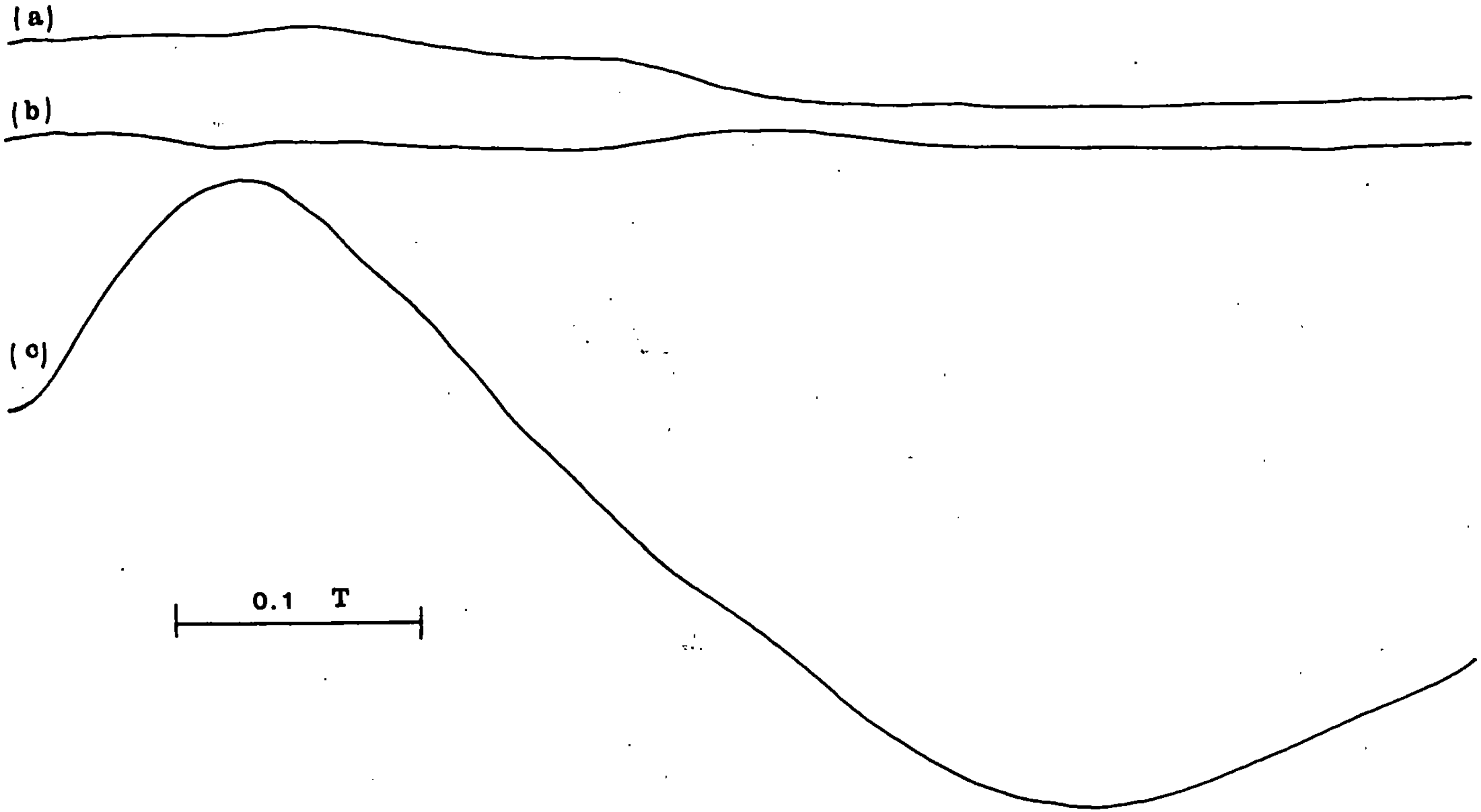

FIG.5.9. E.S.R. spectra recorded at room temperature from 0 to 0.6 tesla for synthetic goethite:
(a) untreated, (b) heated at 673 K in air for 1 hour,
(c) heated at 723 K in hydrogen for 1 hour.

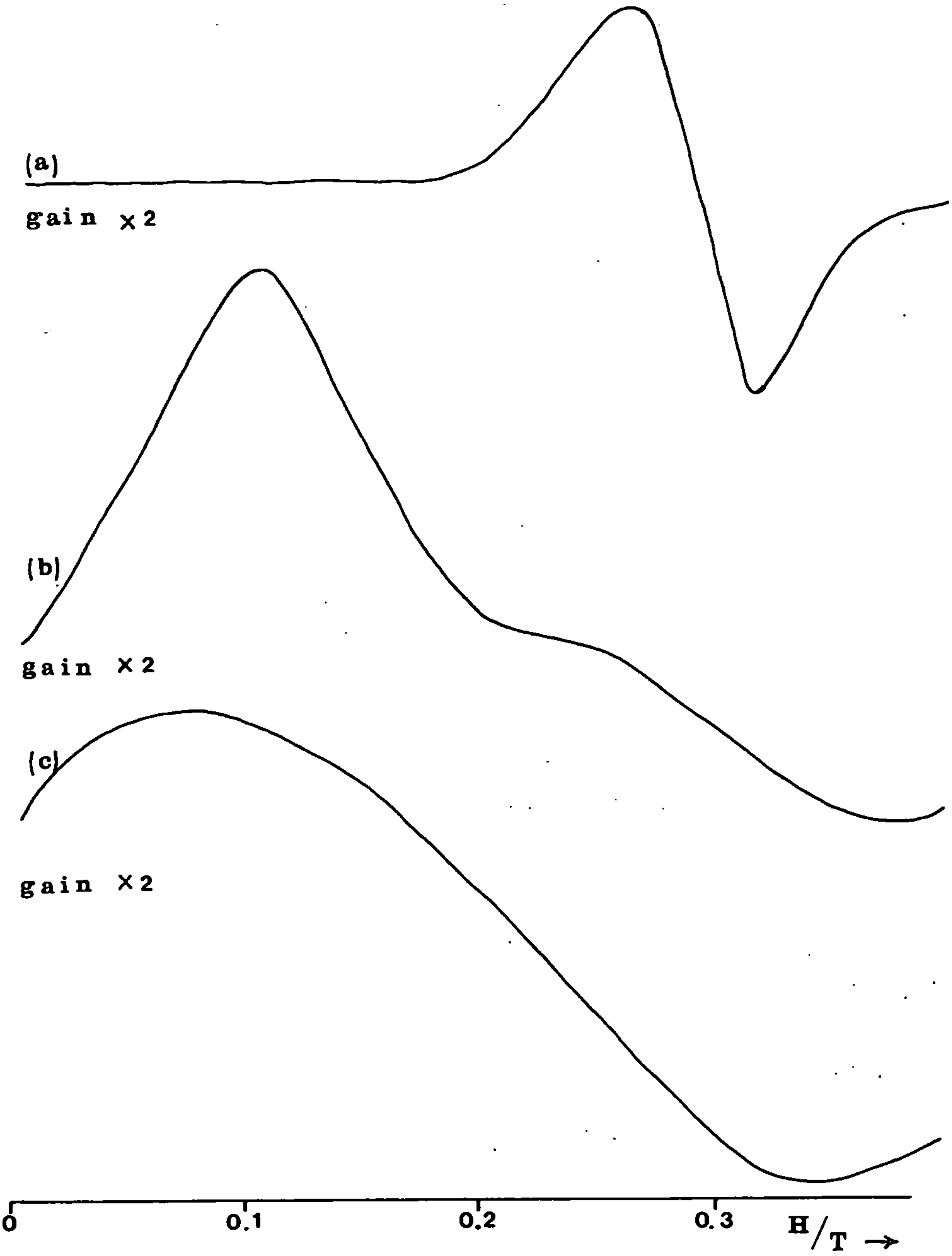

FIG.5.10. E.S.R spectra at room temperature of synthetic lepidocrocite:
(a) untreated, (b) heated in air at 673 K for 1 hour.
(c) heated in hydrogen at 723 K for 1 hour.

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CHAPTER 6.

FINAL SUMMARY AND DISCUSSION.

6.1 Vanadium in Kaolinites.

The E.S.R. study of two suites of naturally occurring kaolinites from Georgia, U.S.A., and from the South West peninsula of England has shown that only the American samples exhibit a weak resonance centred at $g = 2$ which comprises a maximum of 16 features and has been attributed to tetravalent vanadium. By following the changes in the E.S.R. spectra of the Georgia kaolinites caused by magnetic separation, thermal and chemical treatments, preferential orientation and relative humidity, it was concluded that vanadium is substituted in the kaolinite structure and is not associated with either the kaolinite surface or mineralogical impurities (mainly anatase).

In order to support the conclusions drawn from the study of naturally occurring samples, a method of synthesis of vanadium-doped kaolinites was developed. It was found that the synthesised kaolinites, which had not been heated, exhibited vanadium resonances exactly superposable on those of Georgia kaolinites. Furthermore, by repeating the experiments which had been developed for the natural samples, it was concluded that vanadium is also substituted in the kaolinite structure of these synthetic samples.

However, the vanadium-doped synthetic kaolinites produced contrasting results compared with the natural Georgia kaolinites following thermal treatment. For the natural samples, the vanadium resonance collapsed on preheating at temperatures above 773 K, which causes dehydroxylation of the kaolinite to form metakaolinite. The vanadium resonance of the synthetic kaolinites did not decrease in intensity below preheating temperatures of approximately 1273 K, when metakaolinite is known to be transformed into either a spinel-type phase or mullite. The difference in behaviour patterns can be accounted for by postulating that vanadium is located at different sites in the kaolinite structure for natural and synthetic kaolinites.

Dehydroxylation of kaolinite causes a major alteration of the octahedral layer, but the tetrahedral layer remains essentially unchanged.[1] As dehydroxylation has such a pronounced effect on the vanadium resonance of naturally occurring kaolinites, it was deduced that vanadium is substituted in the octahedral layer for these samples. However, when metakaolinite is converted into new crystalline phases at elevated temperatures it is known that the tetrahedral layer is modified[2] thus leading to the conclusion that vanadium is substituted in the tetrahedral layer of the synthetic kaolinites. Synthesis of vanadium-doped boehmite, a mineral which has a structure similar to that of the octahedral layer of kaolinite, provided further evidence for substitution of vanadium in the octahedral layer of natural kaolinites. The behaviour of the vanadium resonance with respect to thermal treatment was found to be similar in both samples.

Using the methods of synthesis and doping described in this work, it was not possible to prepare synthetic kaolinites which, following thermal treatment, produced behaviour patterns identical to the natural samples. However, it is clear from the very large volume of literature,[3,4] which is available on the genesis and synthesis of kaolinites, that the chemistry and thermodynamics of the reactions involved are not fully understood. One of the major constraints inherent in the study of the reactions would seem to be the amorphous nature of the alumino-silicate gels, which do not lend themselves to examination by recognised chemical and physical techniques to determine their structure. It was appreciated from a consideration of the literature that the processes involved in the genesis of the natural kaolinites were probably different to those used in the laboratory. However, it was considered unwise at the present time to postulate reaction mechanisms which would account for the formation of kaolinite with vanadium in either octahedral or tetrahedral sites in the two sets of samples.

Possible mechanisms for the collapse of the vanadium resonance in heated samples of both natural and synthetic kaolinites include:

(a) oxidation of V^{4+} to V^{5+}, which is diamagnetic and not observable by E.S.R.;

(b) reduction of V^{4+} to V^{3+}, which would not be detected by E.S.R. at room temperature.

However, the details and true nature of these mechanisms are not understood.

On the basis of ionic size considerations, it was inferred that vanadium is present in the kaolinite structure as the V^{4+} ion and not as $(VO)^{2+}$. However, bearing in mind the structure of vanadium oxides,[5] it is anticipated that one of the V-O bonds would have more double bond character than the others in the VO_x unit (where $x = 4$ for substitution in the tetrahedral layer and $x = 6$ for substitution in the octahedral layer) and, therefore, V^{4+} substituted in kaolinites might show some resemblance to the vanadyl ion.

Hydrogen treatment of Georgia kaolinites at 723 K produced a significant increase in the intensity of the vanadium resonance. The increase was explained by assuming that these samples contained V^{5+}, which is not detectable by E.S.R. but is reduced to V^{4+} by the hydrogen treatment. Heating in oxygen at similar temperatures had no measurable effect on the vanadium resonance. It might be deduced, therefore, that V^{3+} is not present in kaolinite as one would expect V^{3+} to be readily oxidised to V^{4+},[5] resulting in an increase in the intensity of the resonance.

It was also shown that vanadium (IV) may be adsorbed on the surface of both synthetic and natural kaolinites, regardless of their origin. It was demonstrated that by comparing E.S.R. spectra of samples equilibrated in atmospheres with low and high values of relative humidity it was easy to distinguish between vanadium substituted in the structure and vanadium adsorbed on the surface.

6.2. Resonance A at g = 2 in Kaolinite.

Previous work in this laboratory had shown that the resonance at g = 4 in natural kaolinite could be assigned to Fe^{3+} [4,5,6,7] and that resonance A could be attributed to a paramagnetic defect which was produced by X-irradiation and stabilised by substitution of Mg^{2+} for Al^{3+}.[7,8,9] Although it had been suggested that, on the basis of ionic charge and comparable ionic radius, Fe^{2+} might perform the same function as Mg^{2+}, previous attempts to synthesise Fe^{2+}-doped kaolinite had been unsuccessful.[7]

In this work it was shown that it was possible to synthesise a kaolinite doped with Fe^{2+}, which, following X-irradiation and annealing, exhibited an asymmetric two-line resonance at g = 2 identical to that observed in natural kaolinites. Therefore, it is now feasible to interpret the two main groups of resonances common to natural kaolinite in terms of either iron substitution alone or iron and magnesium substitution.

It has been found previously that resonance A collapses in both natural[4] and synthetic[5] kaolinites on dehydroxylation at temperatures above 773 K. However, it was noted during this work that, when natural kaolinites were heated in hydrogen at 723 K, resonance A was removed. In addition it was found that resonance A could be reformed only in a sample which had been evacuated prior to X-irradiation and annealing. If occluded hydrogen were not removed, it was not possible to reform resonance A. Jones[10] postulated two models for the paramagnetic defect responsible for resonance A:

(a) On X-irradiation hydrogen atoms are removed from some of the hydroxyl groups in the vicinity of the substituted Mg^{2+} or Fe^{2+} resulting in formation of O^- ions, which, if adjacent, form $(O_2)^{2-}$ ions. On further irradiation an electron is lost to stabilise the charge imbalance due to Mg^{2+} or Fe^{2+} substituting for Al^{3+} and thus creating the superoxide ion, $(O_2)^-$, which would be trapped within the kaolinite structure.

(b) On X-irradiation a hole is trapped on the oxygen bridging the Si^{4+} and Mg^{2+} or Fe^{2+} ions. However, Jones[8] presented no experimental evidence in preference of either model. The results obtained from hydrogen treatment of natural kaolinites are consistent with the assumption that X-irradiation removes a proton or a hydrogen atom from the kaolinite structure. Furthermore, the presence of occluded hydrogen has been shown to prevent the defect forming. As the removal of hydrogen would seem to be critical to formation of the defect, the results obtained in this work support model (a) more than (b).

In Georgia kaolinites, it was also noted that the effect of heating in hydrogen at 723 K, as well as removing resonance A, also caused the isotropic line at $g = 4$ to increase in intensity. It is tempting, therefore, to assume that changes in the resonance at $g = 4$ are related to annealing of the defect responsible for resonance A. Indeed, if resonance A were attributable to a defect stabilised by Fe^{2+} substituting for Al^{3+} and the defect were annealed, one might expect Fe^{2+} to be converted to Fe^{3+}, which would account for the observed change in the $g = 4$ resonance. However, for English kaolinites heated in hydrogen no corresponding change in the $g = 4$ resonance was observed when resonance A collapsed. Considering the chemical analysis of the samples, it might be argued that, in the English kaolinites, Mg^{2+}, as opposed to

Fe^{2+}, acts as the precentre and, therefore, prevents the formation of more Fe^{3+} and a change in the $g = 4$ signal. However, when Georgia kaolinites were heated in air at 723 K, a similar increase in the isotropic line at $g = 4$ was also noted, but with no corresponding decrease in resonance A. No changes were observed in the E.S.R. spectra of English kaolinites heated at 723 K in air. Hence, the results from the samples heated in air invalidate the hypothesis that, for resonance A, Fe^{2+} is indirectly responsible in the Georgia kaolinites and Mg^{2+} in the English samples.

It is known that dehydroxylation of kaolinite at 773 K causes an increase in the isotropic resonance at $g = 4$ accompanied by a decrease in resonance A.[6] However, as X.R.D. spectra of Georgia kaolinites heated at 723 K in air were found to be identical to those of untreated samples and as resonance A had not been reduced in intensity, it was assumed that dehydroxylation had not occurred. To date, no satisfactory explanation has been found for the change in the resonance at $g = 4$ observed on heating Georgia kaolinites below their dehydroxylation temperatures.

6.3 Iron Oxide Phases Associated with Kaolinite.

It was found from the preliminary E.S.R. studies of English and American kaolinites that all the samples exhibited a broad resonance, F1, to varying extents. On heating at 673 K for one hour in air, oxygen or nitrogen, English kaolinites produced a more intense broad resonance, F2. Resonance F2 was also found in two of the American samples, but separate studies using magnetic filtration and X.R.D. analysis showed that resonance F2 in these samples was associated with anatase impurities and not the kaolinite fraction. The results obtained from the application of magnetic refining to the samples also demonstrated that resonance F2 in English kaolins was common to both the kaolinite fraction and the mica impurity. Both Georgia and English kaolinites, however, produced an intense broad resonance F3 when they were heated in hydrogen at 723 K.

To establish whether the resonances F1, F2 and F3 were possibly caused by iron oxide impurities associated with the kaolinite, samples were deferrified to remove surface iron oxides. This treatment had a negligible effect on resonance F1 in Georgia kaolins, and reduced, but did not remove it completely in the English samples. It was, therefore, concluded that resonance F1 could not be attributed wholly to surface iron oxides associated with the kaolinites. However, it was found that English kaolinites, which had been deferrified, produced neither resonance F2 on heating at 673 K in air nor resonance F3 following hydrogen treatment at 723 K. Therefore, it was deduced that resonances F2 and F3 in English kaolins were due to iron oxides which could be removed by deferrification.

In contrast, it was found that American kaolinites, which had been deferrified, continued to produce resonance F3. This being so, it was assumed that the iron oxides associated with American kaolinites were not readily removed by deferrification. It was clear that the iron oxides associated with the English kaolinites were very different from those associated with the American samples.

To seek a means of identifying the possible different iron oxide phases, samples of an English kaolinite, which had previously been deferrified to remove the iron oxides, were coated with various iron hydroxides by methods described by Greenland and Oades.[11] These methods involved:

(a) precipitation of goethite at pH 8;

(b) precipitation of lepidocrocite at pH 3;

(c) precipitation of amorphous hydroxides at pH = 3,5 and 7.

In their original paper, Greenland and Oades claimed to have identified goethite and lepidocrocite by X.R.D. powder photography, but, in this work, with the X.R.D. methods available (a diffractometer and proportional counter) it was not possible to distinguish any crystalline iron compounds deposited on the kaolinite surfaces. However, it was found that samples coated with hydroxides precipitated at low pH values displayed resonance F2 on heating in air at 673 K and resonance F3 on heating in hydrogen at 723 K. In contrast, when higher pH values were used, resonance F2 was not observed on heating in air, though resonance F3 was still exhibited on heating in hydrogen. It was apparent that samples coated with hydroxides precipitated at low pH values behaved similarly to the English kaolinites while those coated with hydroxides formed at higher pH values resembled the American kaolinites.

As no crystalline iron compounds had been identified in the study of coated kaolinites, the effect of thermal treatments in air and in hydrogen was investigated for naturally occurring iron oxides and hydroxides. Lepidocrocite had a behaviour pattern similar to that of the oxides associated with English kaolinites, while goethite and hematite resembled the oxides associated with the American kaolinites. From the above results it was inferred that the oxide associated with English kaolinites is probably similar, if not identical to, lepidocrocite. Equally the oxides associated with the American samples were attributable to goethite- or hematite-like phases.

It is generally accepted that deferrification by de Endredy's method[12] consists of dissolution in Tamm's solution involving a chemical reaction which is photosensitive to U.V. and de Endredy[12] has claimed that this method removes both the crystalline and the amorphous oxides of iron. However, it has been found that only amorphous and poorly crystalline iron oxides are soluble in Tamm's solution in the dark.[13] Samples of lepidocrocite, goethite and hematite which were deferrified in this laboratory showed that lepidocrocite dissolved in about 2 hours while the others persisted even after 24 hours. These results provide further evidence in support of the suggestion that the English kaolinites are coated with a lepidocrocite-like phase, which is removed on deferrification, whereas the American kaolinites are coated with a goethite-or hematite-like phase, which is less readily extracted.

The difficulty which arises from the above conclusions, bearing in mind the known transformations of the oxides and hydroxides of iron (see Fig.6.1), is that at 673 K both lepidocrocite and goethite are known to be transformed to hematite.[14] It is, therefore, not clear why lepidocrocite at 673 K should produce resonance F2 while goethite and hematite do not. However, X.R.D. studies of lepidocrocite heated at 673 K for one hour in air showed the presence of magnetite or maghemite in addition to hematite and both of these oxides being ferrimagnetic could account for resonance F2. Owing to the broadness of the peaks and their relatively low intensity it was not possible to distinguish between magnetite and maghemite by X.R.D. However, it was deduced that the oxide was more probably maghemite for the following reasons:

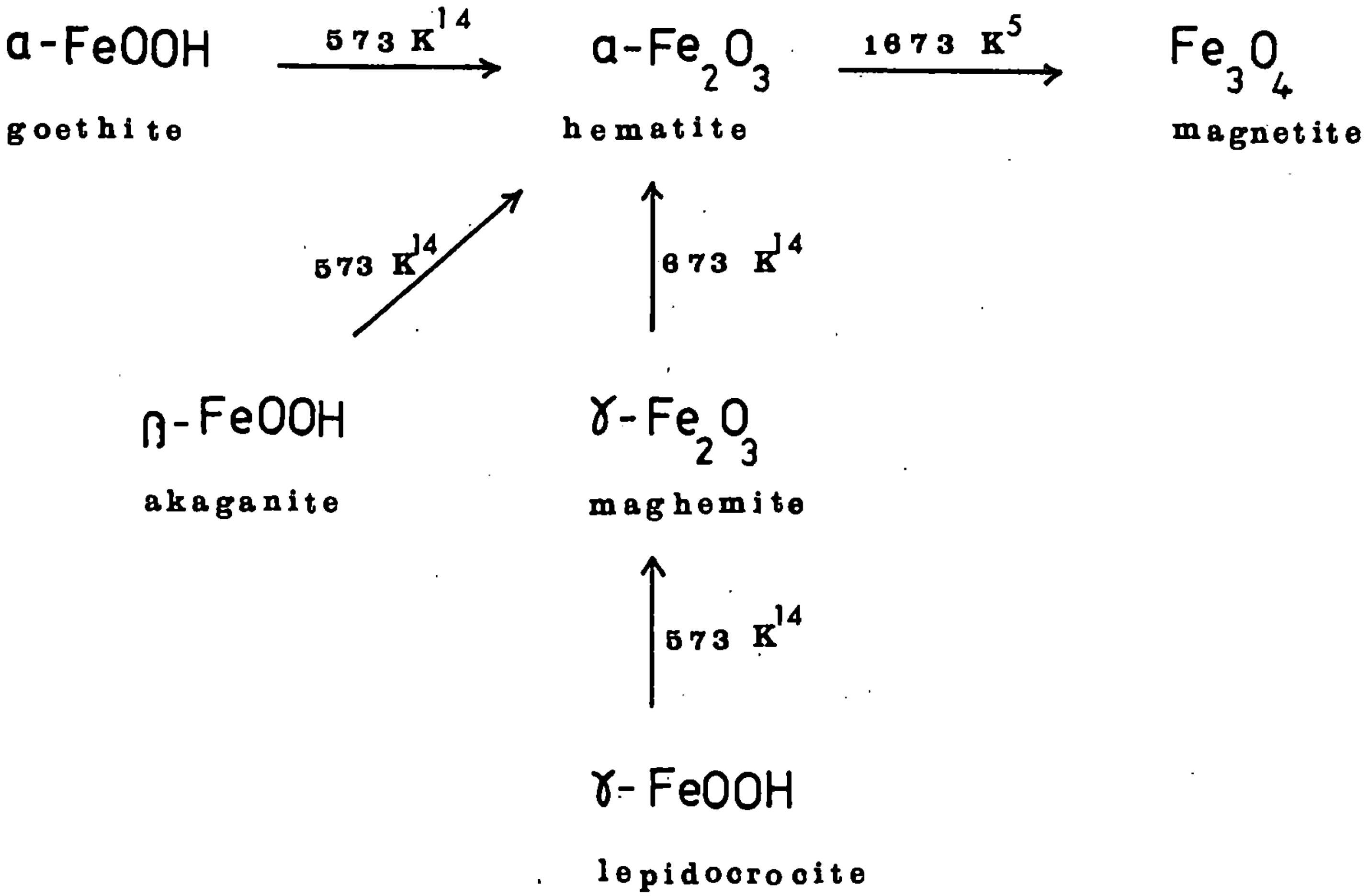

FIG. 6.1. The thermal transformations of naturally occurring iron oxides and hydroxides.

(a) the linewidth of resonance F2 was found to increase with decreasing temperature whereas it is known that the linewidth of the magnetite resonance decreases with decreasing temperature;[15]

(b) magnetite would not be expected to be formed from the other oxides at temperatures below 1673 K in air[5] (see Fig.6.1).

On the other hand it is not apparent why maghemite should remain stable at 673 K when it might be expected to have been converted to hematite.

With regard to resonance F1, which in English kaolinites is partially reduced in intensity on deferrification, the removable component can be attributed to the lepidocrocite-like phase, which would be extracted by deferrification and which is known to be paramagnetic at temperatures above 70 K. It must be emphasised that a paramagnetic resonance is approximately three orders of magnitude less intense than a ferrimagnetic resonance for the same number of spins.[16] The difference accounts for the much greater intensity of resonance F2, which has been attributed to a ferrimagnetic phase. In Georgia kaolinites, resonance F1 was not affected by deferrification so this resonance (and the residual part of resonance F1 in English kaolinites) is probably due to interaction between adjacent Fe^{3+} ions which are known to be substituted in the kaolinite structure.[7,8,9]

Resonance F3 is formed by all the kaolinites on heating in hydrogen at 723 K. X.R.D. studies of kaolinites coated with amorphous iron hydroxides and of naturally occurring iron oxides and hydroxides thus treated show the presence of hematite, magnetite and iron. Therefore, resonance F3 has been attributed to magnetite and/or iron.

Isolated lepidocrocite is normally metastable and readily transforms to its stable polymorph, goethite. However, lepidocrocite is known to occur as a stable compound in soils (particularly in humid, temperate regions).[17] The relative stability of lepidocrocite in soils has been studied in detail and has been shown to be dependent on the amount of organic matter[13] and the concentration of silicon cations,[18] which might be present. The chemical analyses of the samples indicate that the English kaolinites contain more silica than the American kaolinites. Also, organic matter is generally more abundant in English kaolins. It seems reasonable, therefore, to suggest that English kaolinites in a temperate climate are associated with an iron oxide which is similar to lepidocrocite. Hematite rarely occurs in soils of temperate regions, but mixtures of hematite and goethite are common in warmer regions.[19] A reasonable inference, therefore, is that American kaolinites are associated with hematite- or goethite- like phases.

6.4 Brightness Values of Kaolinites.

During the course of the E.S.R. studies of the English and American kaolinites, the effects of the various physical and chemical treatments on the brightness values of the samples was examined. It was found that deferrification improved the brightness of all the English kaolins, but produced no measurable effect in the American samples. This behaviour pattern is expected as iron oxide impurities are known to form one of the major non-white components of kaolins.[20] Deferrification using de Endredy's treatment was shown by the E.S.R. studies to be effective only for the English kaolinites. Organic material is also thought to have a deleterious effect on the brightness of clays. However, in this work, removal of organic impurities by hydrogen peroxide treatment had a negligible effect on the brightness values of the kaolinites studied.

It was noted that the brightness of all the kaolinites decreased appreciably following thermal treatment at 673 K for one hour. Moreover, the heated samples were found to have significantly lower brightness values when the heating had been preceded by chemical treatment. This result was most unexpected and was not readily explained. The only change in the E.S.R. spectrum, which was exhibited hematite- or goethite- like phases.

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It was noted that the brightness of all the kaolinites decreased appreciably following thermal treatment at 673 K for one hour. Moreover, the heated samples were found to have significantly lower brightness values when the heating had been preceded by chemical treatment. This result was most unexpected and was not readily explained. The only change in the E.S.R. spectrum, which was exhibited by all the samples on heating at 673 K, was the collapse of the resonance attributed to B-centres. It is known that B-centres can be reformed on X-irradiation, but in this work no accompanying increase in brightness was observed. It can only be assumed that the effect of heating on the brightness of kaolinite is related to the surface of kaolinite, which remains an area of intense study in many industrial laboratories. To date, the true nature and surface chemistry of kaolinites is not fully understood. In this respect it is hoped that the results presented in this thesis may be of assistance.

6.5. Suggestions for Future Work.

It is suggested that an extension of the present studies of vanadium associated with kaolinite might involve the investigation of the effect of adsorption of vanadium ions on the rheological properties of kaolinite. It might also be interesting to study the rheology of kaolinites with respect to other adsorbed ions.

Further information regarding the iron oxide phases associated with English and American kaolinites may be found by comparing magnetic susceptibility measurements for samples following chemical and thermal treatments. Also an investigation of the effect of other methods of iron oxide removal, in particular the dithionite-citrate-bicarbonate method of Mehra and Jackson,[21] on the American kaolinites might prove useful.

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PAPERS SUBMITTED AND ACCEPTED FOR PUBLICATION

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Paper presented at the 3rd Meeting of the European Clay Groups, Oslo, June 1977.

Electron spin resonance studies of iron oxides associated with kaolinite.
Draft of paper to be submitted for publication in Clay Minerals.

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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 subsitution of Fe^{3+} amd 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 $g = 2.0$ 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 (Hall, 1973) and a survey of a large number of samples established, without exception, the existence of fairly intense signals. 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

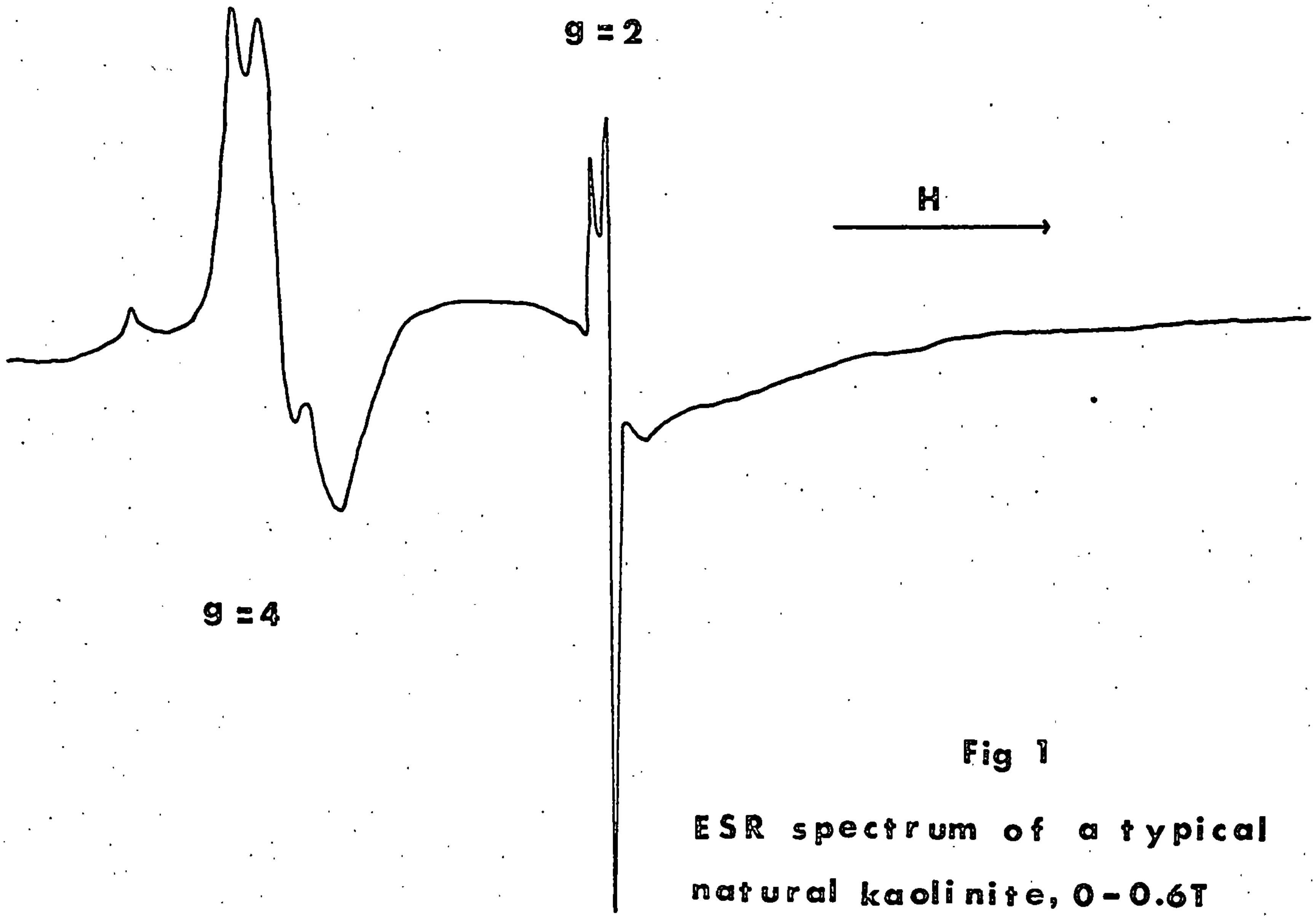


Fig 1

ESR spectrum of a typical natural kaolinite, 0–0.6T contaminants (Angel and Hall, 1972). 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 organic fraction (Hall, Angel and Braven, 1974). This being so, it seemed feasible to seek the sourse of the resonances from comparisons of the chemical analysis of natural samples with the known structure of kaolinite and the results indicated that iron was most probably responsible. Castner et al (1960) have shown that glasses doped with iron produce intense resonance signals at g = 4.0 and it has been shown by Angel et al (1974) using iron doped synthetic kaolinites that the g = 4.0 resonance in kaolinite can be assigned to iron substituted in the strucure. 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. Furthermore, Angel et al (1974) found that intercalation of kaolinite with dimethysulphoxide 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 (Orton, 1968) 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 stablise in a number of different ways, depending on the relative strengths of the interactions and the geometry of the crystal field. At room temperature either groups of lines at g = 4.0 are observed or at least five lines at g = 2.0. 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. It is difficult to see how much 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 (Griffiths, Owen and Ward, 1955; Joffe, 1967; Marfunin et al, 1970). 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. The pre-centre often takes the form of a foreign ion substituting within the crystal structure and requiring charge compensation. For kaolinite divalent magnesium or divalent 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 indentical to that observed in natural kaolinites.

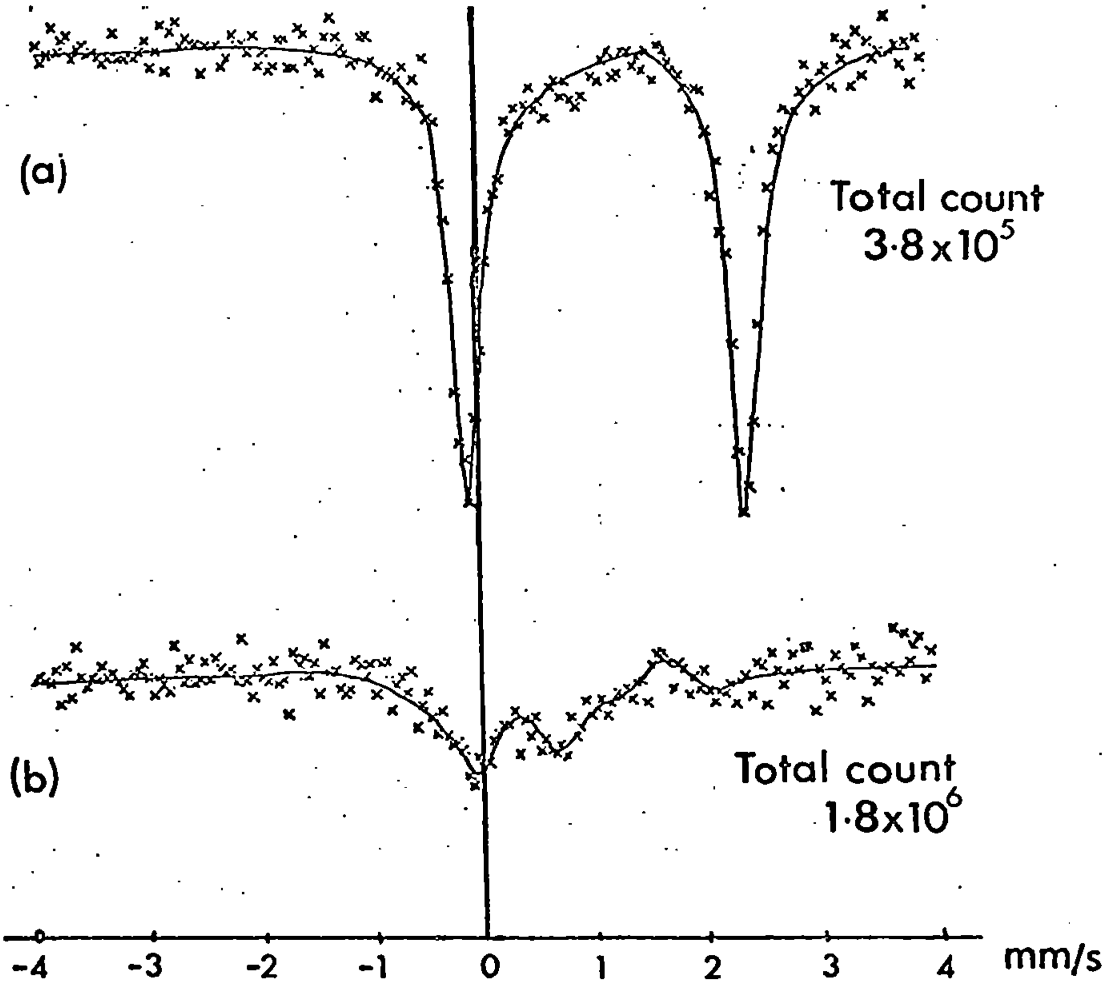
These results suggested that Fe^{2+} might be able to perform the same function as Mg^{2+} and it now seemed possible that both groups of resonances at g = 4.0 and at g = 2.0 migh be caused by iron impurities. Clearly, evidence for Fe^{2+} producing the g = 2.0 signal in kaolinite could be obtained from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

In order that Fe^{2+} could be detected directly in kaolinite samples Mössbauer spectroscopy was used. 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 2.24% abundant, is detectable. A typical clay, which might contain up to 2% total impurity, will therefore 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 inpterpretation. 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 $^{57}Fe^{2+}$ - Doped Kaolinites; Results and Discussion

In order to dope a kaolinite with ^{57}Fe a number of practical difficulties arise. In their experiments, Angel et al (1975) adopted a method of doping with iron using commercially available ferric chloride from which ferric benzoate was prepared. 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



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

Fig 2

of the solution was raised to a value of 5 with sodium acetate before adding ammonimum benzoate solution. The precipitation 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 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 smaple 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 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 interpreted in more detail. The results of this study are to be presented in a separate paper.

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The attached transcript was read at the third meeting of the European clays groups in Oslo, Norway, in June 1977. Only twenty minutes were allowed for the presentation (ten minutes were allowed for discussion). A similar paper will be presented under the same circumstances at the 26th annual U.S. clay minerals conference in Jamaica in August 1977. Due to the time limitation the paper describes the extremes of behaviour patterns which have been observed for different species of iron oxides on American and English kaolinites. A full description of the results is contained in a more detailed paper which is to be submitted for publication.

B R Angel

Dr. B. R. Angel

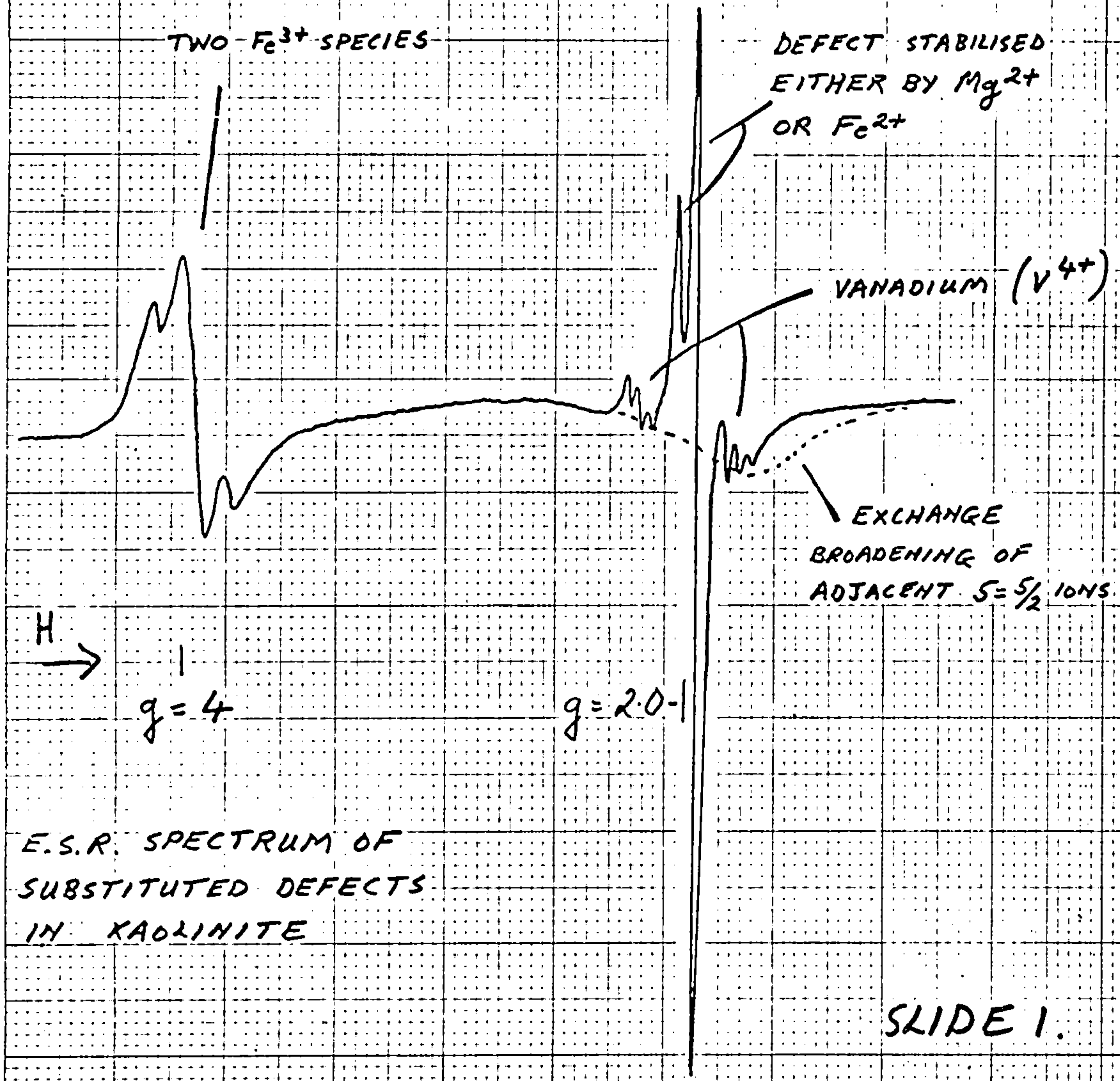
Electron spin resonance studies of surface iron associated with kaolinite.

B. R. Angel and W. E. J. Vincent

Department of Mathematical Sciences, Plymouth Polytechnic.

In slide 1, the room temperature X-band spectrum of a highly crystalline kaolinite from Georgia is reproduced. The main groups of lines centred at $g = 4.0$ and $g = 2.0$ have been studied in detail in our laboratory in recent years and by synthesising and selectively doping kaolinites we have been able to assign all the resonance lines to a number of distinct paramagnetic centres all of which have been shown to substitute in the structure of kaolinite. The paramagnetic centres include Fe^{3+} in a number of different configurations, defects stablised at Mg^{2+} or Fe^{2+}, hole centres trapped by Al^{3+} or hydroxyl vacancies, and V^{4+} or $(VO)^{2+}$. The results of this work have been published. It is worth noting that most kaolinites regardless of location produce similar resonances except that English kaolinites from the South West peninsula do not produce any resonance lines attributable to vanadium.

It was during the course of our studies of the substituted defects in kaolinite that we often found samples which when heated in air at 400°C for an hour produced intense broad resonances at $g = 2.0$. For English kaolinites it was found that samples which had been bleached to remove surface iron contaminants for the purposes of commercial beneficiation did not produce the broad resonance when heated. This being so, we equipped ourselves with two sets of kaolinites from St. Austell and Georgia, U.S.A. which were guaranteed not to have been treated chemically in any way to remove surface iron oxides. In this respect we gratefully acknowledge the supply of samples



E.S.R. SPECTRUM OF SUBSTITUTED DEFECTS IN KAOLINITE

SLIDE 1.

by English China Clays, St Austell and the U.S. Georgia Kaolin Company. For all the samples chemical analysis and particle size distributions were known.

Each set of kaolinites comprised a broad cross section of samples in terms of varying crystallinity and mineralogical impurities. It is well known that in general, the English kaolins contain more mica compared with the American kaolins which in turn contain more anatase and rutile.

The results obtained by heating an English sample in air at 400°C for one hour are presented in slide 2. The main points to note are:

(1) a broad resonance which is produced by heating in air at 400°C can be prevented from forming if the sample is pre-treated by de Endredy's method (combination of Tamm's solution and U.V. light) to remove surface iron oxides.

(2) the broad resonance having been formed is removed if the sample is treated with Tamm's solution.

(3) no significant changes occur in the spectra of the substituted defects.

Similar effects were observed using oxygen or nitrogen at 400°C for one hour.

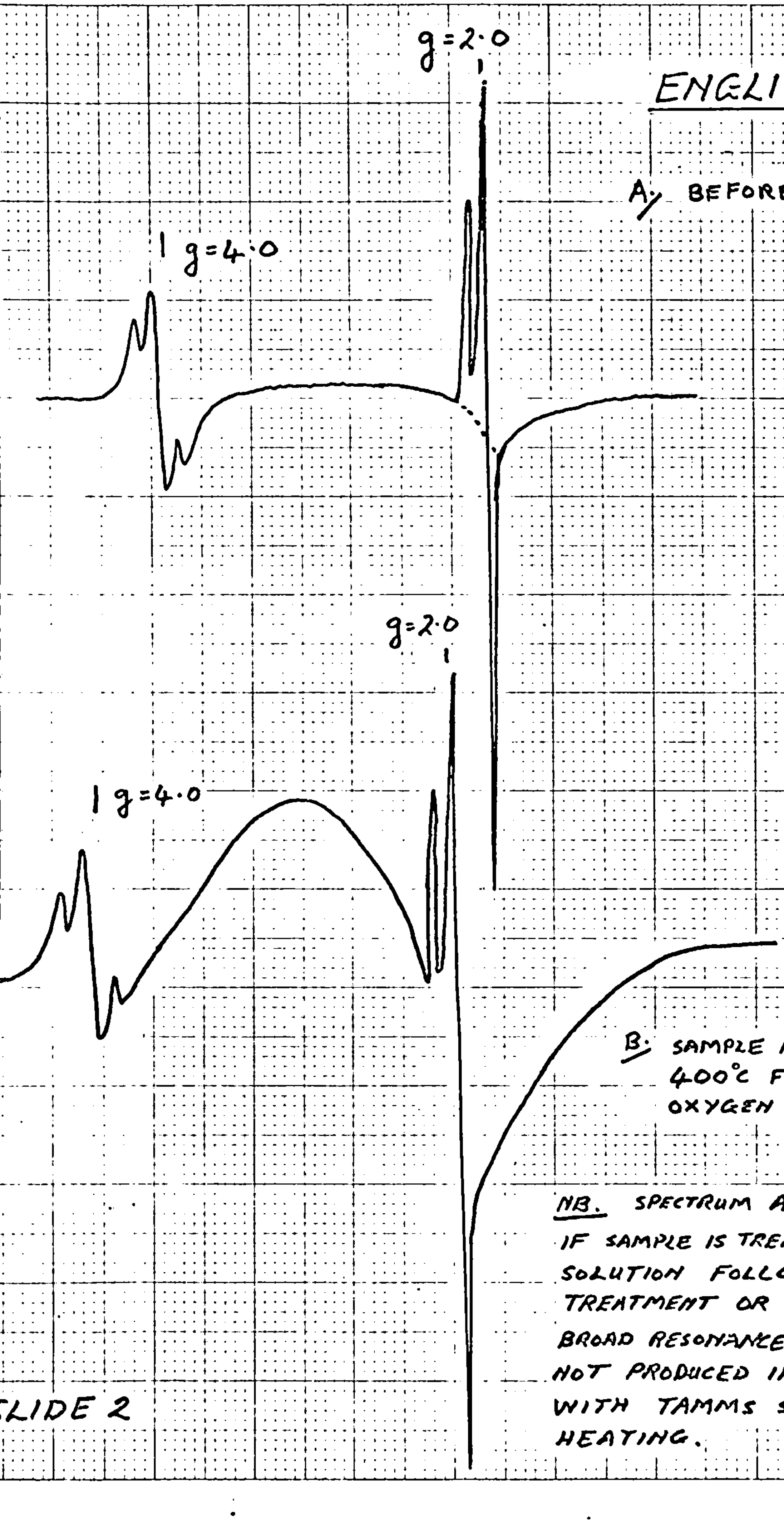
The effect of hydrogen, however, was more striking. In slide 3 we can see that a broad resonance occurs which is more intense and again may be prevented or destroyed by Tamm's solution. In addition, we now find that the resonance of centres at $g = 2.0$ stablised either by Mg^{2+} or Fe^{2+} is reduced in intensity but no change occurs in the signals at $g = 4.0$.

On the basis of the chemical analysis of the samples we had at our disposal we anticipated that similar results would be obtained from the American kaolinites. We were somewhat surprised to find that this was certainly not so.

In contrast to the English samples, we found that heating in air, oxygen or nitrogen at 400°C for prolonged periods beyond one hour did not produce a broad resonance. However, the broad resonance did appear when the

ENGLISH KAOLINITE

A/ BEFORE ANY TREATMENT

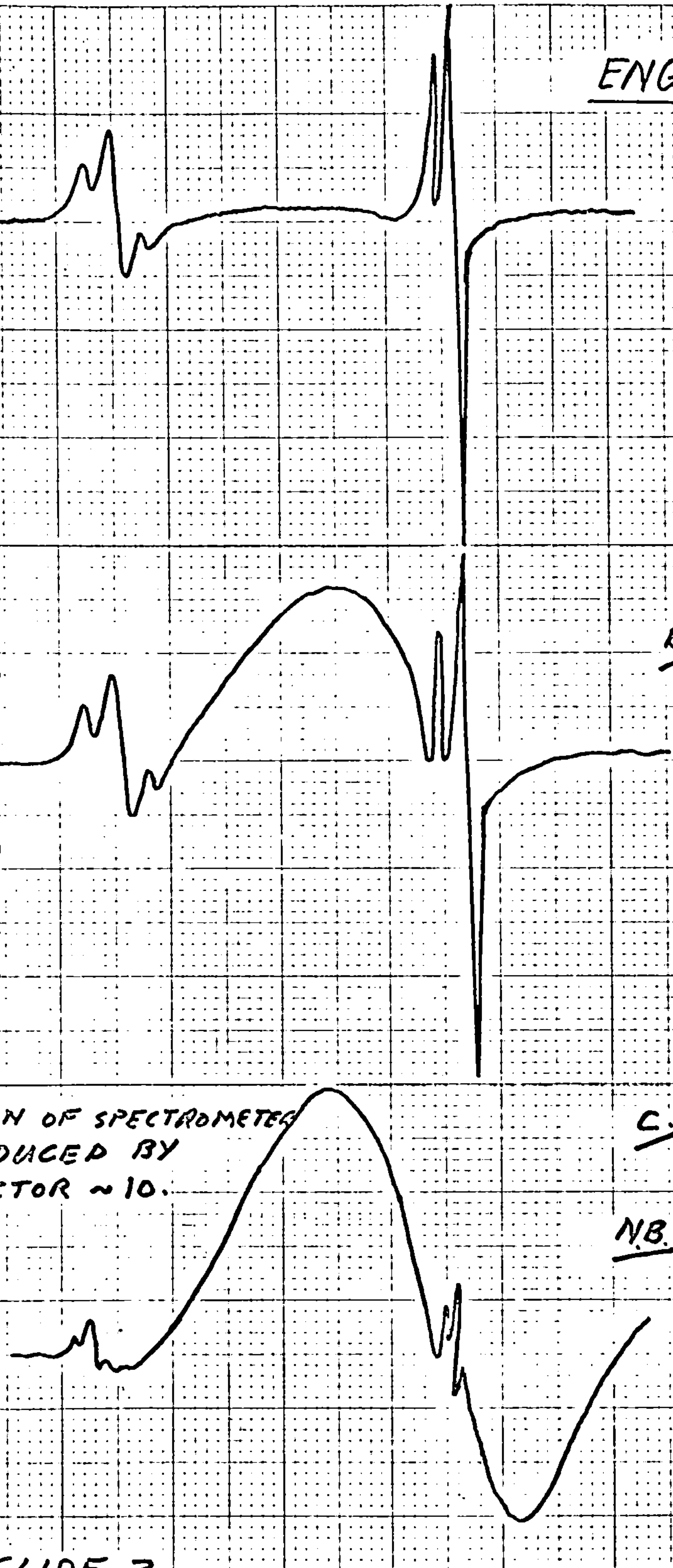


B: SAMPLE HEATED AT 400°C FOR 1 HR IN AIR, OXYGEN OR NITROGEN.

NB. SPECTRUM A IS REPRODUCED IF SAMPLE IS TREATED WITH TAMMS SOLUTION FOLLOWING HEAT TREATMENT OR ALTERNATIVELY THE BROAD RESONANCE IN SPECTRUM B IS NOT PRODUCED IF SAMPLE IS TREATED WITH TAMMS SOLUTION BEFORE HEATING.

SLIDE 2

ENGLISH KAOLINITE.



A. BEFORE ANY TREATMENT

B. HEATED IN AIR FOR 1 HOUR AT 400°c.

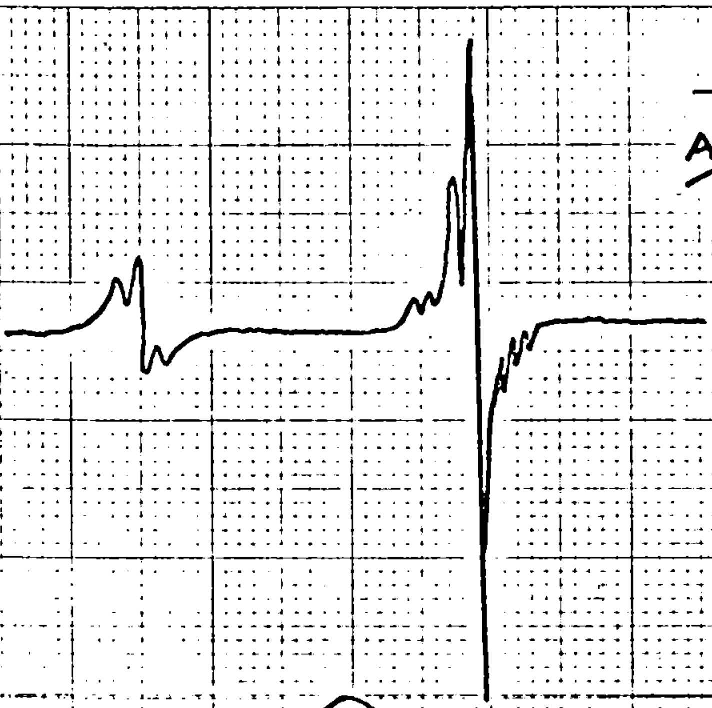
C. HEATED IN HYDROGEN FOR 1 HOUR AT 400°c

N.B. BROAD RESONANCE IS MORE INTENSE. SIGNAL AT $g=2\cdot0$ IS REDUCED BUT SIGNAL AT $g=4\cdot0$ IS UNCHANGED.

N OF SPECTROMETER
DUCED BY
CTOR ~ 10.

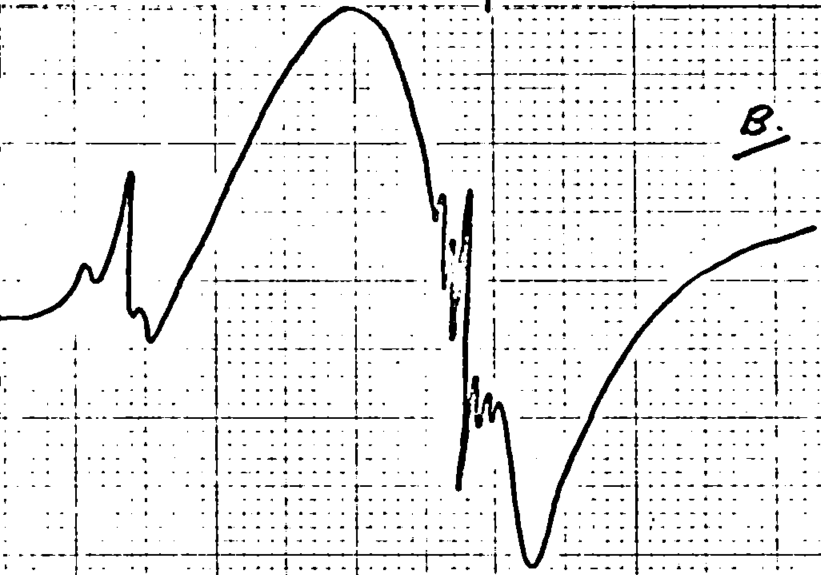
SLIDE 3.

AMERICAN KAOLINITE



A. SAMPLE BEFORE ANY TREATMENT.

SAME RESULT PRODUCED WHEN HEATED IN AIR OXYGEN OR NITROGEN AT 400°C FOR 1 HOUR.



B. SAMPLE HEATED IN HYDROGEN AT 400°C FOR 1 HR.

SAME RESULT IS OBTAINED IF SAMPLE IS PREVIOUSLY TREATED WITH TAMMS SOL^{N}

SIGNAL AT $g = 2.0$ DUE TO HOLE CENTRE IS REDUCED BUT VANADIUM SIGNAL INCREASES

SIGNAL AT $g = 4.0$ HAS CHANGED.

C. SAME SAMPLE AS IN B, BUT WARMED IN CONC. HCl FOR A FEW MINUTES.

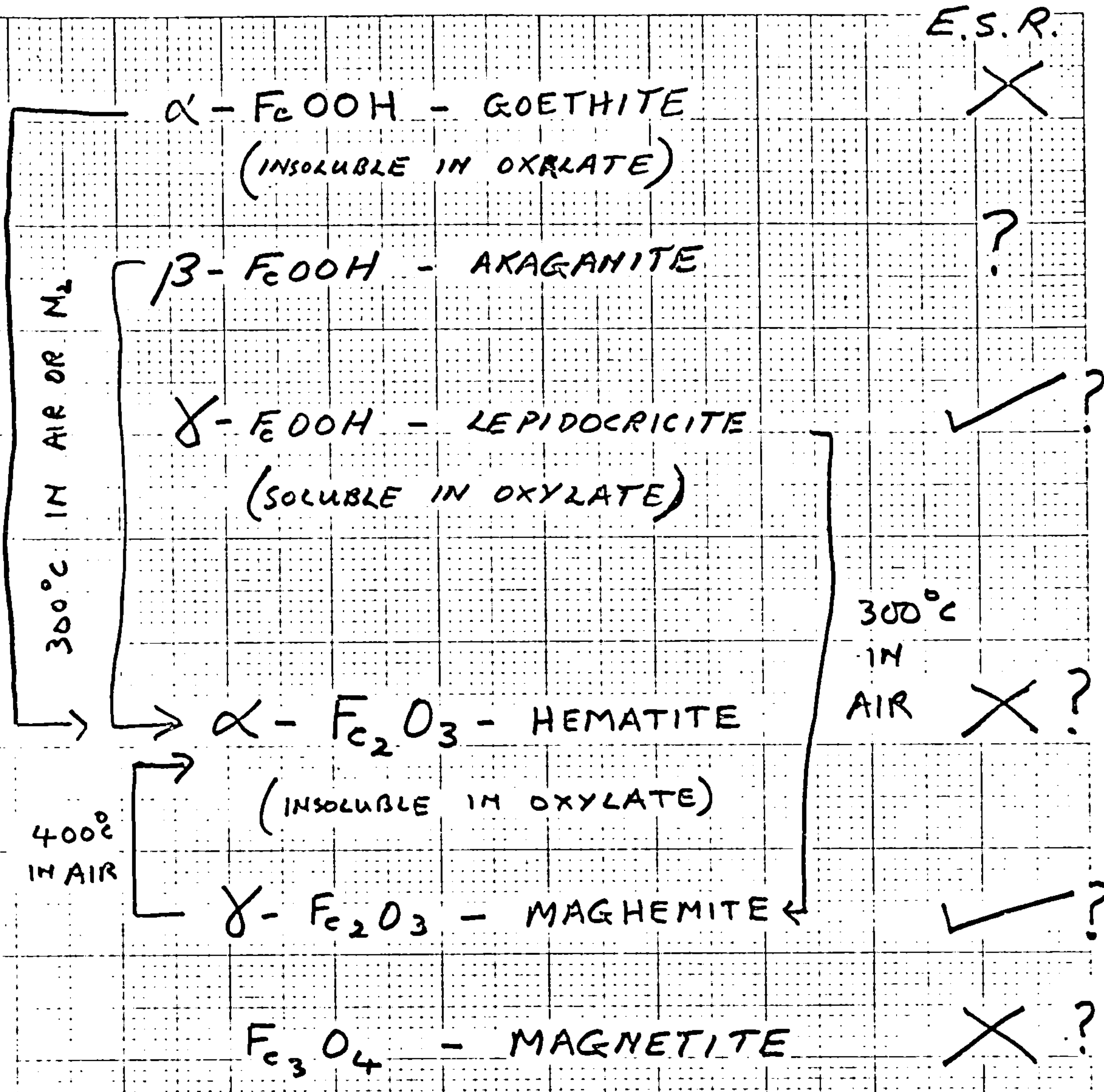
SLIDE 4

samples were heated in hydrogen. Nevertheless, in contrast to the English kaolins, we found that pre-treating the samples by de Endredy's method did not prevent the formation of the resonance in hydrogen. In addition, as we can see from slide 4, the resonance at g = 4.0 has changed as well as the A-centre resonance at g = 2.0 and there is a marked increase in intensity of the vanadium resonance. Hence, to summarise for heating effects at 400°C:

> English kaolins produce a broad resonance in air which does not occur in the American samples. Although it is possible to produce the broad resonance in all samples using hydrogen, it is possible only in the English kaolins to prevent the resonance forming by treating the samples with Tamm's solution and U.V. light. Although in both sets of samples using hydrogen the A-centre resonance at g = 2.0 is reduced in intensity, it is only in the American samples that changes in the signals at g = 4.0 are observed.

Perhaps the most obvious difference between the two sets of samples which might provide an explanation of the results is obtained by considering the mineralogical impurities of the samples. As mentioned previously, it is well known that the principal components are mica and anatase for the English and American kaolinites respectively. However, in this work we have carried out intensive magnetic refining of the samples and shown that the results I have presented are characteristic of the kaolinites. This being so, we have to seek an explanation for the results by considering in more detail the nature of iron oxides which are likely to be associated with the raw kaolinites.

The chemistry of iron and its components is complicated and there is a very large volume of relevant literature available. In slide 5 I have summarised the nomenclature used to describe the various oxides along with



E.S.R.

α-FeOOH - GOETHITE ✗

(INSOLUBLE IN OXALATE)

β-FeOOH - AKAGANITE ?

γ-FeOOH - LEPIDOCRICITE ✓?

(SOLUBLE IN OXYLATE)

α-Fe_2O_3 - HEMATITE ✗?

(INSOLUBLE IN OXYLATE)

γ-Fe_2O_3 - MAGHEMITE ✓?

Fe_3O_4 - MAGNETITE ✗?

N.B. HEMATITE WHEN HEATED IN H_2 AT 400°C IS KNOWN TO PRODUCE BROAD E.S.R. SIGNALS BUT THE STRUCTURE OF THE CENTRES PRODUCING THE EFFECT IS UNKNOWN.

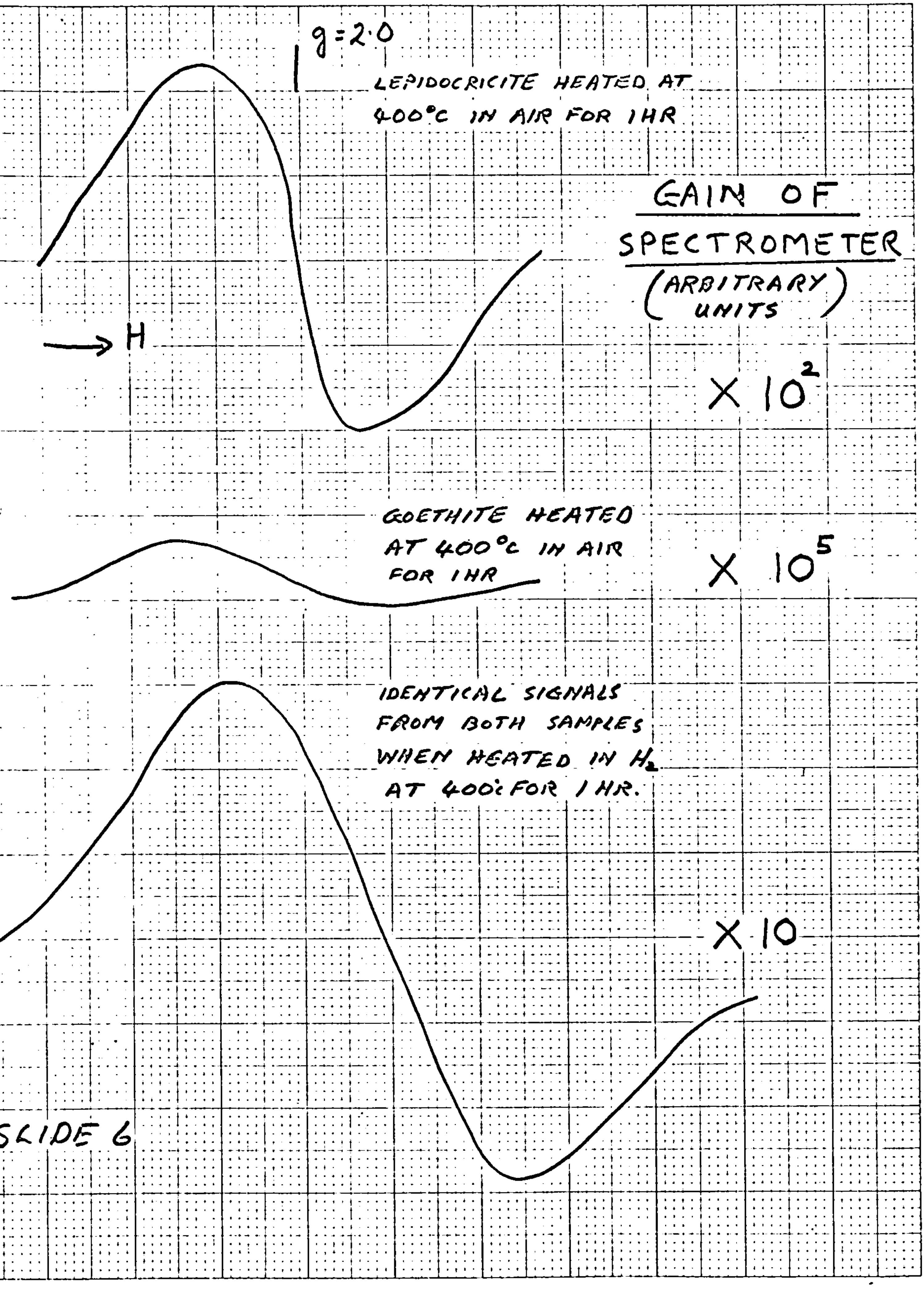
SLIDE 5.

some of the known transformations which occur through heat treatments. Reports of E.S.R. signals associated with the various oxides are confusing and there is some discrepancy in the literature as to whether resonances from hematite would be detectable at room temperature. However, taking into account past work and combining it with independent studies we have made on samples of naturally occurring iron oxides and pure samples of synthetic goethite and lepidocrocite kindly supplied by Professor Udo Schwertmann we can provide a reasonable explanation of the results on the following basis.

We suggest that the American kaolinites are most probably coated with, or have associated with them, goethite or hematite and the English kaolins are probably coated with lepidocrocite or an amorphous iron oxide. Convincing evidence for this assignment is presented in slide 6 where the E.S.R. results from the synthetic oxides are presented. From the gain settings of the spectrometer it is clear that for both these oxides large signals are produced by heating in hydrogen at 400°C but only the lepidocrocite produces a signal when heated in air at 400°C. Furthermore, we have found that the lepidocrocite is more soluble than goethite in Tamm's solution.

In addition, it is worth considering the location of the two sets of kaolinites. The kaolinites from Georgia exist in a sub-tropical climate and is known that they contain very small or indetectable amounts of organic matter. In contrast, the English samples are contained in a more temperate climate and contain easily measurable amounts of organic matter. Also, for the English kaolins, there have been a number of reports in recent years which suggest the possible existence of a gel layer containing silica on the particles. Indeed, Dr. Jepson and Dr. Ferris from English China Clays are presenting a paper at this meeting in which they discuss the possibility of an amorphous gel layer on the surface of English kaolins.

Professor Schwertmann has shown recently that in the presence of either


g=2·0
LEPIDOCRICITE HEATED AT 400°C IN AIR FOR 1HR
GAIN OF SPECTROMETER (ARBITRARY UNITS)
H
× 10²
GOETHITE HEATED AT 400°C IN AIR FOR 1HR
× 10⁵
IDENTICAL SIGNALS FROM BOTH SAMPLES WHEN HEATED IN H₂ AT 400°C FOR 1 HR.
× 10

SLIDE 6

organic matter or silicon cations the relatively unstable lepidocrocite becomes very stable and does not transform into goethite and hematite. It is possible, therefore, that the unexpected existence of a normally unstable oxide such as lepidocrocite would be stablised on the English kaolin either by the excess silica in the suggested gel layer or organic matter or a combination of both.

Finally, I would like to comment briefly on the changes in the signals of substituted species following the hydrogen treatment. Time does not allow a detailed explanation.

The increase in intensity of the vanadium resonance in the American clays can be reconciled with the fact that some V^{5+} which is non-paramagnetic and which may exist in the kaolinites is reduced by the hydrogen to paramagnetic V^{4+}.

In order to understand how for both sets of kaolinites under hydrogen treatment a decrease in the intensity of the A-centre resonance is observed but only in the American kaolinites an accompanying change in the Fe^{3+} spectrum at g = 4.0 occurs, it is necessary to appreciate that the A-centres may be stablised either by Fe^{2+} or Mg^{2+}. We suggest therefore, that possibly in the American kaolinites there are more A-centres stablised by Fe^{2+} compared with the English kaolinites in which the A-centres are probably stablised by Mg^{2+}. Chemical analyses support this view.

It is possible, therefore, that, with a larger concentration of substituted iron in the structure, the American kaolinites produce measurable changes in the g = 4.0 spectrum following the hydrogen treatment. The mechanisms responsible for the changes are not clear and are to be discussed in a detailed publication.

I would like to emphasis that in this paper we have outlined the extremes of behaviour patterns we have observed in the E.S.R. spectra of iron oxides associated with these kaolins. We anticipate publishing this work in detail in the very near future.

Thank you.

The attached manuscript is a draft of a paper which is to be submitted for publication in Clay Minerals.

B R Angel

B.R.ANGEL.

Electron Spin Resonance Studies of iron oxides associated with the surface of kaolins

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INTRODUCTION

Previous E.S.R. studies of natural and selectively doped synthetic kaolinites in this laboratory[1,2,3] have been confined mainly to paramagnetic ions which substitute in the structure. In particular, iron has been shown to substitute in kaolinite in a number of different configurations.

Other workers[4,5,6] have shown that iron substitutes in the structure of ancillary minerals such as anatase, rutile, quartz and micas which are often found in kaolinite deposits.

Iron impurities in kaolin deposits can also exist as discrete particles in the form of oxides and hydroxides[7,8,9] or alternatively as coatings which are bound to the surfaces of both the kaolinite and any ancillary minerals which may be present. Iron impurities of this type are often quoted as "free iron oxides".

Considerable research efforts have been made to study the effective removal of free iron oxides from kaolin as they are detrimental in the application of kaolin in the paper coating industry. The various methods of removal have been reviewed by a number of research authors[9-13].

The possible nature of the chemical bonding of iron oxides and hydroxides to kaolinite surfaces has formed the basis of a number of publications[7,13,14,15,16]. In general, electron microscopy, X-ray diffraction and chemical analysis have been applied to study samples of kaolinite on which hydroxides of iron have been precipitated.

On a more general basis the fundamental properties of bulk samples of iron compounds have been aimed at identifying and characterising the various precipitation products from iron (II) and iron (III) salts in solution[22-30]. These studies have supplemented work which has been concerned with the nature of iron impurities in soils[17-21].

Previous E.S.R. studies of iron oxides in synthetic zeolites[31,32,33] and lunar samples[34-42] demonstrate the potential application of a similar approach to kaolinite.

DESCRIPTION OF SAMPLES

Sixteen kaolinite samples were studied of which ten (Avant, Chambers, Champion, Gray, Wrens, Mines 11,15,24) came from various locations in Georgia, U.S.A. and were kindly supplied by the U.S. Georgia Kaolin Company. The remaining six kaolinites originated in the South West Peninsula of England and were kindly supplied by English Clays Lovering Pochin & Co. Ltd. They were described as Blackpool, Cholwich Town, Dubbers, Lee Moor, English and Supreme. Chemical analysis and particle size distributions were known for all samples.

PRELIMINARY E.S.R. SURVEY

All of the samples exhibited resonances O & A depicted in Fig. 1 which are centred at $g = 4.0$ & $g = 2.0$ respectively. These resonances are known to be due to substituted defects and have been considered in detail[1-3] elsewhere. At $g = 2.0$ an additional resonance approximately 0.1 tesla in width was present which is labelled F_1. In previous studies F_1 has been found to be relatively weak and has not been studied in detail.

For a number of the kaolinites used in this work various size fractions were immediately available and therefore the possibility of any correlation between the intensity of resonance F_1 and particle size was investigated. The result showed that there were marked variations in the intensity of the signal F_1

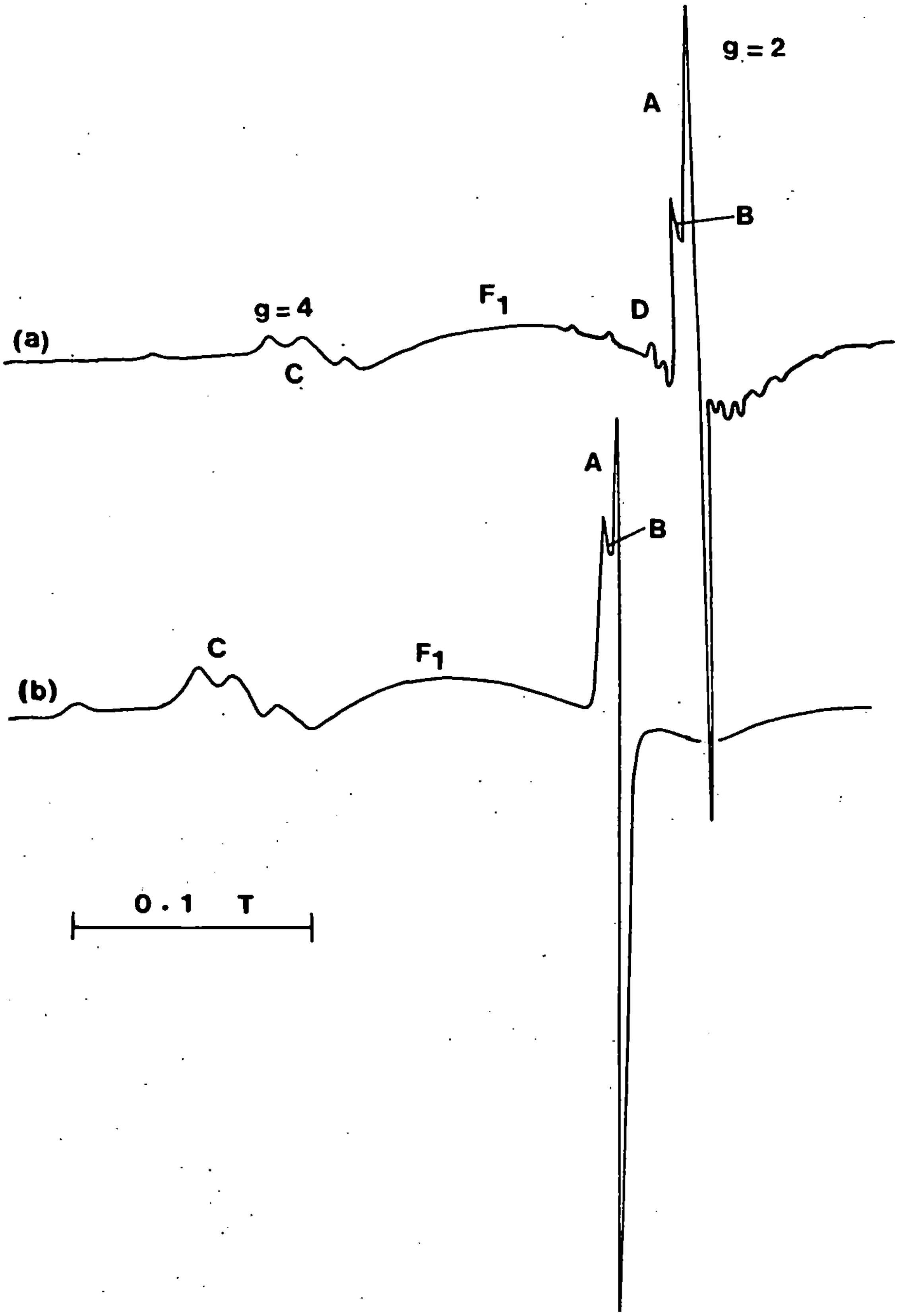

FIG. 1. E.S.R. spectra recorded at room temperature of:
(a)a typical kaolinite from Georgia, U.S.A.
(b)a typical kaolinite from the South-West Peninsula of England.

both for different samples and different size fractions within a sample but these variations could not be correlated with particle size.

The effect of heating only 4 samples at various temperatures between 473K and 1473K for different periods of time from 1 to 24 hours produced interesting and contrasting results which provided the basis for a subsequent study of the effect of heat treatment on all similar kaolins.

In samples mine 15 and Avant no change in resonance F_1 was observed when they were heated in air for periods of at least one hour at temperatures up to 973K. Above this temperature the resonance began to decrease but did not collapse completely. In contrast for samples mine 24 and Blackpool the effect of heating at 473K for one hour in air was to produce an additional fairly intense broad resonance (F_2 in Fig. 2) on the low field side of the resonance F_1. Resonance F_2 increased for preheating times of one hour and temperatures up to a maximum of 673K (Figs. 2 a & b). At 973K the resonance gradually collapsed as the period of heating was increased to 24 hours. In the Blackpool sample resonance F_1 remained after preheating at 1473K but in sample mine 24 P.D.I., it decreased considerably above 1173K.

No changes in the X.R.D. patterns were observed for these 4 samples when heated at 673K for one hour. Prolonged heating above 723K caused a decrease in intensity and above 823K metakaolinite was formed. At 1473K mullite was detected.

Taking into account the chemical and mineralogical analysis, the crystallinity, and the particle size distribution for the 4 samples examined there was no obvious explanation for the contrasting E.S.R. results following the heat treatment. Heating at 673K for one hour was found to be the lowest temperature and corresponding time to promote maximum development of resonance F_2 in the Blackpool and mine 24 kaolinites. The remaining kaolinites were therefore subjected to this type of heat

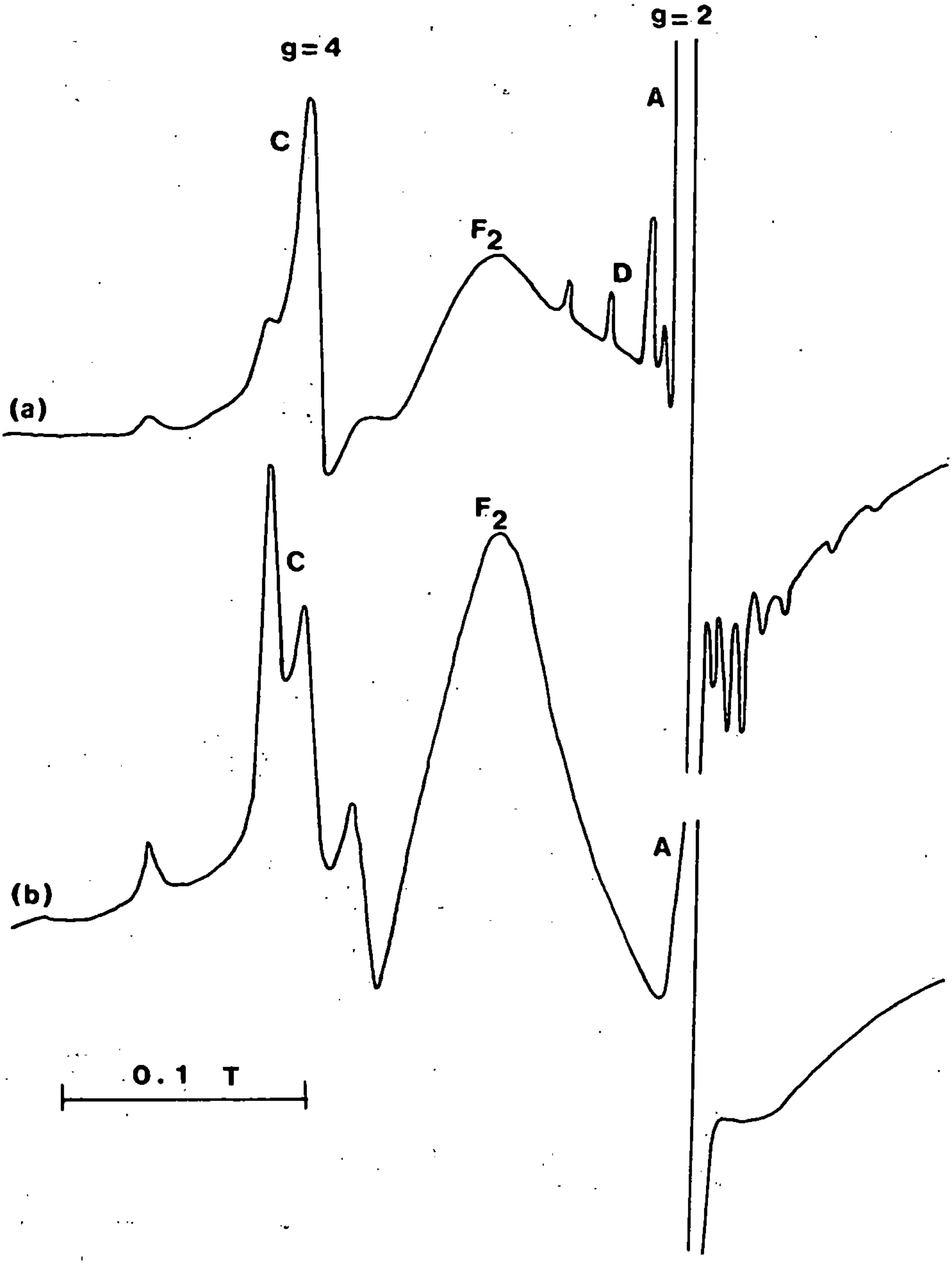

FIG. 2. E.S.R. spectra recorded at room temperature of:
(a) Mine 24 kaolinite heated at 673 K for 1 hour;
(b) Blackpool kaolinite heated at 673 K for 1 hour.

DETAILED E.S.R. STUDIES

It was found that all the English kaolinites from the S.W. peninsula when heated at 673K for one hour produced resonance F_2 but in contrast only two of the kaolinites from Georgia, namely mine 24 and Champion, produced the effect and even then on a much weaker scale. Also, it was found that for each of the English kaolins the intensity of the resonance F_2 (in contrast to resonance F_1) increased with increasing particle size but for the two exceptional American kaolinites there was no obvious relationship between F_2 and particle size. The X.R.D. patterns of the English kaolins showed that resonance F_2 was not related to the crystallinity of the samples and also most probably not related to the mica impurities. It was suspected therefore that the resonance F_2 was directly associated with the surface of the kaolinites.

An observed decrease in the intensity of the resonance F_2 and an accompanying increase in line width with decreasing temperatures (Fig. 3) are behaviour patterns characteristic of ferromagnetic or ferrimagnetic materials[34].

MAGNETIC FILTRATION

As it was suspected that resonance F_2 in the English kaolin was probably associated with the kaolin surfaces and not the mica impurities magnetic extraction was used to refine all the samples. The results obtained from the XRD and ESR analysis of the filtrates and the magnetic residues clearly indicated that in the English samples mica was not responsible for the resonance. However, for the two exceptional American kaolinites which originally produced the F_2 resonance, it was found that after magnetic separation only the magnetic residue which contained mainly anatase produced the resonance. It was clear therefore that resonance F_2 was associated with a surface iron contaminant which was common to the English kaolinites and the anatase fraction to a lesser extent in two of the American kaolins.

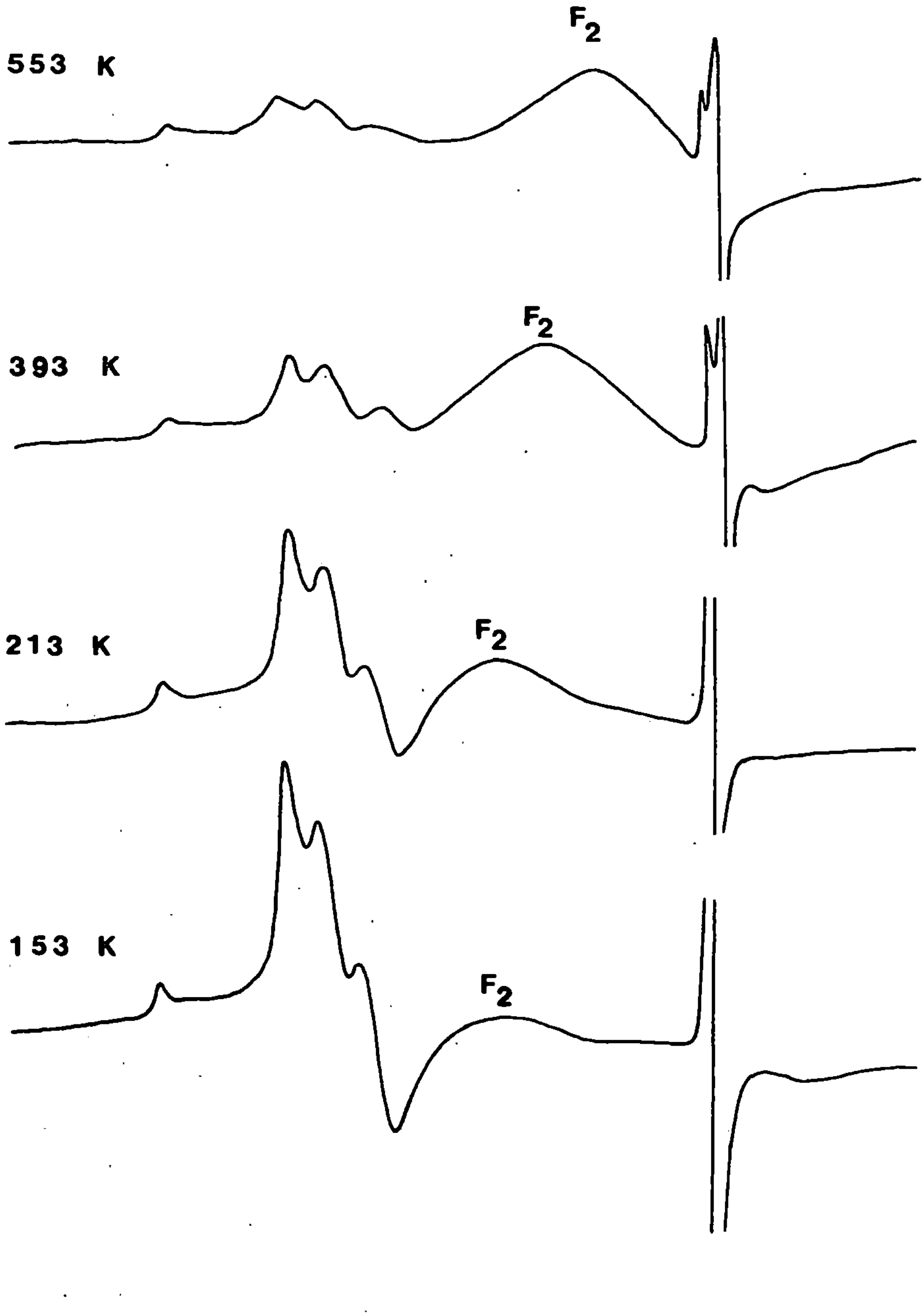

FIG. 3. E.S.R spectra of Blackpool kaolinite heated at 673 K for 1 hour recorded at various temperatures.

In addition to differences between English and American kaolinites with respect to resonance F_2 it was found that after heating the samples at 673K for one hour, the isotropic line of the ESR signal at $g = 4.0$ had increased in intensity in all the American samples but there was no similar change produced in the English kaolinites. These contrasting changes associated with the substituted iron will be considered later.

THE EFFECT ON RESONANCES F_1 and F_2 USING DE ENDREDY'S METHOD TO REMOVE FREE IRON OXIDES

It was anticipated that if either resonance F_1 or F_2 were associated with surface iron contaminants they would most likely be affected by any chemical treatment of the kaolinites which either modifies or removes the iron species. Herbillon et al.[15] in their ESR study of kaolinites from tropical soils found that De Endredy's method[12] for removing iron oxides was more effective than Mehra and Jacksons[11] method. Accordingly, De Endredy's method was adopted in this work.

Suspensions of 2g. of sample in 100 cm^3 of Tamm's solution (0.1 mol $dm^{-3}$with respect to oxalic acid and 0.175 mol dm^{-3} with respect to ammonium oxalate) were stirred magnetically and exposed to ultra-violet radiation from a medium pressure mercury lamp. Exposure times of two hours were not exceeded in order to prevent the precipitation of iron (II) oxalate[5]. The suspensions were then centrifuged and the supernatant tested for iron using the ammonium thioglycollate test[46]. The residues were washed with deionised water and the procedure was repeated until no iron was detectable in the supernatant. At this stage the residues were washed free of oxalate and dried at 383K. It was found that in general the American kaolinites required considerably more extraction cycles compared with the English samples to produce a negative test for iron in the supernatant, a result which gave the first indication that the iron contaminant in the American samples was relatively insoluble in Tamm's solution.

For samples which had been treated by this method no measurable changes were identified in their XRD patterns. For the American kaolins the treatment had no effect on resonance F_1. For the English samples the intensity of the resonance was reduced but not completely removed (Fig. 4).

Resonance F_2 was not reproduced in any of the samples which had been chemically treated and heated in air at 673K for one hour. In addition, it was found that F_2 induced in the English samples by heating could be removed by De Endredy's treatment. To summarise, therefore, both the English and American kaolinites probably have surface iron contaminants associated with them which do not produce significant E.S.R. signals. The effect of heating the English kaolins at 673K for one hour in air is to effect a change in the iron oxide contaminant which then produces an intense broad resonance at $g = 2.0$. However, the same effects are not produced in the American kaolinites. The iron oxides on English kaolins seemed to be different in nature from these on American kaolins and were more soluble in U.V. irradiated Tamms solution

THE EFFECT OF THERMAL TREATMENT IN ATMOSPHERES OF OXYGEN, NITROGEN AND HYDROGEN

In their study of the source of ferromagnetism in zircon, Lewis and Senftle[47] heated zircon specimens in reducing and in oxidising atmospheres at 723K and followed the reactions by magnetisation measurements. They interpreted theresults in terms of an iron oxide coating which consisted mainly of **hematite** together with some maghemite and/or magnetite.

In this work the effect of similar treatments on the American and English kaolinites was examined with the intention of possibly identifying the surface oxides. Samples were heated in oxygen, nitrogen and hydrogen for one hour at temperatures ranging from 473 to 873K. All the samples when heated for one hour in oxygen or nitrogen at 723K, produced similar results to those obtained for samples heated in air. Treatment in hydrogen produced further interesting results. For the English kaolinites, resonance F_2

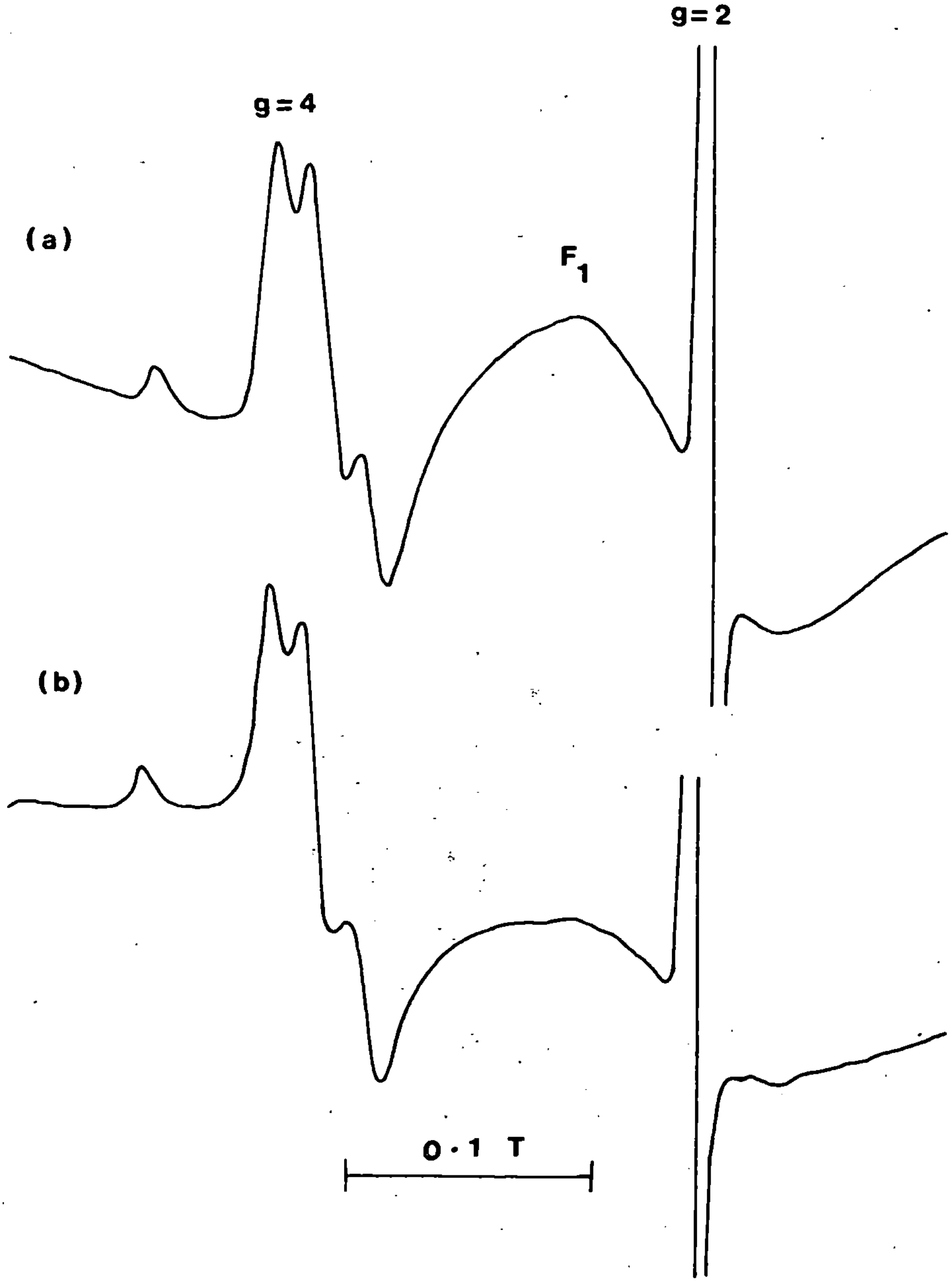

FIG. 4. E.S.R spectra recorded at room temperature of:
(a) untreated English kaolinite;
(b) English kaolinite deferrified using de Endredy's method.

developed at temperatures below 673K (Fig. 5a), but, at this temperature, a much more intense resonance (which will be referred to as F_3) was observed centred at about g = 2.4. The intensity of resonance F_3 reached a maximum value following heating in hydrogen at 723K (see Fig. 5b) and then remained constant up to temperatures of 873K. Georgia kaolinites also exhibited a similar intense resonance on heating in hydrogen (see Fig. 6a), though the signal did not develop below 773K for some of the samples (see Fig. 6b).

It was found that resonance F_3 was readily removed from both English and American kaolinites by warming the samples in hydrochloric acid for two minutes, centrifuging and washing until chloride free (see Fig. 5c and Fig. 6c). Kaolinites from which free iron oxides had been removed by De Endredy's method[12] were also heated in hydrogen at 723K for 1 hour. It was found that resonance F_3 did not develop in English kaolinites, but was produced by the American samples, even after magnetic refining. The very marked difference in behaviour of English and American kaolinites following hydrogen treatment at 723K combined with chemical treatment by De Endredy's method[12] provided more evidence that there were probably different types of iron oxide impurities associated with the two groups of kaolinites.

It was noted that for all of the American kaolinites, which had been heated for 1 hour at 723K in hydrogen, resonance A had decreased in intensity, while resonance D and the isotropic line of resonance B had increased in intensity. No reduction of resonance A was noted in English kaolinites which had been treated similarly, though further heating at 723K in hydrogen resulted in a decrease in resonance A with resonance C remaining unaltered. These effects (except for the change in resonance C in Georgia kaolinites) were not observed in the samples when they were heated at similar temperatures in air.

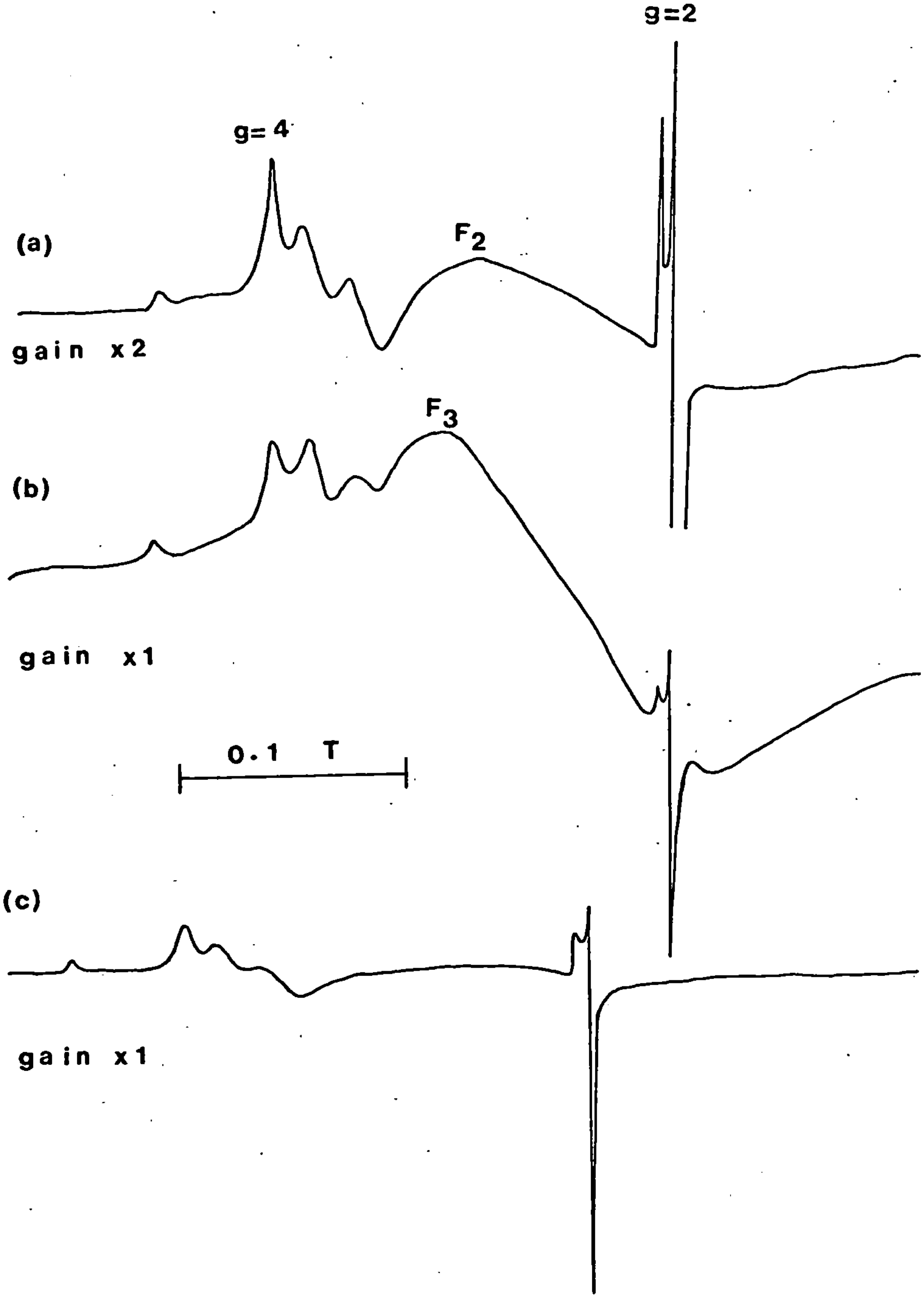

FIG. 5. E.S.R. spectra recorded at room temperature of: Blackpool kaolinite (a) heated at 673 K for 1 hour in hydrogen; (b) heated at 723 K for 1 hour in hydrogen; (c) heated at 723 K for 1 hour in hydrogen, followed by treatment with hydrochloric acid.

STUDIES OF PRECIPITATED IRON HYDROXIDES ON KAOLINITE SURFACES

With a view to identifying the different iron phases present on English and Georgia kaolinites, various kaolinite - iron hydroxide complexes were synthesised. Samples of English kaolinite from Blackpool pit, St. Austell, were treated by De Endredy's method[12] to remove free iron oxides. The samples were then coated with different iron hydroxides using 3 methods described by Greenland and Oades[14].

These methods involved:-

a) precipitation of goethite at pH 8;

b) precipitation of lepidocrocite at pH 3;

c) precipitation of amorphous hydroxides at pH = 3,5 and 7.

The kaolinite-hydroxide complexes were studied using identical methods to those described previously. The results are summarised in Table 1.

TABLE 1: Relative Intensities of Broad Resonances at g = 2 observed for Iron Hydroxides Precipitated on Blackpool kaolinite.

COATING TREATMENT	GOETHITE	LEPIDOCROCITE	AMORPHOUS HYDROXIDES		
			pH3	pH5	pH7
Untreated	Weak+	Medium+	Medium+	Weak+	Weak+
673K 1 hour	Weak+	Very intense+	intense+	medium+	Weak+
723K 1 hour in hydrogen	Very intense^{o}	Very intense^{o}	Very intense^{o}	-	-

Key:- + :- kaolinite only detected by X.R.D.

o :- in addition to kaolinite, hematite and magnetite detected by X.R.

Unfortunately the initial iron hydroxide coatings were not identfiable by X.R.D. However, it was clear from the E.S.R. results that kaolinites coated with hydroxides precipitated at low pH produced resonances similar to those observed previously from natural English kaolinites. In contrast, kaolinites coated with hydroxides precipitated at higher pH produced results similar to those obtained from natural Georgia kaolinites.

STUDIES OF NATURALLY OCCURRING IRON OXIDES AND HYDROXIDES

TABLE 2:- Magnetic Properties of Naturally Occurring Iron Oxides and Hydroxides.

NAME	FORMULA	MAGNETIC PROPERTIES
Amorphous Oxides	-	Paramagnetic[22]
Hematite	$\alpha\text{-}Fe_2O_3$	Weakly ferromagnetic above 263[47]. Controversy in literature regarding observance by E.S.R. at X-band at room temperature[35].
Goethite	$\alpha\text{-}FeOOH$	Antiferromagnetic with Neel temperature of 393K[37].
Akaganite	$\beta\text{-}FeOOH$	Antiferromagnetic with Neel temperature of 293K[49].
Maghemite	$\gamma\text{-}Fe_2O_3$	Ferrimagnetic[48]
Lepidocrocite	$\gamma\text{-}FeOOH$	Antiferromagnetic with Neel temperature of 73K[49]
Magnetite	Fe_3O_4	Ferrimagnetic[48] E.S.R. linewidth decreases with decreasing temperature to 130K[50]

The magnetic properties of naturally occurring iron oxides and hydroxides are summarised in Table 2 where it can be seen that species detectable by E.S.R. at room temperature are amorphous oxides, maghemite, lepidocrocite, magnetite and possibly hematite.

Since resonance F_2 was observed to be either ferromagnetic or ferrimagnetic in nature and its linewidth increased with decreasing temperature, it may be assigned to only maghemite or hematite. Resonance F_2 is produced when English kaolinites are heated at 673K in air and maghemite is known to be transformed into hematite at this temperature[51]. It seems reasonable, therefore, to attribute resonance F_2 to hematite, However, there is a divergence of opinion in the literature[37,38] as to whether hematite would be detectable at room temperature by E.S.R.

To clarify the situation a study was made of some available iron oxides and hydroxides. Samples of naturally occurring magnetite and hematite obtained from the Department of Geology, Plymouth Polytechnic, and synthetic goethite and lepidocrocite kindly donated by Professor U. Schwertmann of Technische Hochscule, Munich. The results are summarised in Table 3.

TABLE 3:- Relative Intensities of Broad Resonances at about g = 2 Observed for Iron Oxides and Hydroxides.

TREATMENT/ SAMPLE	GOETHITE	LEPIDOCROCITE	HEMATITE	MAGNETITE
Untreated	Weak	Medium	Medium	Intense
673K 1 hour	Weak^{h}	Very intense	Medium^{h}	Intense^{h+a}
723K 1 hour	Very intense^{h,a,f}	Very intense^{h+a+f}	Intense^{h+a+f}	Intense^{h+a+f}

Key:- a - magnetite ; b - maghemite
f - iron ; h - hematite

It was found that hematite exhibited a broad resonance, but not with sufficient intensity to account for resonance F_2 in kaolinites. However, lepidocrocite produced an intense broad resonance on heating both in air and in hydrogen, a behaviour pattern which is similar to that observed in the English kaolinites.

In contrast, the E.S.R. spectra of both goethite and hematite were unaffected by heating in air at 673K, but an intense broad resonance developed on heating in hydrogen; a behaviour pattern which resembles that of Georgia kaolinites. Therefore, it may be reasonable to infer that English kaolinites are associated with a lepidocrocite like phase while Georgia kaolinites are associated with a goethite - hematite - like phase. The results are considered in more detail in the discussion.

SUMMARY AND DISCUSSION

The various heat treatments applied to the kaolinites used in this work produced significant changes in the E.S.R. features associated with substituted defects as well as interesting results with regard to surface iron oxides. Previous work[45] has shown that the resonance at $g = 4.0$ in natural kaolinites is composite and can be unequivocably assigned to two Fe^{3+} species in different sites and resonance A may be attributed to a defect which can be produced by X-irradiation and stabilised by Mg^{2+} or Fe^{2+}. Resonance D which is common only to the American kaolinites is attributable to V^{4+} and is the subject of a separate publication[52]. In all kaolinites containing the A-centre resonance it is found that by expanding the spectrum it is possible to identify additional paramagnetic species which have become known as B-centres and produce weak resonance peaks between the two main lines of the A-centre resonance.

Heating the American kaolinites in hydrogen at 723K produced a significant increase in the intensity of resonance D, but oxygen had no effect. Since neither V^{5+} nor V^{3+} are detectable at room temperature and only hydrogen causes an increase in the concentration of V^{4} it is logical to conclude that the American kaolinites probably contain mainly V^{4+} ions, a smaller number of V^{5+} ions and no detectable V^{3+} ions. The possible situation of the vanadium ions either on the surface or within the structure of kaolinite forms the basis of a separate paper[52].

It is known[43] that resonance A in natural kaolinites normally collapses if samples are heated in air at 773K when dehydroxylation occurs. For samples heated in hydrogen resonance A collapsed at temperatures of 723K but it was not possible to detect any dehydroxylation effects by X-ray diffraction.

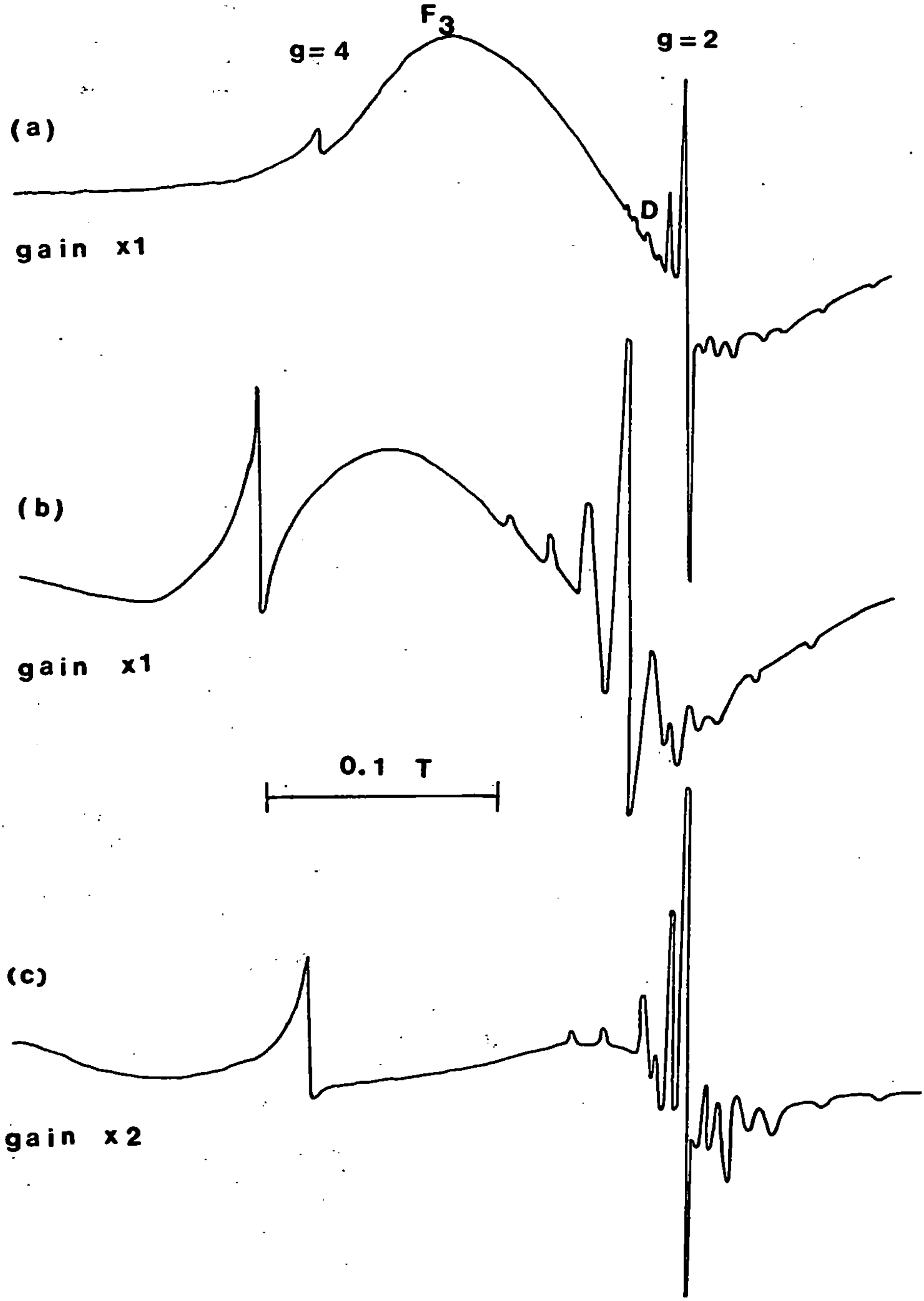

FIG.6. E.S.R. spectra recorded at room temperature of:
(a) Mine 11 kaolinite heated at 723 K in hydrogen for 1 hour,
(b) Mine 15 kaolinite heated at 773 K in hydrogen for 1 hour,
(c) Mine 11 kaolinite heated at 723 K in hydrogen for 1 hour, then treated with hydrochloric acid.

Furthermore, it was found in this work that resonance A could only be reformed in samples which had been treated in hydrogen provided that prior to X-irradiation and annealing they were evacuated to remove any occluded hydrogen. It is known[1,2] that at least X-ray energies are required to produce defect A and ultra-violet radiation is ineffective. On the basis therefore of recoil energies involved in an elastic collision it is reasonable to suggest that the defect is formed by removal of a proton or a hydrogen atom. The results from the hydrogen treated samples support this hypothesis on the basis that occluded hydrogen prevents the defect reforming.

In his previous work on the A centre Jones suggested models for the defect which involved either the formation of $(O_2)^-$ created by the initial removal of hydrogen atoms through X-irradiation or alternatively the production of trapped holes. Although it may be argued that removal of protons or hydrogen atoms might conceivably lead to the formation of trapped holes, the results obtained here indicate the importance of hydrogen in the formation and annealing of resonance A and therefore support explanation in terms of formation of $(O_2)^-$.

In American kaolinites, it was also noted that the effect of heating in hydrogen at 723K, as well as removing resonance A, also caused the isotropic line at $g = 4$ to increase in intensity. It is tempting, therefore, to assume that changes in the resonance at $g = 4$ are related to annealing of the defect responsible for resonance A. Indeed, if resonance A were attributable to a defect stabilised by Fe^{2+} substituting for $A\ell^{3+}$ and the defects were annealed, one might expect Fe^{2+} to be converted to Fe^{3+}, which would account for the observed change in the $g = 4$ resonance. However, for English kaolinites heated in hydrogen no corresponding change in the $g = 4$ resonance was observed when resonance A collapsed. Considering the chemical analysis of the samples, it might be argued that, in the English kaolinites, Mg^{2+}, as opposed to Fe^{2+}, acts as the precentre and therefore does not create more

Fe^{3+} and a change in the g = 4.0 signal. However, in contrast to English kaolinites in which no changes are observed, for the Georgia kaolinites, heated in air at 723K, an increase in the isotropic line at g = 4 was also noted, but with no corresponding decrease in resonance A. These results suggest that changes in the Fe^{3+} distribution are independent of any Fe^{2+} which stabilizes the A centres.

It is known[43] that dehydroxylation of kaolinite at 773K causes an increase in the isotropic resonance at g = 4 accompanied by a decrease in resonance A. However, as X.R.D. spectra of Georgia kaolinites heated at 723K in air were found to be identical to those of untreated samples and as resonance A had not been reduced in intensity, it was assumed that dehydroxylation had not occurred. To date, no satisfactory explanation has been found for the change in the resonance at g = 4 observed on heating Georgia kaolinites below their dehydroxylation temperatures.

The preliminary E.S.R. studies of English and American kaolinites established that all samples exhibited a broad resonance, F_1, to varying extents. On heating at 673K for one hour in air, oxygen or nitrogen, English kaolinites produced a more intense broad resonance, F_2. Resonance F_2 was also found in two of the American samples, but separate studies using magnetic filtration and X.R.D. analysis showed that resonance F_2 in these samples was associated with anatase impurities and not the kaolinite fraction. Magnetically refining samples also demonstrated that resonance F_2 in English kaolins was common to both the kaolinite fraction and the mica impurities. Both Georgia and English kaolinites, however, produced an intense broad resonance F_3 when they were heated in hydrogen at 723K.

Since deferrification by De Endredy's method had a negligible effect on resonance F_1 in Georgia kaolins, and reduced, but did not remove it completely, in the English samples, it was concluded that resonance F_1 could not be attributed wholly to surface iron oxides associated with the kaolinites. However, it was found that English kaolinites, which had been deferrified produced neither resonance F_2 on heating at 673K in air nor resonance F_3 following hydrogen treatment at 723K. Therefore, it was deduced that resonances F_2 and F_3 in English kaolins were due to iron oxides which could be removed by deferrification. In contrast, it was found that American kaolinites, which had been deferrified, continued to produce resonance F_3. This being so, it was clear that iron oxides associated with American kaolinites were not effectively removed by the deferrification process used, and were probably different to those on the English kaolins.

Although using kaolins selectively coated with hydroxides at different pH values it was possible to produce similar behaviour patterns to those found in the naturally occurring kaolins it was not possible to positively identify the true nature of the oxide coatings. However, the conclusions which might have been drawn from these experiments were substantiated on a more definite basis from the results obtained from the samples of raw oxides. Combining the two sets of results it seems reasonable to conclude that the iron oxide associated with the English kaolinites is very similar if not identical to lepidocrocite. On a similar basis goethite or hematite is associated with the American kaolins.

It is generally accepted that deferrification by De Endredy's method[12] consists of dissolution in Tamm's solution involving a chemical reaction which is photo-sensitive to U.V. and De Endredy has claimed that his method removes both the crystalline and the amorphous oxides or iron. However, it has been found more recently that only amorphous and poorly crystalline iron oxides are soluble in Tamm's solution in the dark[23].

Samples of lepidocrocite, goethite and hematite treated by De Endredy's method in this laboratory showed that lepidocrocite dissolved in about 2 hours while the others persisted even after 24 hours. These results provide further evidence in support of the suggestion that the English kaolinites are coated with a lepidocrocite-like phase, which is removed on deferrification, whereas the American kaolinites are coated with a goethite - or hematite-like phase, which is less readily extracted.

The main difficulty which arises from the above conclusions, bearing in mind the known transformations of the oxides and hydroxides of iron (see Fig. 6.1) is that heating at 673K in air both lepidocrocite and goethite are known to be transformed to hematite[58]. It is, therefore, not clear why lepidocrocite at 673K should produce resonance F_2 while goethite and hematite do not. However, X.R.D. studies of lepidocrocite heated at 673K for one hour in air showed the presence of magnetite or maghemite in addition to hematite and both of these oxides being ferrimagnetic could account for resonance F_2. Owing to the broadness of the peaks and their relatively low intensity it was not possible to distinguish between magnetite and maghemite by X.R.D. However, it was deduced that the oxide was more probably maghemite for the following reasons:-

(a) The linewidth of resonance F_2 was found to increase with decreasing temperature whereas it is known that the linewidth of the magnetite resonance decreases with decreasing temperature[54];

(b) Magnetite would not be expected to be formed from the other oxides at temperatures below 1673K in air[55](see Fig. 6.1). On the other hand, it is not clear why maghemite should remain stable at 673K when it might be expected to have been converted to hematite.

With regard to resonance F_1, which in English kaolinites is partially reduced in intensity on deferrification, the removable component can be attributed to the lepidocrocite-like phase, which would be extracted by De Endredy treatment and which is known to be paramagnetic at temperatures above 70K. It must be emphasised that a paramagnetic resonance is approximately three orders of magnitude less intense than a ferrimagnetic resonance for the same number of spins[36]. The difference accounts for the much greater intensity of resonance

F_2, which has been attributed to a ferrimagnetic phase. In Georgia kaolinites, resonance F_1 was not affected by De Endredy treatment so this resonance and part of resonance F_1 in English kaolinites is probably due to the interaction between adjacent Fe^{3+} ions, which are known to be substituted in the kaolinite structure[1,2].

Resonance F_3 is formed by all the kaolinites on heating in hydrogen at 723K. Kaolinites coated with amorphous iron hydroxides and naturally occurring iron oxides and hydroxides thus treated show the presence of hematite, magnetite and iron. Resonance F_3 is, therefore, attributed to magnetite and/or iron.

Isolated lepidocrocite is normally metastable and readily transforms to its stable polymorph, goethite. However, lepidocrocite is known to occur as a stable compound in soils (particularly in humid, temperate regions)[25]. The relative stability of lepidocrocite in soils has been studied in detail and has been shown to be dependent on the amount of organic matter[23] and the concentration of silicon cations[24], which might be present. The chemical analyses of the samples indicate that the English kaolinites contain more silica than the American kaolinites. Also, organic matter is generally more abundant in English kaolins. It seems reasonable, therefore, to suggest that English kaolinites in a temperate climate are associated with an iron oxide which is similar to lepidocrocite. Hematite rarely occurs in soils of temperate regions, but mixtures of hematite and goethite are common in warmer regions[29]. It is reasonable therefore to assume that the American kaolinites are associated with hematite or goethite-like phases.

During the course of the E.S.R. studies of the English and American kaolinites, the effects of the various physical and chemical treatments on the brightness values of the samples was examined. It was found that deferrification improved the brightness of all the English kaolins, but produced no measurable effect in the American samples. This behaviour pattern is expected as iron oxide impurities are known to form one of the major non-white components of kaolins[61]. Deferrification using De Endredy's treatment was shown by the E.S.R. studies to be effective only for the English kaolinites. Organic material is also thought to have a deleterious effect on the brightness of clays. However, in this work, removal of organic impurities by hydrogen peroxide treatment had a negligible effect on the brightness values of the kaolinites studied. It was noted that the brightness of all the kaolinites decreased appreciably following thermal treatment at 673K for one hour. Moreover, the heated samples were found to have significantly lower brightness values when the heating had been preceded by chemical treatment. This result was most unexpected and was not readily explained. The only change in the E.S.R. spectrum, which was exhibited by all the samples on heating at 673K, was the collapse of the resonance attributed to B-centres. It is known that B-centres can be reformed on X-irradiation, but in this work no accompanying increase in brightness was observed. It can only be assumed that the effect of heating on the brightness of kaolinite is related in some way to the surface of kaolinite. To date, the true nature and surface chemistry of kaolinites is not fully understood. In this respect is is hoped that the results presented in this paper may be of assistance.

Further information regarding the iron oxide phases associated with English and American kaolinites might be found by comparing magnetic susceptibility measurements for samples following chemical and thermal treatments. Also an investigation of the effect of other methods of iron oxide removal, in particular the dithionite-citrate-bicarbonate method of Mehra and Jackson[11], on the American kaolinites might prove useful.

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