

MÖSSBAUER EFFECT AND NUCLEAR RESONANCE
IN LATERITIC MINERALS

by

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To Miriam Angeli

ABSTRACT

The possible usefulness of several methods of measuring hyperfine fields in the appraisal of lateritic materials has been explored. An aluminium laterite, two nickel laterites and a number of synthetic and natural pure minerals were studied. The methods used were Fe^{57} Mössbauer effect, wide-line nuclear magnetic resonance (NMR) of H^1 and Al^{27} , and zero field NMR of Ni^{61} and Fe^{57} in addition to ordinary methods of determinative mineralogy. The experiments supplied fundamental information about the magnetic and structural properties of individual lateritic minerals and provided measurements of direct interest for the processing of laterites. These measurements included: a. - the relative proportions of iron-bearing minerals, b. - the particle size distribution of these minerals in sizes below about 18 nm, and c. - evidence that some of the valuable elements contained in the laterites are substitutionally or interstitially contained in the structures of hematite and goethite. The results have also shown the limitations of present day instrumentation in these fields in the study of lateritic materials.

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CHAPTER I

INTRODUCTION

Lateritic mineral deposits are an important present and future source of raw materials to the modern world. Nickeliferous laterites constitute about 80% of the known terrestrial reserves of nickel, the largest known reserves of cobalt and are also major potential sources of chromium and iron. In addition, virtually the entire world's production of aluminium is derived from the treatment of lateritic bauxites.

A major problem in prospecting, evaluating and treating lateritic mineral deposits is the limitation of present-day techniques of laterite appraisal. This is a consequence of the inherent properties of lateritic materials which make them difficult to study by ordinary methods of determinative mineralogy.

An examination of the problem has shown that chemical and mineralogical techniques currently used cannot provide all the required information and that research for, and development of, new methods and techniques for the appraisal of lateritic mineral deposits are required. As a consequence this work has been concerned with evaluating the possible use of techniques of hyperfine field measurements as tools for mineral appraisal of lateritic materials.

The subject material in this work has been arranged as follows: Chapter I is concerned with the background of the problem including a description of lateritic deposits, the way they are treated and a short review of current methods of laterite appraisal. This is followed, in Chapter 2, by the result of a study by these current methods of three lateritic mineral samples. The results of hyperfine field measurements

carried out in lateritic, as well as in pure natural and synthetic mineral samples, is reported in the next three chapters. The methods of hyperfine field measurement used were Mössbauer effect spectroscopy, wide-line nuclear magnetic resonance and zero-field nuclear magnetic resonance. All the background theoretical considerations are collected in Chapter 3. Chapter 4 contains a description of the instruments used and Chapter 5 contains all results and discussion of the results.

1.1 Origin and description of laterites

Laterites are residual mineral deposits developed in humid, tropical or subtropical regions by the weathering of underlying rocks by surface waters. In the process silicates and other minerals are decomposed and soluble components such as silicon and magnesium are leached out and carried away leaving higher concentrations of certain elements, such as Fe, Al, Ni, Co, Cr, Th, Nb and rare earths, in the residues. Iron is the most abundant element in the majority of laterites, but it is the relatively high concentration of the other, more valuable, elements which attract attention to laterites as possible sources for these elements.

A laterite is a surface phenomenon which results in a deposit normally varying from 5 to 15 metres in depth, which in exceptional cases may reach 100 metres. (Figure 1.1). Studies of the relative concentrations of various elements in the lateritic profile and in the underlying rocks have indicated that a laterite of about 14 m depth may be the residue from the weathering of up to 240 m of rock. (Esson

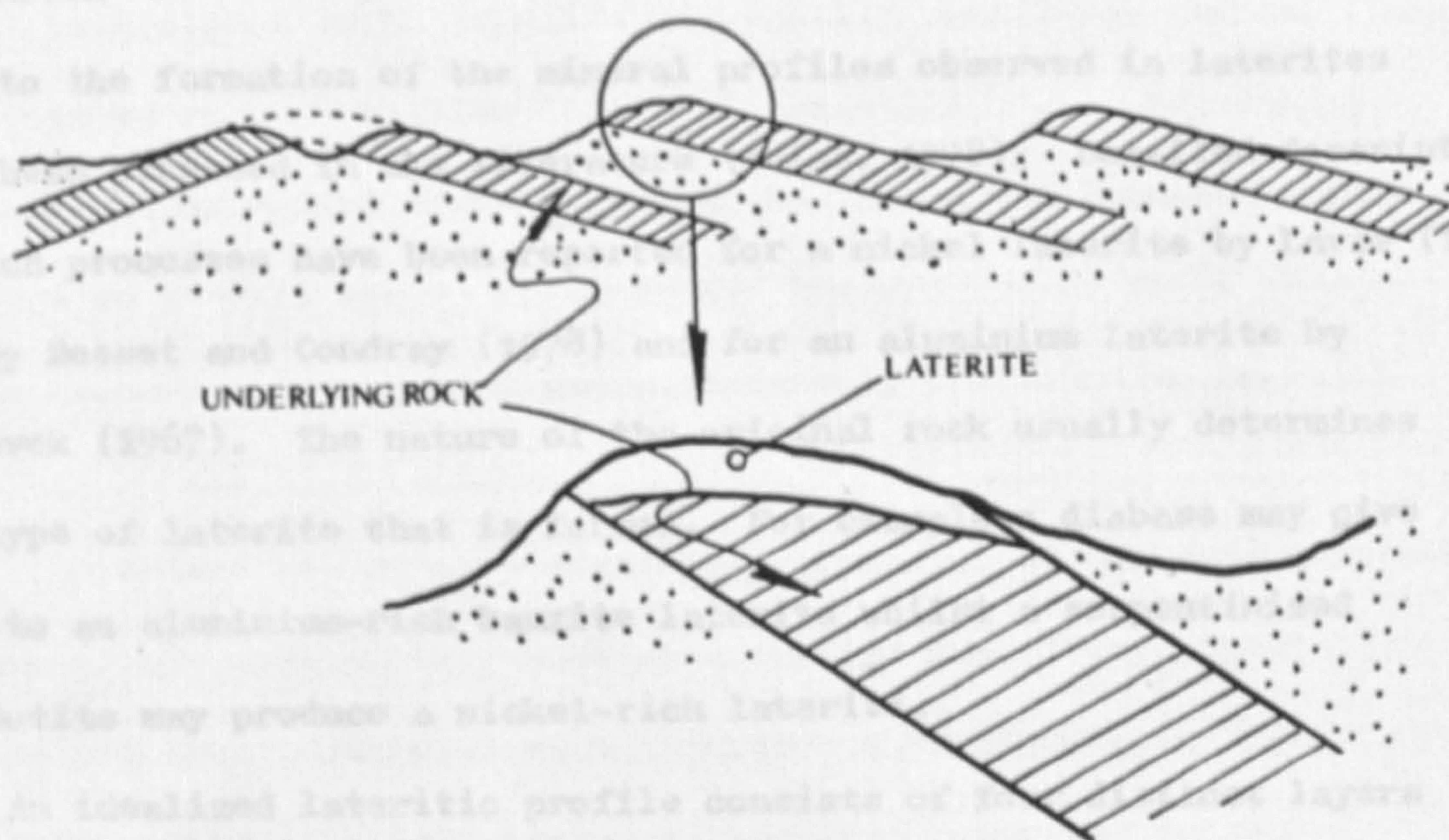


Figure 1.1 Section through a typical lateritic deposit indicating the location of a weathered zone.

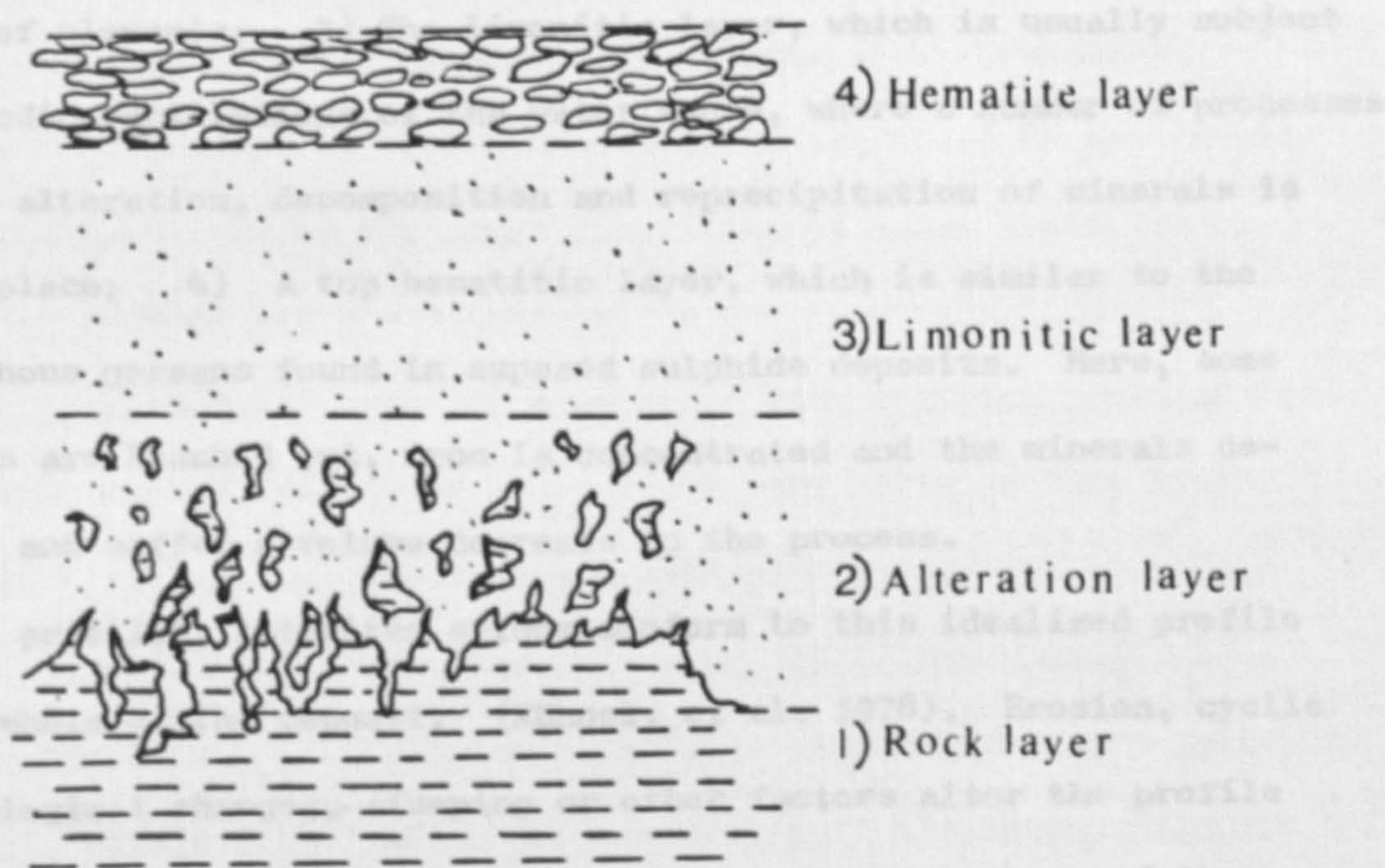


Figure 1.2 Section of an idealized lateritic profile.

and Surcan dos Santos, 1978). Numerous models of the processes that lead to the formation of the mineral profiles observed in laterites have been proposed in the literature (Avias, 1978). Detailed descriptions of such processes have been reported for a nickel laterite by Lavie (1967) and by Besset and Condray (1978) and for an aluminium laterite by Sinkovek (1967). The nature of the original rock usually determines the type of laterite that is formed. For example a diabase may give rise to an aluminium-rich bauxite laterite whilst a serpentized peridotite may produce a nickel-rich laterite.

An idealized lateritic profile consists of four distinct layers as shown in Figure 1.2. (Roorda and Quenau, 1973). These layers, from bottom to top, are 1) A relatively unaltered rock layer which is undergoing a process of hydration, volume increase and consequent breakage; 2) An alteration layer in which the underlying rocks are in a process of further alteration with dissolution and migration of a number of elements; 3) The limonitic layer, which is usually subject to periodic oscillations of the water table, where a number of processes such as alteration, decomposition and reprecipitation of minerals is taking place; 4) A top hematitic layer, which is similar to the ferruginous gossans found in exposed sulphide deposits. Here, some elements are leached out, iron is concentrated and the minerals dehydrate and suffer a volume decrease in the process.

In practice, laterites seldom conform to this idealized profile in the whole of the deposit. (Kühnel, et al. 1978). Erosion, cyclic climatological changes, slumping or other factors alter the profile and produce a characteristic variability of the mineralogy of the deposit in a horizontal as well as in a vertical direction (Power and Geiger, 1977).

Lateritic mineral deposits are usually very large and can contain up to 1000 million tonnes of potential ore. They occupy relatively extensive areas which can be from a few thousand square metres to several square kilometres. These deposits range in age from Precambrian to Recent and occasionally are found to be still in the process of formation.

Laterites are usually classified according to the main valuable element that they contain such as aluminium laterites, nickel laterites etc. Within Ni-rich laterites a distinction is made between garnieritic laterites and limonitic laterites according to the dominant type of material in the deposit. In this context it is useful to introduce the following definitions due to the confusion in the literature between past and present usage of the terms.

Bauxite: a term used for a lateritic material containing a mixture of the hydrated aluminium oxide minerals. Gibbsite, $\alpha\text{-Al(OH)}_3$; diaspore, $\alpha\text{-AlO OH}$, and boehmite, $\beta\text{-AlO OH}$, are usually the main constituents but minor quantities of other lateritic minerals such as clays and iron oxides are common.

Garnierite: generic name for a material that contains green nickel-magnesium hydrous silicates which occur very often in fine grains, with poor crystallinity and as intimate mixtures of two or more components. (Brindley and Pham Thi Hang, 1973; Esson and Carlos, 1978; Maksimovic, K. in Brindley, 1978). In the idealized lateritic profile, garnierite is found preferentially in the second, alteration, layer of the deposit.

Limonite: generic name for a material containing a mixture of yellowish-brown iron oxide minerals usually of fine particle size and often of poor crystallinity (Roorda, 1977). In the idealized lateritic profile, limonite is the main constituent of the third limonitic layer, and also of the fourth hematitic layer.

Garnieritic laterite: The term is used to describe a nickel-rich laterite in which the material has a predominance of garnierite and whose overall chemical assay has high proportion of silica (40 - 55% SiO_2) and magnesia (25 - 38% MgO) and a lower proportion of iron (8 - 18% Fe_3O_4) (Power and Geiger, 1977).

Limonitic laterite: This term describes a laterite in which the material is predominantly limonite and consequently the overall chemical assay shows a high proportion of iron (35 - 60% Fe_2O_3) and lower proportion of magnesia and silica (0.2 - 6% MgO , SiO_2) (Power and Geiger, 1977).

Real laterites seldom conform to these definitions and in practice a laterite which is described as a garnieritic laterite, for example, may contain pockets or lenses of predominantly limonitic material irregularly located within the predominantly garnieritic material, resulting in an overall composition that contains a sizeable proportion of limonitic material.

1.2 Laterite treatment

Lateritic mineral deposits are usually worked by open pit methods after removal of the overburden and hematite layer.

The material is seldom amenable to physical methods of producing mineral concentrates, and hence treatment involves light comminution, screening and blending followed by chemical processing. The material

is usually friable and comminution requires very moderate energy expenditure. The methods used for chemical treatment are highly dependent on the particular deposits, especially when dealing with nickel laterites.

Aluminium laterite treatment

With aluminium laterites the majority of deposits worked are high quality bauxites in which aluminium is contained in gibbsite, boehmite or diaspora. With these bauxites the usual treatment (Budgen, 1947) consists of two stages:

- 1) Attack with alkali hydroxide at high temperature and pressure: this takes into solution the aluminium from its oxides and hydroxides and the residues are then separated by filtration. The extracted aluminium is recovered by recrystallization and separation of bayerite, $\beta\text{-Al(OH)}_3$ at low temperature and pressure. The separated bayerite is finally converted to alumina by calcination. (Bayer process).

- 2) The alumina is reduced to aluminium by electrolysis at high temperature (Hall process).

Modifications of the first stage are sometimes applied with success when a proportion of the aluminium is associated with silicate minerals such as halloysite, kaolinite or clays; but, for lower grade ores where a significant amount of aluminium is contained in silicates and the Fe content is high (> 10%), alternative methods have been the subject of much research and evaluation. For instance: in the "H+ process", the Bayer process stage is replaced by a two-step acid leach which removes aluminium from the ore and produces alumina

suitable for electrolysis (Fallwell, 1975). In other proposed methods, totally different processing routes have been considered which usually include a chlorination stage at high temperature. A review of these alternatives has been reported by Peacey and Davenport (1974).

Nickel laterite treatment

The great variability of nickel-bearing laterites and the influence of economic, political and other factors has resulted in a large number of chemical methods being proposed for the treatment of these materials.

The subject has been reviewed in the literature by Boldt (1967); Canteford, (1975); Jeffes and Monhemius (1976); Roorda (1977) and Pazour (1979).

Four different processes are presently used in commercial practice. These have been reviewed in detail by Boldt (op. cit.) and recent innovations discussed by Canteford (op. cit.).

The large number of treatment processes proposed, including the ones in current use, can be classified as:

1) Pyrometallurgical, 2) Hydrometallurgical and 3) Gaseous phase.

The pyrometallurgical processes include matte smelting and ferronickel smelting. (see below)

The hydrometallurgical processes include sulphuric acid leaching at high pressure, reduction/ammonia leaching, sulphidisation at high temperature followed by acid leaching (Barbery, et al. 1977), sulphuric acid leaching at atmospheric pressure (Canteford, 1978a) and hydrochlorination at atmospheric pressure (Roorda and Queneau, 1973).

The gaseous phase processes include chlorination and carbonylation. These are processes based on vapour transport reactions (Alcock and Jeffes, 1967) whereby the valuable elements in the ore are reacted with a gas to produce a gaseous compound which is then separated from the ore.

Of these processes only four are in current use. These are:

1) Matte smelting. This is carried out in Russia, New Caledonia and Japan. The process is similar to the one used for sulphide minerals and consists of the addition of sulphur or a source of sulphur, to the ore and smelting to produce a matte or mixture of sulphides from which the nickel sulphide is separated.

2) Ferronickel smelting. This is carried out in New Caledonia, Japan, Brazil, USA, Greece and Russia. It consists of smelting and reducing the ore to produce a ferronickel alloy which can have a variety of grades.

3) Sulphuric acid leaching at high pressure is carried out at Moa Bay in Cuba. This involves attacking the material with sulphuric acid at 513°K under pressure. Nickel and cobalt go into solution leaving the iron in the residue. Nickel and cobalt are recovered from the leach solution as a sulphide concentrate by precipitation with H_2S under pressure.

4) Reduction roasting followed by ammonia leaching is used at Nicaro, Cuba, the Philippines, Australia and Guatemala. In this process the ore is reduced under carefully controlled conditions so that nickel is selectively reduced to nickel metal and most of the iron reduced to Fe_3O_4 . The calcined material is then leached and

nickel and cobalt are selectively dissolved. Recent advances in this process have been reviewed by Power and Geiger (1977) and Pazour, (1979).

Amenability studies indicate that the broad mineralogical characteristics can sometimes be used to indicate which process is likely to be more successful with a particular ore. Thus, it has been found that nickel extraction with hydrochloric and with sulphuric acids leaching at atmospheric pressure is more readily achieved from garnieritic ores than from limonitic ores, (Rice and Strong, 1974) while the reduction/ammonia leaching process for the extraction of nickel is more successful with limonitic ores. (Canteford, 1978a; Canteford, 1978b). Nevertheless little success has been obtained in attempts to quantitatively correlate the mineralogy and chemistry of nickel laterites with the response of the material to a given chemical treatment. (Limerick, 1978). This worker found, for example, that there was no reason to expect the measured mean value of a mineralogical property of a sample to correlate with the process response of that sample and that chemical analysis of an ore is a poor guide to its likely response to any particular process. These results agree with those of Canteford (1978b) who found that variations in process behaviour can be expected when the feed is blended purely on the basis of chemical composition.

The recent several-fold increase in the cost of energy and the enforcement of pollution control measures has changed considerably the economics of the various alternative processes. (Roorda, 1977).

At present the selection of a treatment process for a particular orebody must be made in the light of these changing conditions.

1.3 Appraisal of Laterites

This section deals with some of the information required to evaluate the amenability of a lateritic material for processing and with the relative merits of the various techniques which are currently available to collect this information.

Information required

The chemical and mineralogical characteristics of an ore play major roles in determining its response to chemical or physical processes of mineral beneficiation. While the characteristics of the ore that determine its response to a physical process (e.g. density, magnetic susceptibility, etc.) are reasonably well understood, the situation is not so clear as to the characteristics that determine its response to a chemical process. It is even unlikely that any single property or a simple combination of properties, can be established which will allow the prediction of the behaviour of a laterite under a wide variety of chemical processes. Nevertheless a short list of the chemical and mineralogical information required is given below.

Chemical data

Due to the compositional variations in lateritic deposits particular care must be taken in sampling to avoid errors when collecting the chemical and mineralogical data.

A complete and accurate overall chemical analysis for at least the following elements is required: Ni, Cr, Co, Al, Pt, Fe, Si, Mg, Mn. This analysis will determine not only the amounts of the valuable elements but also the presence and amounts of possibly troublesome elements. In addition it is desirable to establish the variability of chemical composition both horizontally and vertically within a deposit. If the deposit approximates to the idealised profile discussed above, two or more different compositional populations are likely to be found. Such a result might imply that different mining and processing methods should be used for the different populations or that blending to form a constant feed should be provided.

Mineralogical data

The mineralogical data should include the following:

- 1) Mineral identities and their variability of crystallinity and composition.
- 2) Proportions of each mineral.
- 3) Partition of the valuable elements in the various minerals and the nature of the association of the valuable elements with the minerals
- 4) Size distribution of the whole of the material and of each mineral.
- 5) Mineral associations and textural features.
- 6) The variability of these features in different parts of the deposit.

The comments regarding the possibility of more than one compositional population mentioned above are also relevant in the mineralogical study.

Analytical techniques

Chemical methods

A combination of X-ray fluorescence (XRF) and atomic absorption spectrophotometry (AA) has been used in the past with success in the study of laterites. XRF is a fast and convenient technique for establishing the major, minor and trace elements, (Norrish and Chappell, 1977) but the need to prepare accurate standards to correct for matrix effects makes this technique inconvenient for precise work because of the compositional variability of laterites. AA (Kirkbright, and Sargent, 1974) has been found to be a straightforward and reliable technique for the majority of the elements found in laterites.

Mineralogical methods

Mineral separations

Mineral separation is based on the concept that well-defined mineral phases exist, but this is not necessarily the case in lateritic deposits due to the variability and alteration usually observed. Standard laboratory methods of mineral separations are based on properties such as density, size, shape, magnetic susceptibility, electrical conductivity and surface wettability. Of these methods size, density and magnetic susceptibility are likely to produce the best results when separating the components

of a laterite. All the methods are hampered by the large proportion of small particles: as much as 60% of the material may be below 5 μm . Other difficulties include the different degrees of alteration of the various minerals, the presence of continuous stages of alteration from one mineral into another and the porosity of the material. Porosity makes it difficult to achieve separations in dense liquids due to the amount of trapped air in the pores. Grain picking under the microscope is possible for the coarser sizes and this method has been useful for producing relatively pure amounts of the optically different minerals which can then be used for mineral identification by other analytical techniques.

Imaging Techniques

Imaging techniques include optical microscopy, electron optical microscopy and electron probe microanalysis.

The use of optical microscopy is hampered by the fact that a large proportion of lateritic material approaches the limit of resolution of the technique. Conventional optical examination of polished and thin sections is also limited by difficulties of producing acceptable specimens. These difficulties are derived from the coexistence of hard minerals such as chromites and hematite with soft friable minerals such as goethite and the garnieritic minerals which lead to unacceptable relief or the loss of the soft minerals from the specimen surface. Optical examination of granular samples is likely to provide more information than the examination of polished or thin sections.

Scanning electron microscopy has been used with some success and because of its great magnification and depth of field it is useful for establishing morphology (Kühnel, et al. 1975) as well as to study the mechanisms of the reactions that take place during processing attempts (Suzuki, et al. 1974).

Electron probe microanalysis (Long, 1977) has been used to establish the intimate association between the valuable elements and the various minerals. (Kühnel, 1972; Kühnel, et al. 1974). This is done by comparing the electron backscatter image with the primary X-ray image of particular grains or by an automatic linear transverse of the specimen with simultaneous recording of the X-ray signals of two or more of the elements on a chart recorder. A variation of this technique called microprobe correlation analysis by Schellmann (1978), consists in connecting the output of the X-ray signals of two elements to the x and y inputs of an x-y plotter while the beam automatically transverses the specimen. The resulting diagrams, after about one hour of measurement, give a visual, statistically more significant, indication of the correlation between any two elements. However the use of the microanalyser is limited by several factors such as: 1) The difficulty of producing acceptable polished samples. 2) The errors introduced by polishing relief. 3) The difficulty of preparing standards for matrix correction. 4) Sampling problems. 5) The limited resolution of the analysis. Because of the resolution of microprobe X-ray analysis (e.g. $\approx 2 \mu\text{m}$) this technique is incapable of solving an important problem in nickel laterite appraisal: what is the nature of the association between nickel and goethite.

The limited resolution of the imaging techniques discussed above, when applied to lateritic materials, result in a corresponding limitation of techniques of automatic image analysis (Jones, 1977) which otherwise would be able to provide quantitative estimations of various mineralogical parameters useful in the appraisal of laterites.

X-ray diffraction

X-ray diffraction (XRD) is the most useful method of mineral identification in laterites. The technique tolerates the use of very small specimens and of simple mixtures. Hence it is possible to use the XRD patterns of a few mineral grains separated under the microscope for mineral identification. Such identification provides a means of later recognising the minerals in grain samples under the microscope. However XRD has a number of limitations when used in the examination of laterite minerals: it is incapable of detecting semi-crystalline or amorphous materials or of detecting a mineral phase that occurs in small proportions* (less than about 5%). These problems are likely to be common during the study of a laterite. The capability of the XRD method in quantifying mineral mixtures (Chung, 1974) cannot be realised with laterites due to the difficulty of producing suitable pure mineral standards with the same crystallinity and particle size as in the unknown specimens. In addition the XRD method is particularly limited for recognizing and quantifying iron

*The limit of detectability depends a great deal on the minerals concerned. A well crystallised mineral under favourable conditions may be detectable below 1% level while large concentrations of amorphous material may be undetected.

minerals in mixtures due to the coincidence of the main X-ray reflection angles. (Kodama, et al. 1977). This limitation is particularly severe with mixtures involving hematite and goethite where the coincidence of the reflection angles is aggravated by the broadening of the lines produced by imperfect crystallinity and small particle size. The broadening of the XRD lines has been used as a means of quantifying the crystallinity of the minerals in laterites by analysing the moments of the X-ray diffraction peaks (Kühnel, et al. 1975).

Selective chemical dissolution of Fe minerals

The limitations of the XRD method in determining the relative proportions of amorphous and crystalline iron oxides in laterites can be partially overcome by a method of selective chemical dissolution of the mineral phases. The method has been developed for the study of soils and consists of a series of treatments that selectively remove the iron oxides. First the proportion of amorphous iron hydroxides is determined by a method called acid-ammonium-oxalate extraction. (Landa and Gast, 1973). This treatment does not extract the iron contained in crystalline minerals. The proportion of crystalline hematite and goethite is then obtained by a method called sodium-dithionate extraction (Aquilera and Jackson, 1953; Mehra and Jackson, 1960) which dissolves these two minerals but does not affect magnetite, ilmenite or chromite. The rest of the iron contained in these minerals can be determined by attacking them with strong acids.

Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are applicable to lateritic minerals because a large number of these minerals show pronounced thermal effects. The hydrated iron and aluminium oxides, the nickel and magnesium hydrated silicates and the clays all show thermal effects which can be used for mineral identification and occasionally, quantification. (Neumann, 1977). Unfortunately endothermal and exothermal peaks are broad and overlap so that it is only in certain cases that mixtures of minerals found in laterites can be elucidated by the use of DTA or TGA. A further difficulty is that thermal peaks are not necessarily constant for a given mineral. For example, goethite shows a wide range of dehydration temperatures which vary from 553°K to 603°K depending on the degree of crystallinity. (v. Oosterhout, 1965). DTA carried out under controlled atmospheres makes the method more diagnostic as demonstrated by Lodding and Hammel, (1960) who report a method for the detection and measurement of gibbsite, $\text{Al}(\text{OH})_3$, regardless of the iron hydroxides present. The method is very useful for laterite mineral identification if it is possible to produce relatively pure mineral phases for analysis by the methods discussed above. This last requirement establishes the limits of the applicability of the method.

Optical and infrared spectroscopy

The situation of infrared (IR) spectroscopy is rather similar to that of thermal analysis as a tool in mineral appraisal of laterites. (Farmer, 1968; Estep-Barnes, 1977). The majority of

lateritic minerals produce an infrared absorption spectrum which is characteristic of the mineral. For example, the spectra of the three hydrated aluminium hydroxides commonly found in bauxites; gibbsite, boehmite and diaspore, are quite different. (Frederickson, 1954) and the infrared absorption spectrum can be used as a fingerprint technique for the identification of relatively pure specimens. But the complex shape and broadness of the IR absorption peaks result in great difficulties in applying this method to mixtures of more than two minerals (Liese 1967).

Spectroscopy in the optical region of the spectrum is an even poorer prospect for the appraisal of laterites. Absorption or reflectance spectra are made up of broad unresolved absorption peaks (Strens and Wood, 1977). These spectra are unlikely to improve with the use of monochromatic tunable laser sources presently available or with new sensitive methods of optical absorption detection such as photoacoustical spectroscopy. (Rosencwaig, 1975; Adams, et al. 1976). This is because optical absorption arises from transitions between the electronic conduction bands, the crystal field levels, the valence band and the electron core bands - all of which are inherently broad (Strens, private communication).

Conclusion

The limited ability of the techniques discussed above to supply the information required for the evaluation of a lateritic material demonstrates the present unsatisfactory state of affairs in the appraisal of laterites. In view of the limitations of the

methods of determinative mineralogy and the evidence of the close interrelationships between value elements and gangue minerals it is probable that new instrumental methods of analysis will be needed in the study of laterites. In particular, analytical methods which supply information on a sub-microscopic, molecular or atomic level are likely to provide information which may be of use in evaluating processing routes. Hence the bulk of this work has been concerned with studying the possible usefulness of techniques that probe the hyperfine fields around nuclei in minerals of lateritic origin.

CHAPTER 2

MINERALOGY AND CHEMISTRY OF THE MATERIALS STUDIED

Introduction

In this chapter are collected the results of a mineralogical and chemical study carried out on three laterite samples. The samples originated in Central and South America and included two nickel-bearing laterites and an aluminium bearing laterite.

The study was carried out in order to establish the main mineral and chemical properties of the materials. Additionally, the study aimed at assessing the usefulness of the various analytical techniques in the appraisal of laterites.

Mineral separations were carried out under laboratory conditions for the purpose of studying the minerals concerned, not for determining the feasibility of beneficiation of the materials. Nevertheless the information gathered which could be used for physical treatment of these laterites has been pointed out.

2.1 Aluminium laterite from Los Guaicas, Venezuela.

Origin of the material.

The material studied consisted of a sample of aluminium laterite from Los Guaicas, Estado Bolivar, Venezuela. The geology of the region has been described by A. Bellizzia (1957). A paper by Sinkovec (1967) describes the geology of the region, the structure of the deposit and proposes a model for the genetic processes that gave rise to the formation of the laterite. The exploration work reported was confined to two zones. Each zone showed slightly different average chemical compositions as follows:

Zone A. Al_2O_3 = 34.5%, Fe_2O_3 = 37%, SiO_2 = 1.73% and TiO_2 = 3.7%.

Zone B. Al_2O_3 = 31.0%, Fe_2O_3 = 43.5%, SiO_2 = 1.43% and TiO_2 = 5.5%.

The reserves of these zones were estimated as Zone A, 26.6 million tonnes and Zone B, 33.4 million tonnes. It is estimated that the total reserves of the Los Guaicas region is probably a few hundred million tonnes of material of rather similar composition.

Figure 2.1 shows the approximate location of the deposit and figure 2.2 shows a diagram of the zone of the deposit studied by B. Sinkovec.

For the present work three samples of Los Guaicas material totalling 13.2 kg were obtained. Of these, one containing 8.9 kg and described as "mixed material" was selected for appraisal. This material was supplied by courtesy of Dr. P. Bolsaitis of the IVIC Research Institute, Caracas, Venezuela.

Appraisal procedure.

The appraisal procedure followed on the lateritic material is indicated schematically on flowsheet No. 2.1. The sample, contained in four plastic bags, consisted of dry lumps and loose material with a general light brown colour with occasional white grains visible in the loose material and in the lumps. Some of the lumps were clearly aggregated material which could be broken by hand. Even the hardest pieces would probably break with only minor energy requirements.

After sampling the material was scrubbed in an 8 inch rod mill with no rods, at a pulp density of about 30% solids, turning at 100 r.p.m. for $\frac{1}{2}$ hour. No dispersant was used.

The scrubbed slurry was wet screened in British Standard screens from B.S.7 (2411 μm) to B.S. 200 (75 μm). The -75 μm slurry was allowed to settle and the clear water decanted. The -75 μm fraction contained in the thickened slurry was weighed and two samples of identical volume were taken during vigorous stirring. The samples were



Figure 2.1 Approximate location of the Venezuelan lateritic deposits studied. A - Los Guaicas aluminium laterite. B - Loma de Hierro nickel laterite.

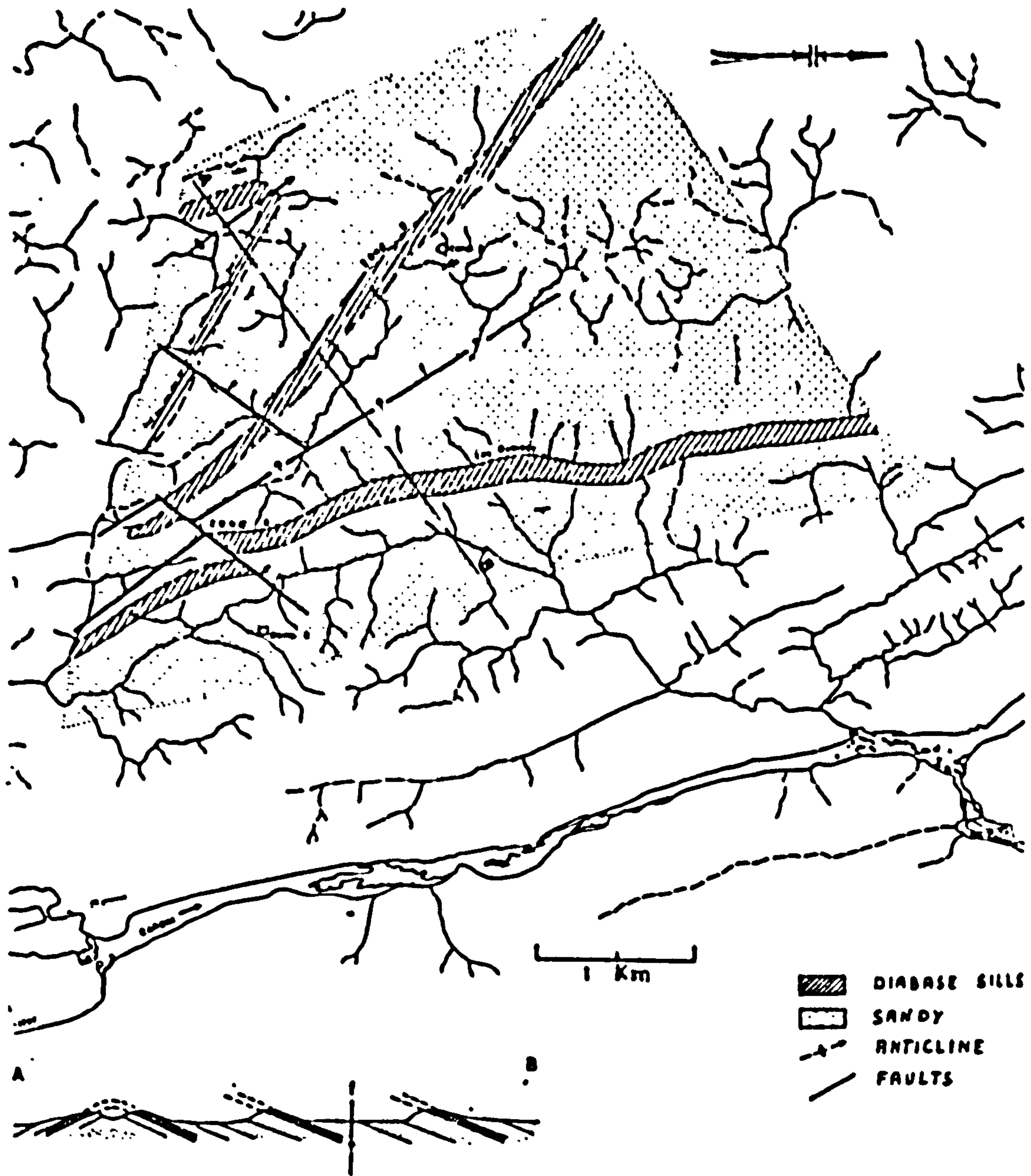
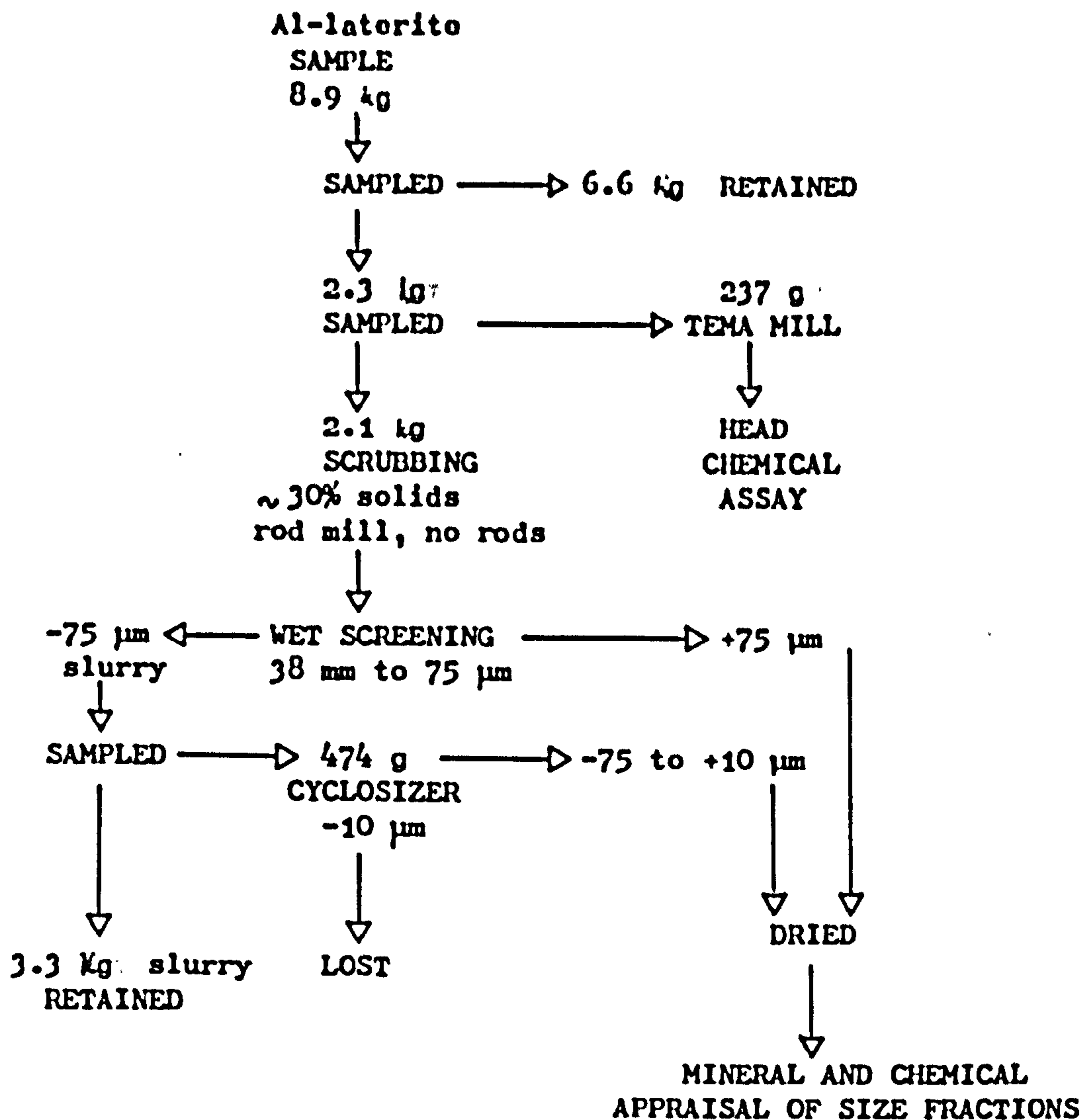


Figure 2.2 Los Guaicas aluminium laterite deposit.
After Simkovec (1967).



Flowsheet No. 2.1 Schematic diagram showing the appraisal procedure followed with the aluminium laterite sample from Los Guaicas, Venezuela.

weighed and one dried while the other was used for further sizing with a Cyclosizer.

Table 2.1 shows the results of the sizing operation and figure 2.3 shows these results in a graph of cumulative percent finer as a function of particle size.

Table 2.1 Results of the sizing operation on the Al-laterite from Los Gualcas, Venezuela.

Size (mm or μm)	Weight g	Weight %	Cumulative % weight finer
-38.1+19 mm	338.5	15.8	99.7
-19 +9.5	93.5	4.4	83.9
-9.5 +2.4	30.8	1.4	79.5
-2.4 +1.18	26.2	1.2	78.1
-1.18+0.6	111.8	5.3	76.9
-0.6 +0.3	194.6	9.2	71.6
-0.3 +0.15	228.3	10.8	62.4
-150 +75 μm	236.6	11.2	51.6
- 75 +44	67.3	3.2	40.4
- 44 +33	75.6	3.5	37.2
- 33 +23	82.5	3.9	33.7
- 23 +15	63.3	3.1	29.8
- 15 +11	35.1	1.6	26.7
- 11	529.8	25.1	25.1
2110.4			

The sample retained for chemical assay was ground in a Tema Mill for $\frac{1}{2}$ hour and used for all chemical assays. A semiquantitative scan for all elements by X-ray fluorescence (XRF) and quantitative assays for Fe, Al, Ti and Si were supplied by Analytical Services, Imperial College. Additionally, assays were carried out by Atomic Absorption Spectrophotometry (AA) for the elements: Fe, Co, Cr, Ti, Mg and Al.

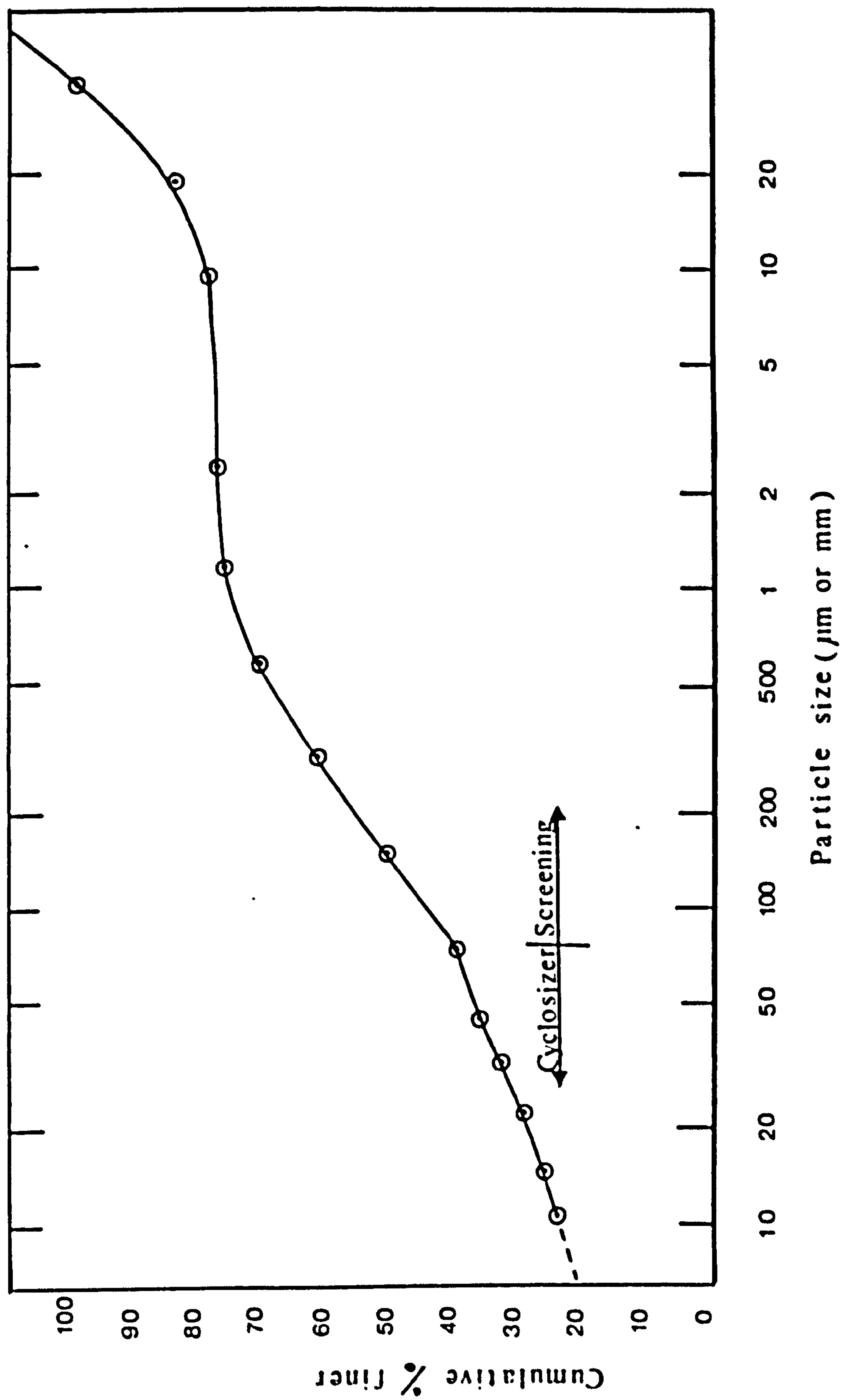


Figure 2.3 Particle size distribution of the aluminium laterite from Los Guaícas, Venezuela.

The AA assays were made by dissolving the solid sample and aspirating the solutions, or suitable dilutions, and comparing the absorption with standard solutions in the usual manner (Kirkbright and Sargent, 1974).

To dissolve the sample several methods were tried including

- 1) Attack with hot concentrated acids (HCl , H_2SO_4 , HNO_3).
- 2) A method suggested by Omang (1969) for the dissolution of silicates and bauxites. This method consists of adding equal quantities of lithium carbonate and boric acid to 1/5th the weight of material. The mixture is melted in a crucible and when cool the melt is dissolved in dilute HCl .
- 3) Melt the material in alkali hydroxide and the melt dissolved in water followed by addition of HNO_3 .

None of these methods produced completely satisfactory results.

Method 1) left up to 31% undissolved solids consisting of aluminium silicates and quartz. Method 2) dissolved a very large percentage of the material but the undissolved solids included at least four different mineral phases and difficulties were encountered in producing standard solutions. Method 3), which was adopted, dissolved at least 90% of the material leaving a solid residue which consisted of magnetite and amorphous silica.

Details of method 3 are as follows: weighed quantities of laterite and Na OH in the ratio 1:1.5 were added to a nickel crucible. The mixture was heated, gently at first, in a Bunsen burner and kept at red hot temperatures in the covered crucible for a few minutes. Distilled water was added during cooling and the crucible placed in a beaker with 100 ml of water. The beaker was then placed in a hot water bath and the crucible removed when free of the melt. This produced an orange slurry. The slurry

was then heated to 100°C and a few ml concentrated nitric acid were added. This produced a vigorous reaction which rendered most of the material soluble. The solution was filtered and made up to volume and the solids dried. These consisted of magnetite and amorphous silica which were magnetically separated and weighed.

The results of all chemical assays are shown in Table 2.2.

Table 2.2 Chemical composition of the Al-laterite from Los Guaicas, Venezuela. AA = Atomic absorption.
NR = Not reported, NA = Not assayed. H_2O calculated by difference.

Element	AA	Analytical Services	Reported by Simkovec (1967) (zone A)	(A-2) ^{b)}
Fe_2O_3	25.0	28.4	37.0	23.6
Al_2O_3	29.1	24.25	24.5	28.9
TiO_2	4.2	3.11	3.7	2.8
SiO_2	NA	24.2	1.73	29.8
NiO	NA	<500 ppm	NR	NR
Cr_2O_3	0.03	NR	NR	NR
MgO	0.009	NR	NR	NR
Traces ^a				
H_2O	17.4	NR	NR	NR

a) Trace elements analysis supplied by Analytical Services include: 0.5 to 0.05%: S, Cl, Mn and Cu
<500 ppm : K, Ca, Ni, Zn, Zr, Pb, Se.

b) The chemical composition of the sample studied is very similar to the assay of sample A-2 "Clay Laterite" reported by Simkovec (1967) in the same deposit. In the laterite profile sample A-2 corresponds to the zone just above the underlying diabase.

Mineral appraisal

Granular samples of the sized fractions were examined by optical microscopy and samples of the different minerals were isolated by the use of several standard techniques including hand picking under the microscope. Mineral identifications were confirmed or carried out with the aid of X-ray diffraction (XRD).

Table 2.3 Minerals identified in the XRD analysis of hand-picked mineral grains from the Al-laterite of Los Guaiacas, Venezuela.

Description of Sample		MINERALS IDENTIFIED (In approximate order of concentration)
Fe ¹⁾ bearing	(Black Mod. Magnetic (Black grains	ilmenite, hematite and magnetite ilmenite, hematite and magnetite
	(Orange concretionary (White grains	gibbsite halloysite (metahalloysite, poorly crystalline)
Al-bearing	(White mineral from (rock samples	kaolinite and quartz
	HCl leach residue	kaolinite, quartz and gibbsite traces
	-75 μ m slimes	gibbsite, kaolinite, goethite, hematite and quartz
	Black Non Magnetic	todorokite, quartz and halloysite.

- 1) No XRD patterns were made of iron bearing mineral grains such as goethite and magnetite which were clearly identifiable in the grain samples.

The following minerals were identified: aluminium-bearing minerals; gibbsite α -Al(OH)₃, kaolinite Al₄ Si₄ O₁₀ (OH)₈, halloysite Al₄ Si₄ O₁₀ (OH)₈ · 8H₂O; iron-bearing minerals; magnetite Fe₃O₄, hematite Fe₂O₃, ilmenite Fe Ti O₃, and goethite α -Fe O OH. The only other minerals identified were quartz SiO₂ and todorokite (Mn, Ca) Mn₅ O₁₁ · 4 H₂O.

All these minerals were clearly identified in XRD patterns. Table 2.3 shows the results of the XRD examination of the samples. In all cases a diffractometer was used and a mineral was considered identified when at least the three most intense lines were found. In fact, all lines with intensity greater than 10 (relative) were accounted for in the diffractometer patterns.

Al-bearing minerals.

The minerals which are commonly found in an aluminium-rich lateritic deposit may be arranged in a sequence which begins with montmorillonite and ends in alumina. See figure 2.4. In this sequence the amount of silica gradually decreases and is substituted by OH ions. The OH ions are later lost and are substituted by oxygen atoms. This sequence fits well within some of the models postulated for the genesis of a bauxite laterite. (Sinkovec, 1967).

The Al-bearing minerals found in the Guaiacas deposit belong to the middle of the sequence referred to above. This suggests that the sample studied may belong to a lower stratum of the deposit where the initial stages of the transfer motion takes place. The overall chemical composition, determined for the sample, supports this assumption. (See footnote to Table 2.2). From the mineral processing point of view this fact is important as it indicates that the material used in this study may not be representative of the full deposit.

The most common Al-bearing mineral is gibbsite and this is intimately associated with goethite. The presence of iron colours the gibbsite grains from bright orange to pale yellow. Under high magnification (X 1600) the orange grains of gibbsite are seen to consist of a mixture of transparent material (gibbsite proper) with yellow or red grains of very small size (goethite or hematite of 0.5 to 5 μm). The optically distinctive characteristic of gibbsite is that the orange or yellow grains look concretionary.

In the finer size fractions (below 150 μm) it is increasingly difficult to differentiate visually between gibbsite and goethite grains as there is a continuous series from what is clearly pure gibbsite to what is clearly pure goethite. Pure liberated gibbsite grains are only

found in very small sizes ($<10\ \mu\text{m}$) while orange-stained grains of gibbsite may be found liberated up to 1-2 mm size.

The next most common Al-bearing mineral is halloysite.

Halloysite grains are easily recognised by their smooth surface appearance and opaque white colour. They are found liberated at sizes below about 2 mm size. In the finer size fractions (less than $150\ \mu\text{m}$) halloysite shows a dull cream or white colour sometimes with a greenish tint (When seen under transmitted light with crossed polars). In this fine size range the grains of halloysite adopt a tabular shape.

The presence of kaolinite in the white minerals associated with the harder rock samples, was found by XRD. This is consistent with the fact that it is one of the initial stages in the sequence shown in figure 2.4. Kaolinite was also detected by XRD in the $-75\ \mu\text{m}$ slimes and in the solids left after HCl treatment of the head sample.

Figure 2.5 shows the XRD patterns of hand-picked samples of the Al-bearing minerals.

Fe-bearing minerals

The minerals ilmenite, hematite and magnetite are intimately associated. They report together in black moderately magnetic grains in which the three different minerals are indistinguishable under the microscope due to the alteration of the mineral surfaces.

Although no proper quantitative measurements have been done of the mineral distribution in the different size fractions it has been observed that the minerals ilmenite and magnetite are present in

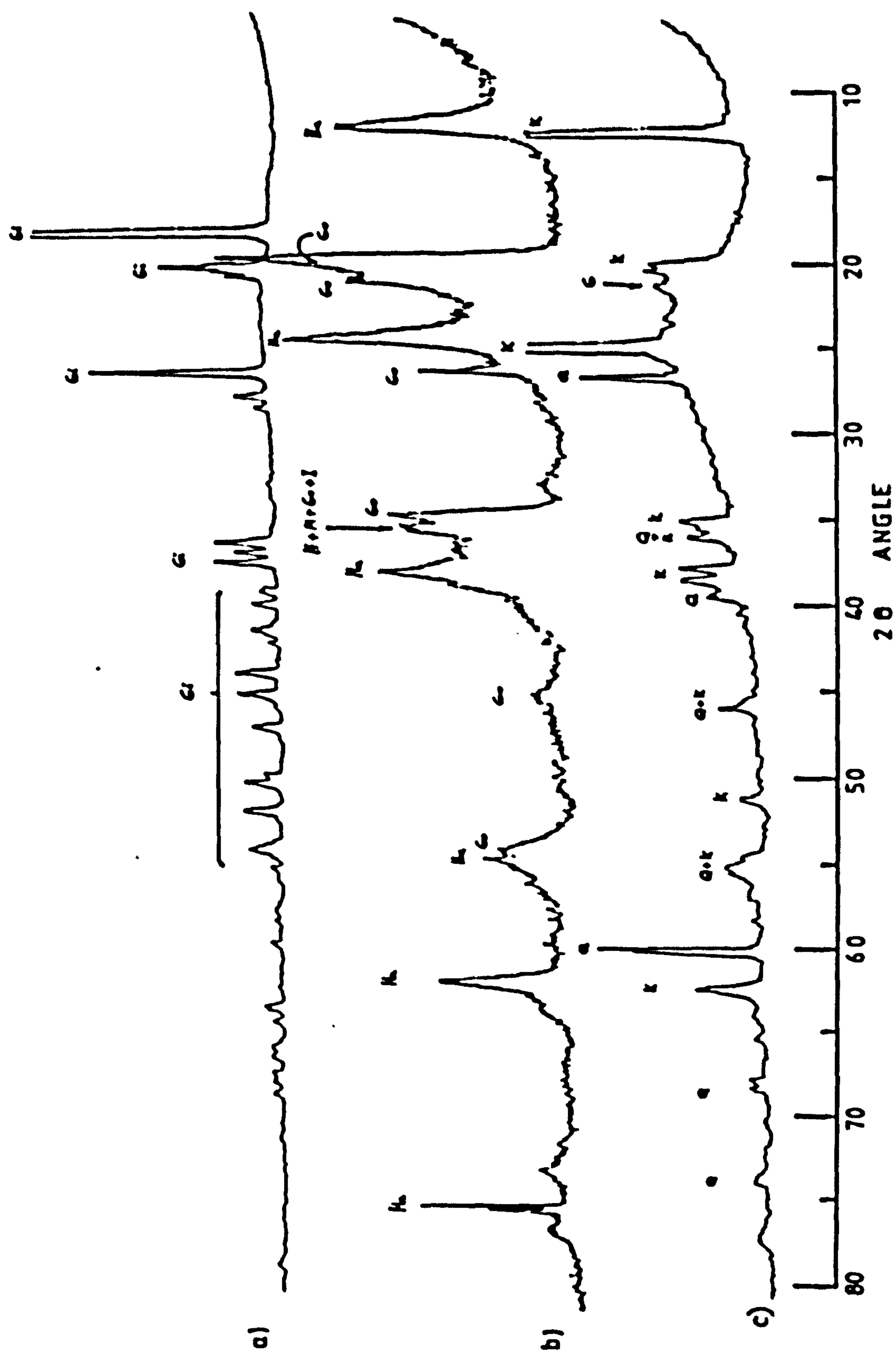


Figure 2.5 XRD patterns of hand picked grains of aluminum bearing minerals from Los Gualacas, Venezuela. Cu K α radiation. a) orange grains, b) white grains, c) white grains from rock. G = gibbsite, Ha = halloysite, K = kaolinite, Go = goethite, M = magnetite, H = hematite, I = ilmenite, Q = quartz, To = todorokite.

greater quantities in the coarser sizes (0.3 to 2.4 mm) than in the finer fractions (less than 0.15 mm). They were not detected in careful XRD analysis of the -75 μ m slimes.

Magnetic separation under laboratory conditions of grain samples in the range -2.4 mm to +75 μ m were carried out with a Cook high intensity magnetic separator. No tests were carried out on sizes above 2.4 mm because the minerals are not liberated above this size. The results are shown in Table 2.4. Optical examination of the magnetic fractions indicate that a concentration of ilmenite, hematite and magnetite was achieved, especially in the sizes above 0.3 mm. This indicates the possibility of removing some of the iron contained in the ore. Any further study of this ore to evaluate the possibility of commercial extraction should pay careful consideration to this possibility.

Hematite and goethite are present in all size fractions. Goethite in the coarser fractions consists of soft grains which readily crumble to slime size particles. These minerals account for the majority of the iron present in the -75 μ m fraction.

Figure 2.6 shows the XRD patterns of hand-picked samples containing the iron bearing minerals, the -75 μ m slimes and black non-magnetic grains which were identified as todorokite, a manganese hydrated oxide $((\text{Mn}, \text{Ca}) \text{Mn}_5 \text{O}_{11} \cdot 4\text{H}_2\text{O})$.

Table 2.5 shows an estimate of the mineral proportions deduced from the mineral appraisal and normative calculations using the results of the chemical assay of the various mineral fractions.

Table 2.4 Results of magnetic separation of the -2.4 mm +75 μ m grain fractions in a Cook high intensity magnetic separator (Fractions in this size range represent 37.5% of the material)

Magnetic fraction	% weight	Cum.% weight
Highly magnetic*	5	5
Moderately magnetic*	2.6	7.6
Weakly magnetic	6.0	13.6
Very weakly magnetic	6.0	19.6
Least magnetic ⁺	18.0	37.6

*These fractions contained from 35 to 100% of magnetite, ilmenite, hematite and goethite.

⁺These fractions contained mostly gibbsite, halloysite, goethite, quartz and todorokite.

Table 2.5 Approximate mineral proportions in the aluminium laterite from Los Guaicas, Venezuela.

Minerals	Proportions % weight
Magnetite, Ilmenite, goethite, hematite	30
Gibbsite Al(OH)_3	31
Halloysite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}$	15
Kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	11
Todorokite $(\text{Mn,Ca})\text{Mn}_5\text{O}_{11} \cdot 4\text{H}_2\text{O}$	1
Quartz SiO_2	12

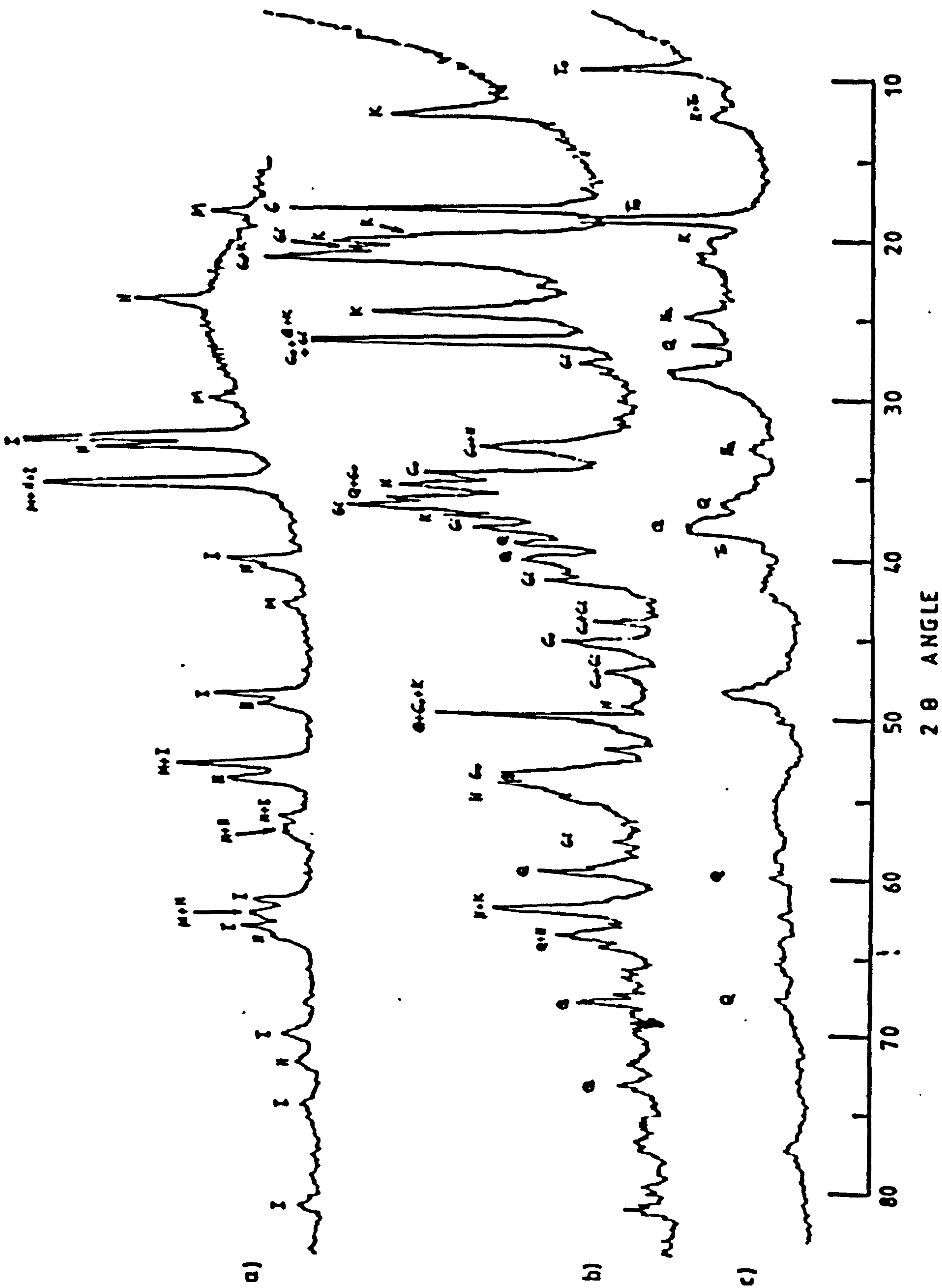


Figure 2.6 XRD patterns of minerals from Los Guaiacas, Venezuela. a) black moderately magnetic, b) -75 μm , c) black non-magnetic. Symbols as in Figure 2.5. Cu $K\alpha$ radiation.

Chemical distribution

Chemical analysis was carried out, using AA, for the elements Fe, Al and Ti of four size fractions: -75 μm material, two fractions of approximately equal proportional weights between 75 μm and 2.4 mm, and clearly unliberated +2.4 mm material. The grade and distribution of the elements in these four fractions are shown in Table 2.6 and figure 2.7.

Table 2.6 Grade and distribution of Fe, Al and Ti in size fractions of the Al-laterite from Los Guaicas, Venezuela.

Size mm or μm	% weight %	Grade %			Distribution () = Cum. % finer		
		Fe	Al	Ti	Fe	Al	Ti
+2.4 mm	21.7	14.7	17.5	2.2	17.8(99.8)	25.3(99.9)	18.3(99.9)
-2.4+0.3 mm	15.7	21.5	14.2	4.2	18.8(82.0)	14.8(74.6)	25.8(81.7)
-300+75 μm	22.1	21.0	11.2	3.4	25.9(63.2)	16.5(59.8)	28.9(55.8)
-75 μm	40.5	16.5	16.0	1.7	37.3(37.3)	43.3(43.3)	26.9(26.9)
Calculated head		17.9	15.0	2.5			
Measured head		17.5	15.4	2.5			

The results of the chemical distribution together with the results of the mineral appraisal indicate a very intimate association between the iron and aluminium minerals, the presence of a large proportion of aluminium contained in silicate minerals and a high proportion of the values contained in the -75 μm slimes. Aside from the possibility of reduction of the Fe content by magnetic separation already discussed, the results of the appraisal suggest that the material is a very poor prospect for any form of physical beneficiation.

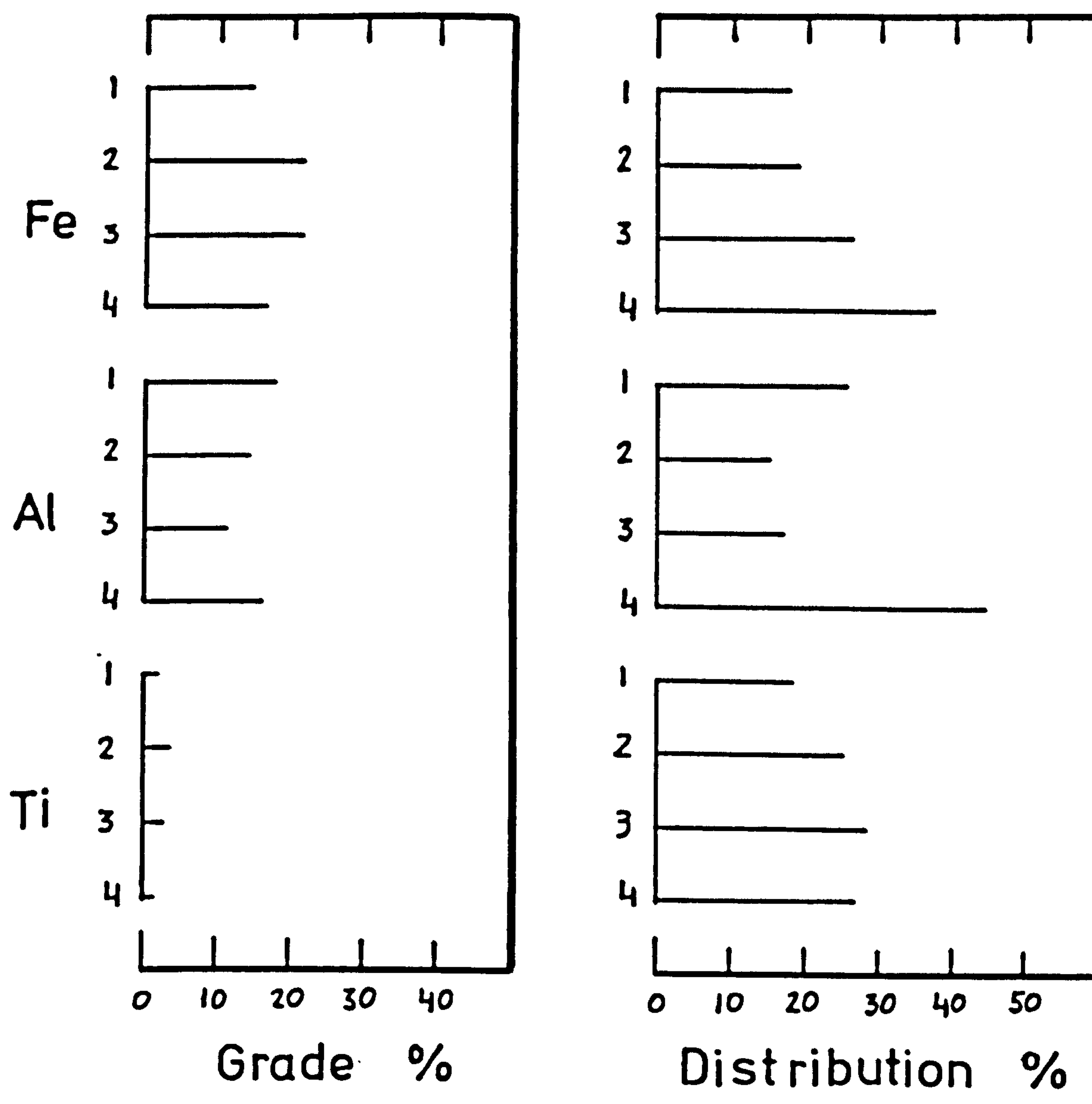


Figure 2.7 Diagram showing the grade and distribution of the main elements in the particle size fractions of the laterite from Los Guaicas, Venezuela, 1 = $-19+2.4$ mm, 2 = $-2.4+0.3$ mm, 3 = $-300+75$ μ m, 4 = -75 μ m.

The large amount of iron and the proportion of aluminium contained in the silicate minerals indicate that the material does not lend itself to conventional Bayer process aluminium extraction.

2.2 Ni-laterite from Loma de Hierro, Venezuela.

Origin of the material.

The material consisted of a sample of a nickel laterite deposit located at Loma de Hierro, Estado Miranda, Venezuela. (Figure 2.1).

Previous work on this deposit by Lavie (1967) deals mainly with a description of the deposit and the exploration work done to determine the extent and distribution of the valuable elements. This work was carried out by the Venezuelan Government and included the analysis of 8545 samples. The results indicate a total of 38.2 million tonnes of dry ore with an average nickel content of 1.52 percent.

Previously International Nickel Corp. held a concession on the deposit (from 1946 to 1960) but no information is available of the work done by this company.

The sample studied consisted of four bags containing a total of 6.7 kg of material. This material was supplied by the mining division of the Ministry of Mines and Hydrocarbons of the Venezuelan Government.

One bag containing 2.1 kg of material consisted of unaltered rock. Apart from selecting a small sample for the preparation of polished specimens, no further work was done on this unaltered rock material.

The rest of the sample consisted of lateritic material which was dry and had a brown earthy appearance. The contents of the bags with lateritic material were mixed and used for the appraisal procedure.

Appraisal procedure

The appraisal procedure is indicated schematically in flowsheet No. 2.2.

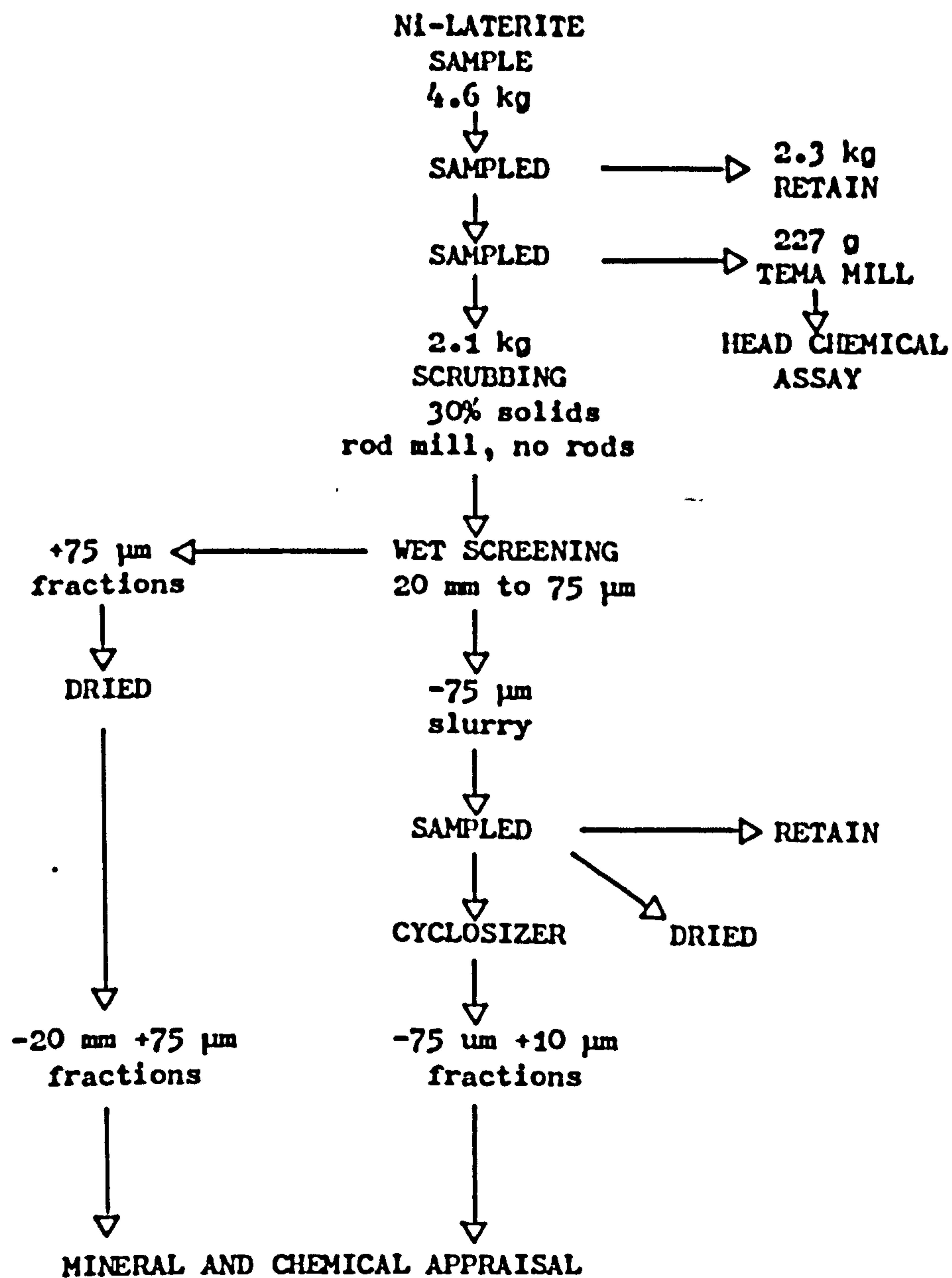
Wet scrubbing was done in order to disperse the fine particles attached to the mineral surfaces. It was accomplished in an 8 inch rod mill with no rods turning at 100 r.p.m. for $\frac{1}{2}$ hour. For scrubbing approximately 30% solids was used and no dispersant was added.

The scrubbed slurry was wet screened in British Standard screens from B.S.7 (2411 μm) to B.S. 200 (75 μm). The -75 μm slurry was allowed to settle and the clear water decanted. The thickened slurry was weighed and sampled by taking volumes of slurry during vigorous stirring. Two identical weights of slurry were taken, one was dried and weighed while the other was used for further sizing in the subsieve range with a Cyclosizer. This procedure allows the calculation of the percentages of each size fraction by subtraction without the need to dry the whole of the -75 μm slurry or to recover the Cyclosizer undersize.

Table 2.7 shows the results of the sizing operation and figure 2.8 shows the same results in a graph of cumulative percent finer as a function of particle size.

A representative sample of material was ground in a Tema mill for $\frac{1}{2}$ hour and used for chemical assay.

A semiquantitative scan for all elements by X-ray fluorescence and quantitative analysis for Fe, Ni, Cr and Al was supplied by Analytical Services, Imperial College. Additionally assays by Atomic Absorption spectrophotometry (AA) was made for the elements Fe, Ni, Co, Cr, Ti, Mg and Al.



Flowsheet No. 2.2

Schematic diagram showing the appraisal procedure followed with the Ni-laterite from Loma de Hierro, Venezuela.

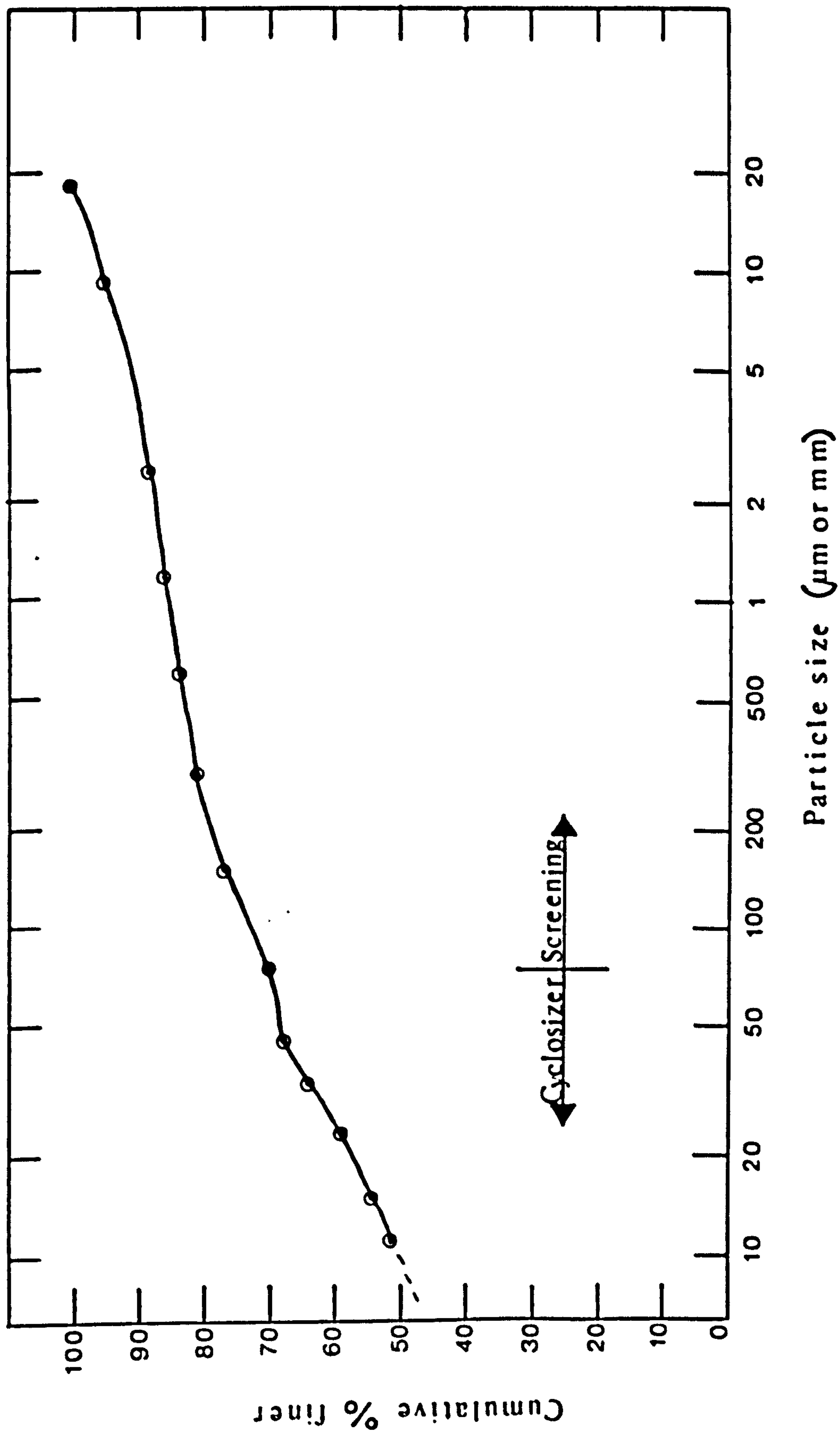


Figure 2.8 Particle size distribution of the nickel laterite from Loma de Hierro, Venezuela.

Table 2.7 Particle size distribution of the Ni-laterite from Loma de Hierro, Venezuela.

SIZE (mm or μm)	weight (g)	weight (%)	Cum. % Finer
-19 +9.5 mm	89.9	4.4	99.3
-9.5+2.4	154.7	7.5	94.9
-2.4+1.2	44.0	2.1	87.4
-1.2+ .6	50.4	2.4	85.3
- .6+ .3	52.4	2.5	82.9
- .3+150 μm	89.2	4.3	80.4
-150+75	141.8	6.8	76.1
- 75+44	46.2	2.2	69.3
- 44+33	73.2	3.5	67.1
- 33+23	111.4	5.4	63.6
- 23+15	97.9	4.7	58.2
- 15+11	58.5	2.8	53.5
- 11	1041.0	50.7	50.7

The AA assays were made by dissolving the material and assaying the solution by the usual method of comparing the absorption obtained with the absorption produced by standard solutions of the elements. The dissolution of the sample was achieved by attacking with concentrated HCl and evaporating to dryness several times. This treatment dissolved the majority of the material. The undissolved solids were recovered by filtering, dried and separated by panning into two pure mineral phases. These were identified by XRD as undissolved silica (amorphous) and a spinel-type mineral later recognised as chromite. This mineral was assayed by electron probe microanalysis and the results added to the previous chemical assay.

The results of all chemical assays are collected in Table 2.8.

Table 2.8 Chemical composition of the Ni-laterite from Loma de Hierro, Venezuela.

Element	% weight oxide	Analytical services a)	Lavie (1967) b)
Fe_2O_3	50.41	51.61	28.8
SiO_2	15.3	11.1	33.38
MgO	10.25	NA	19.40
NiO	2.30	2.33	2.11
Cr_2O_3	1.87	2.05	2.73
Al_2O_3	NA	6.21	2.91
CoO	0.24	NA	0.038
MnO_2	0.01	NA	NR
		-	-

a) Minor and trace elements reported are S, Cl, K, Ca, Ti, V, Cu, Zn, Sc.

b) Average reported by H. Lavie (1967) for "Area 1" of the deposit.

Mineral Appraisal

The sized fractions were examined by optical microscopy and samples of different minerals isolated by the use of magnetic separation and hand-picking under the microscope.

Extensive use was made of XRD on the hand-picked mineral grain samples as an aid in the identification of the minerals. Table 2.9 shows the results of XRD of different samples. A diffractometer was used in all cases and a mineral was considered identified when at least the 3 most intense lines were found.

Table 2.9 Results of X-ray diffraction of hand-picked grains from the Ni-laterite from Loma de Hierro, Venezuela

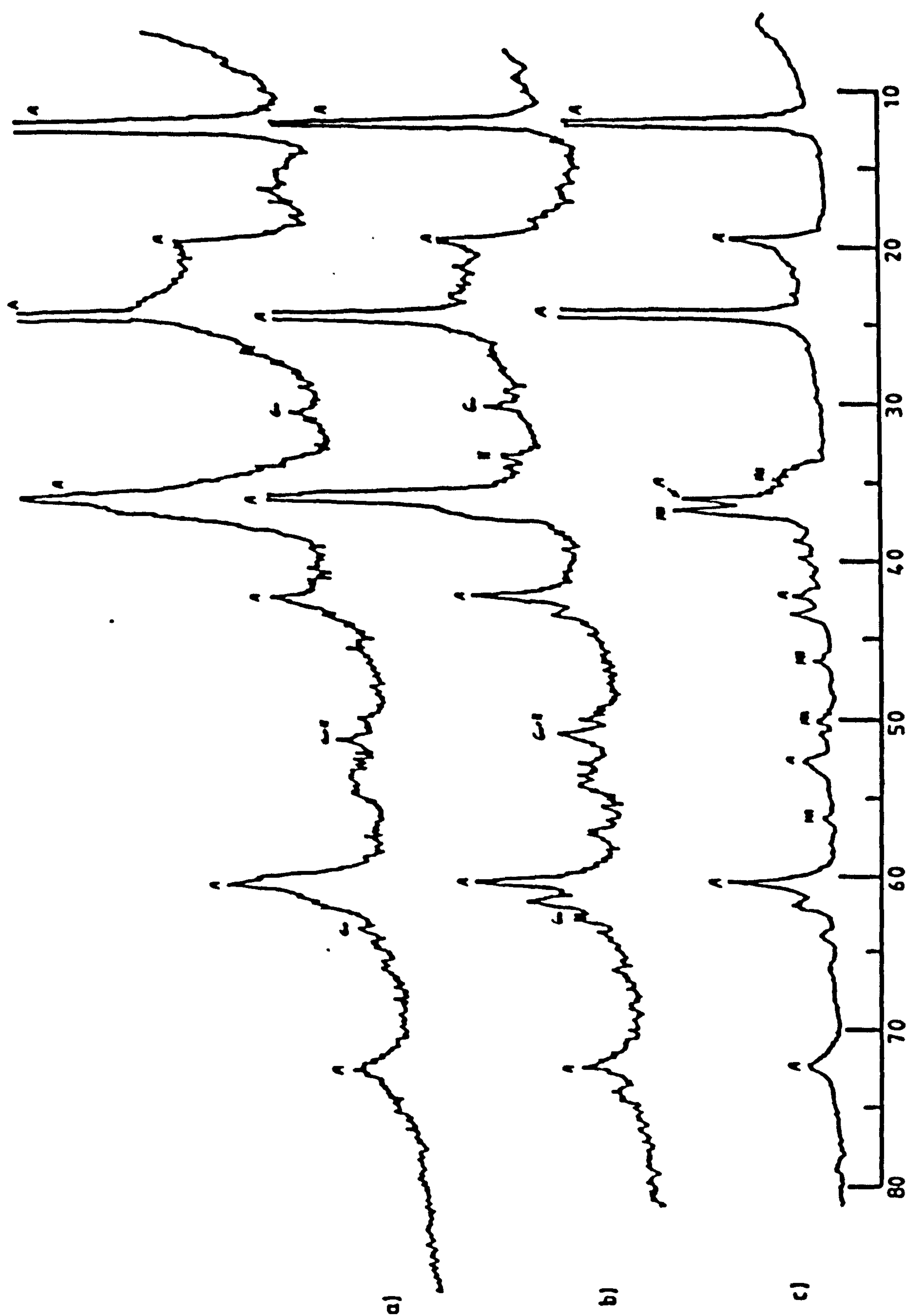
SAMPLE DESCRIPTION		MINERALS IDENTIFIED
Fe minerals	Black flaky (highly magnetic)*	Magnetite
	Black irregular (moderately magnetic)*	Spinel type (chromite)
	Composite dark brown*	Goethite, Hematite
	Composite light brown-yellow*	Goethite, Hematite
Garnierite	Green platy antigorite*	Ni-antigorite, traces Mg antigorite (highly crystalline)
	White tabular	Ni, Mg-antigorite (low crystallinity)
	White speckled yellow veins*	Ni Antigorite, Goethite, Hematite
	Mixed light coloured* (moderately magnetic)	Amorphous + Ni-Antigorite "Garnierite" pattern
	-200 mesh slimes*	Goethite, Hematite, Antigorite, Magnetite
	HCl leach solids*	Amorphous, Chromite

*XRD pattern shown

The following minerals were identified. Iron minerals: goethite, hematite, magnetite. Nickel minerals: Ni-antigorite. Others: Mg-antigorite, quartz, chromite.

Nickel minerals

Nickel antigorite and magnesium antigorite $(\text{Ni, Mg})_3 \text{Si}_2\text{O}_5 (\text{OH})_4$ occur in several different forms. They both vary in colour from light green, for pure well crystalline Ni-antigorite (XRD pattern c Fig. 2.9), which occurs as tabular grains, to white or cream colour for less crystalline nickel and magnesium antigorite. Brindley and Phan Thi Hang (1973) have established the existence of a linear relationship between



2 θ ANGLE

Figure 2.9 XRD patterns of nickel-bearing minerals from Loma de Hierro, Venezuela. Cu K α radiation.
a) light coloured, moderately magnetic. b) white speckled. c) green platy.
A = Ni-antigorite, MA = Mg-antigorite, C = chromite, H = hematite, M = magnetite.

the "greenishness" of garnierite minerals measured by the value of $(u-20) r/z$ and their NiO content. The variables u , r and z are parameters in the Munsell colour scheme where u = hue, r = chroma and z = lightness.

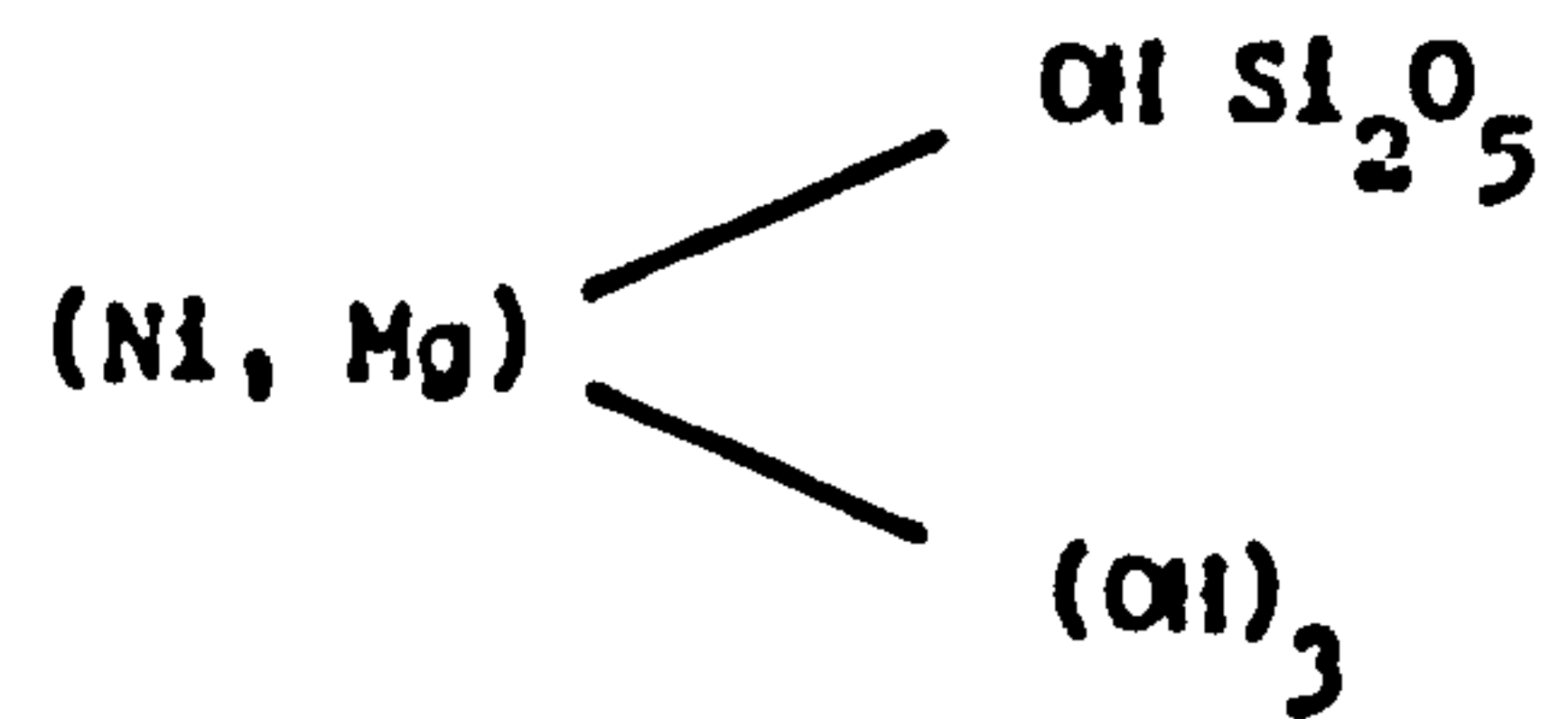
Light-coloured grains of antigorite with decreasing amounts of NiO as determined by colour estimation also show a decrease in the degree of crystallinity as measured by XRD (pattern b and pattern a, Fig. 2.9).

The XRD patterns shown in Figure 2.9 are very similar to some of those reported by Brindley and Phan Thi Hang (1973) and which they have named $7\text{\AA}$ garnierite, particularly pattern (a) which was produced by a mixture of light-coloured minerals.

Fully liberated grains of antigorite are found up to 3 or 4 mm in size, in the form of greenish white plates (exceptionally up to 15 mm), but magnetic separation shows a large percentage of, apparently liberated, antigorite reporting in the highly or moderately magnetic fractions. This is due to the presence of very fine particles of magnetite or veins of iron minerals trapped in the antigorite grains. In some cases the magnetic behaviour is due to surface coatings of iron minerals over the antigorite mineral surface. Magnetic susceptibility tests on predominantly antigorite grains showed that they contained iron minerals in very small particles and that true liberation is not significantly achieved even in 75 μm particle size.

Based on the head chemical assay a ratio of Ni to Mg antigorite was established as: Ni/Mg antigorite = 0.30 i.e.: 30% of the overall antigorite is probably Ni-antigorite.

Antigorite has the general formula



According to Martin, et al. (1967) the structure of Ni antigorite is derived from that of the hydroxide in which certain of the (OH) are substituted by SiO_4 tetrahedra.

Magnesium and nickel substitute isomorphically in the structure of antigorite due to their similar ionic radii ($\text{Ni}^{2+} = 0.69 \text{ \AA}$, $\text{Mg}^{2+} = 0.69 \text{ \AA}$) and the practical consequence is the existence of a continuous compositional series from pure Ni antigorite at one end to pure Mg antigorite at the other. This fact makes it very difficult to differentiate between members in the series or to affect a separation.

Iron minerals

The main iron-bearing mineral is goethite which is easy to recognise in grain samples. Under the microscope the goethite grains appear as brown to yellow grains or as yellow coatings on the surface of other minerals. Goethite grains from relatively coarse fractions are really just agglomerates of very fine particles. They frequently contain inclusions of other minerals such as magnetite or hematite and these are responsible for the fact that magnetic separation results in a large percent of goethite reporting either as highly magnetic or moderately magnetic.

In figure 2.10, XRD patterns c) and b) are of apparently liberated grains of goethite with slightly different colour. The XRD method shows them to be composite grains containing hematite and chromite in addition to goethite. The more reddish or darker brown grains contain greater amounts of hematite and chromite.

XRD pattern a) in figure 2.10 made of a sample of -75 μm material shows goethite as the main mineral in the fine fractions.

The other Fe-bearing minerals are hematite and magnetite. Visually it is not easy to distinguish these minerals from each other in grain samples due to the advance alteration that they show. Magnetite occurs either as very small inclusions in other phases, notably in antigorite, or in the form of plates or scales which are highly magnetic. An examination of these highly magnetic grains show that they are very soft (<3) and slowly soluble in HCl. The XRD pattern of these platy grains shows very clearly the presence of well crystalline magnetite (figure 2.11 pattern c)). The observations suggest that these grains are composed of an XRD-amorphous phase which contains magnetite as inclusions. Visual examination shows this form of "magnetite" to be present in all the size fractions.

Hematite is also present in all the size fractions. It occurs as a dark mineral with varying degrees of alteration which makes it very difficult to identify visually in grain samples from the other dark minerals (magnetite and chromite). In very fine fractions under transmitted light hematite can be identified by a dull red colour while goethite grains are light yellow and other minerals appear opaque. Hematite was clearly identified in several XRD patterns made from dark coloured minerals (Figure 2.10 and 2.11).

Other minerals

The only other mineral phases found, apart from the nickel and iron minerals already discussed, are quartz and a spinel-type mineral identified as chromite.

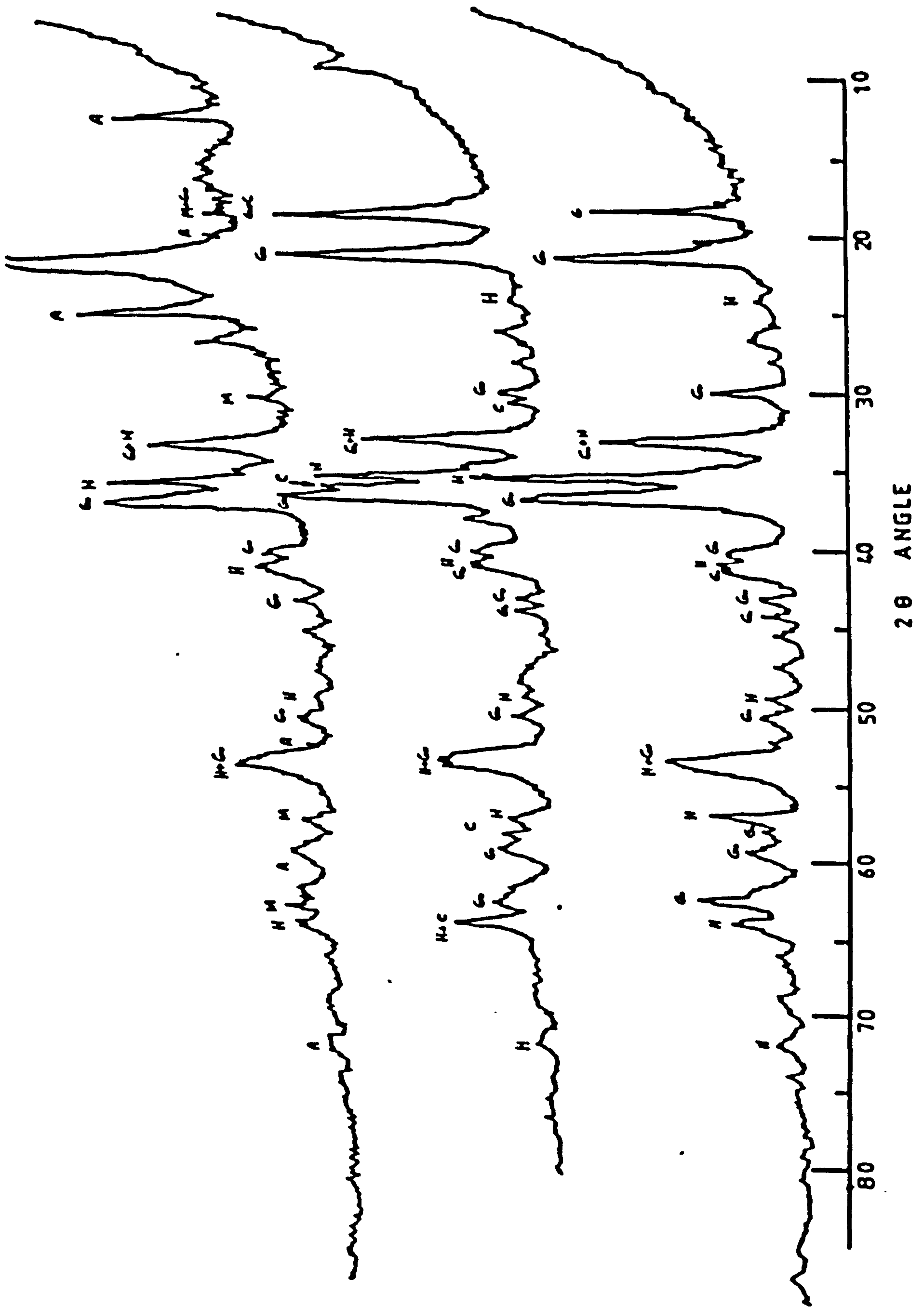


Figure 2.10 XRD patterns of iron-bearing minerals from Loma de Hierro, Venezuela. Cu K α radiation.
a) -75 μ m, b) composite dark brown, c) composite light brown. Symbols as in Figure 2.9.

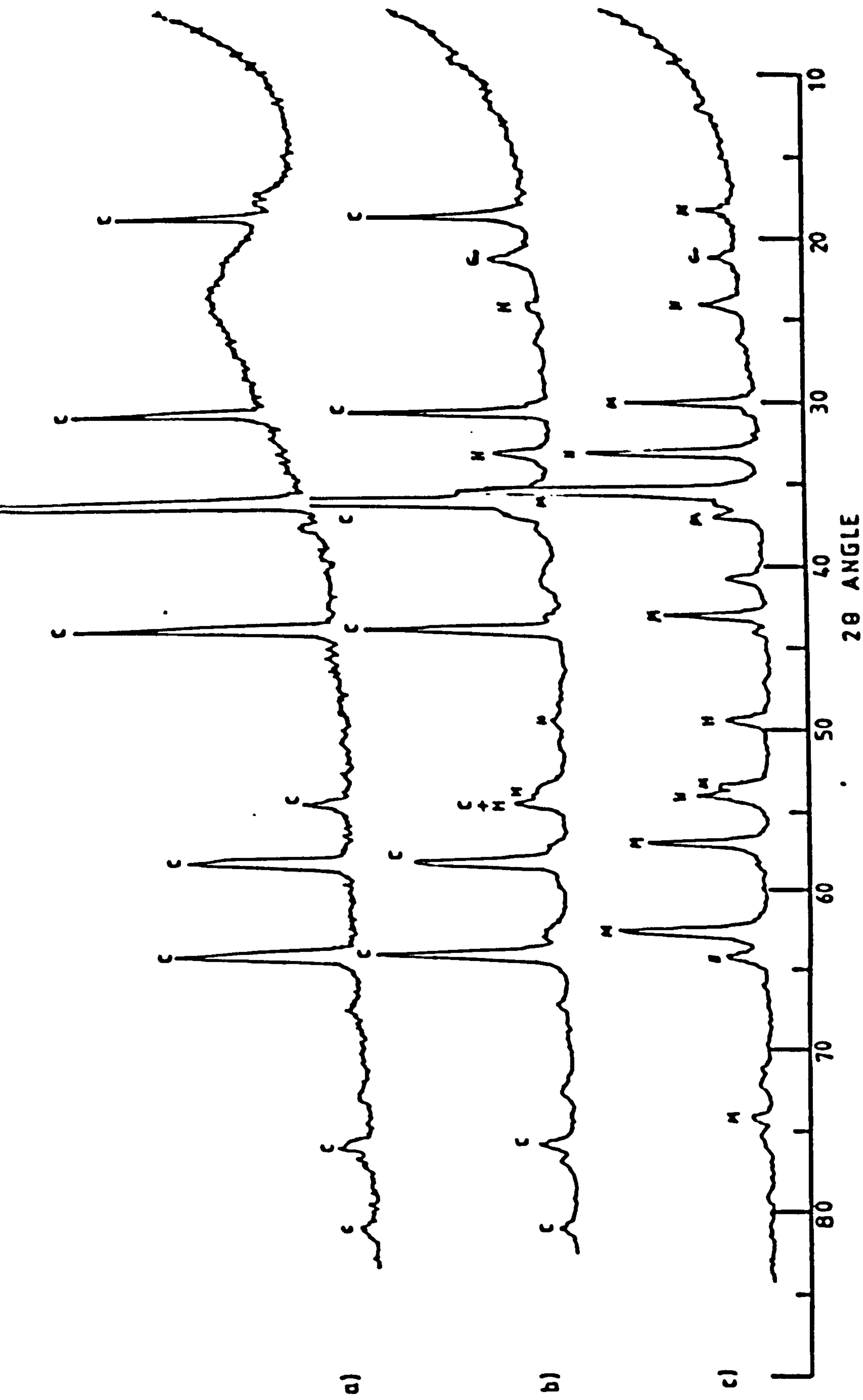


Figure 2.11 XRD patterns of spinel-type minerals from Loma de Hierro, Venezuela. Cu K α radiation.

Symbols as in Figure 2.9. a) HCl leach solids, b) Black moderately magnetic, c) Flaky highly magnetic

Chemical distribution

Chemical assays by atomic absorption were carried out on the different size fractions in order to establish the distribution of the valuable elements. All the size fractions were assayed by grouping into four fractions and taking representative samples. These fractions were dissolved and assayed in the same manner as the overall chemical assay. The results are shown in Table 2.11 and figure 2.12.

Analysis of the figures shows that, although there seems to be an increase in the grade of nickel in the coarse fraction and of cobalt in the middle range fractions, the bulk of the metal values are contained in the $-75\ \mu\text{m}$ fraction.

The results of the mineral and chemical appraisal indicates that the laterite sample studied conforms to what is described in the literature as a "garnieritic" laterite. (Brindley 1978; Kühnel et al. 1978) This is due to the high proportion of Ni and Mg silicates where the bulk of the nickel is contained.

The results of the work carried out indicate that the sample of material studied cannot be effectively treated by physical means for the recovery of the nickel, chromium and cobalt contained. This is due to the continuous solid solution of the Ni and Mg silicates, the large proportion of the valuable elements contained in the fine fractions and the intimate associations and advanced state of alteration of the minerals present in the material.

Very little quartz is present. Only a few grains of clear quartz are found among the non-magnetic fractions. By grain counting it was estimated that quartz accounts for less than 0.5% of the material.

Chromite was found in the moderately magnetic fractions and among the solids left after HCl attack. Figure 2.11 pattern A) shows the results of XRD of the solids left after HCl treatment of the -2.4 +0.3 mm size fraction. All the peaks in this pattern were identified as belonging to a spinel-type phase. The background signal in this pattern is due to amorphous silica left after the breakup of the antigorite structure by the acid treatment.

A very similar spinel-type mineral was found in the study of the nickel laterite from Guatemala. Further discussion of these minerals is presented in Section 2.3 and 5.4.

Based on the information obtained in the mineralogical appraisal and on the results of chemical analysis an overall mineral composition of the laterite was calculated. Table 2.10 shows the results.

Table 2.10 Approximate mineral composition of the Ni-laterite from Loma de Hierro, Venezuela.

Mineral	Proportion %
Fe oxides: goethite, hematite and magnetite	56
Mg-Antigorite	23
Ni-Antigorite	4
Chromite	2
Hydrated Al silicates and clays	13
Quartz	0.5

Table 2.11 Grade and distribution of various elements in the size fractions of the nickel laterite from Loma de Hierro, Venezuela.

size (mm or μm)	weight (%)	GRADE %				DISTRIBUTION %					
		Ni	Cr	Mg	Co	Fe	Ni	Cr	Mg	Co	Fe
- 19+2.4mm	12.0	4.5	.23	19.1	.06	8.1	18.8	5.4	41.3	3.9	2.8
-2.4+0.3	7.2	1.4	.26	8.2	.34	21.3	6.3	3.6	10.6	13.5	4.5
-300+75 μm	11.2	1.4	.34	7.8	.43	37.5	9.9	7.4	15.7	26.6	12.4
- 75 μm	69.6	1.5	.61	2.6	.14	38.7	65.0	83.6	32.4	57.0	80.
Calculated		1.56	0.51	5.54	0.18	33.6					
Measured		1.8	0.64	6.0	0.15	35.0					

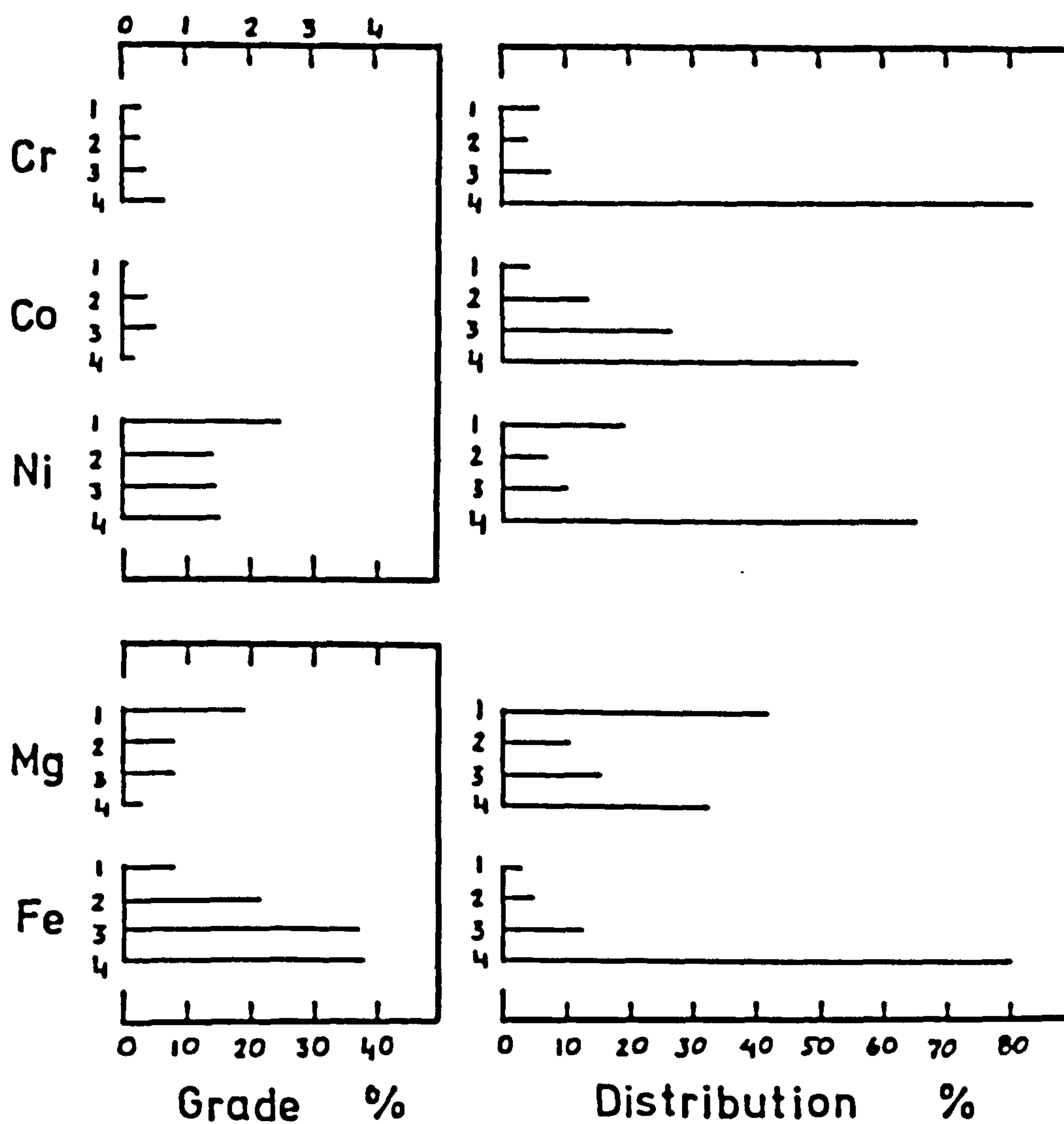


Figure 2.12 Diagram showing the grade and distribution of the main elements in the particle size fractions of the laterite from Loma de Hierro, Venezuela.
 1 = $-19+2.4$ mm, 2 = $-2.4+0.3$ mm, 3 = $-300+75$ μ m,
 4 = -75 μ m.

2.3 Nickel laterite from Guatemala.

Origin of material

The material used for this study consisted of two bags with a total weight of 4 kg. The origin of this material is uncertain. It was supplied by courtesy of Charter Consolidated, as a sample of nickel laterite from Guatemala.

The material as received was contained in sealed plastic bags each about 2 kg and identified as follows:

P41 -10D (1910 g of material)

P41 - 6B (2058 g of material)

Appraisal procedure

The material as received was very wet, almost muddy, of yellowish brown colour with the characteristic smell and appearance of humic dark brown earth.

The contents of both bags were mixed thoroughly and lumps broken by hand to pass a B.S. 18 screen (0.853 mm). One half of the material was used for mineral appraisal. The appraisal procedure is shown in flowsheet No. 2.3.

The 2 kg of material used for appraisal was sampled and split into three fractions: one was used for moisture content determination, one for chemical assay and one for sizing.

The sample used for moisture content determination was first dried in an oven at 110°C for a period of 24 hours. This showed a loss of weight of 39.8%. Part of the material dried at 110°C was heated in a crucible for 20 minutes under a Bunsen burner (dull red). This process produced a further weight reduction of 14.4%. These results are summarised as follows:

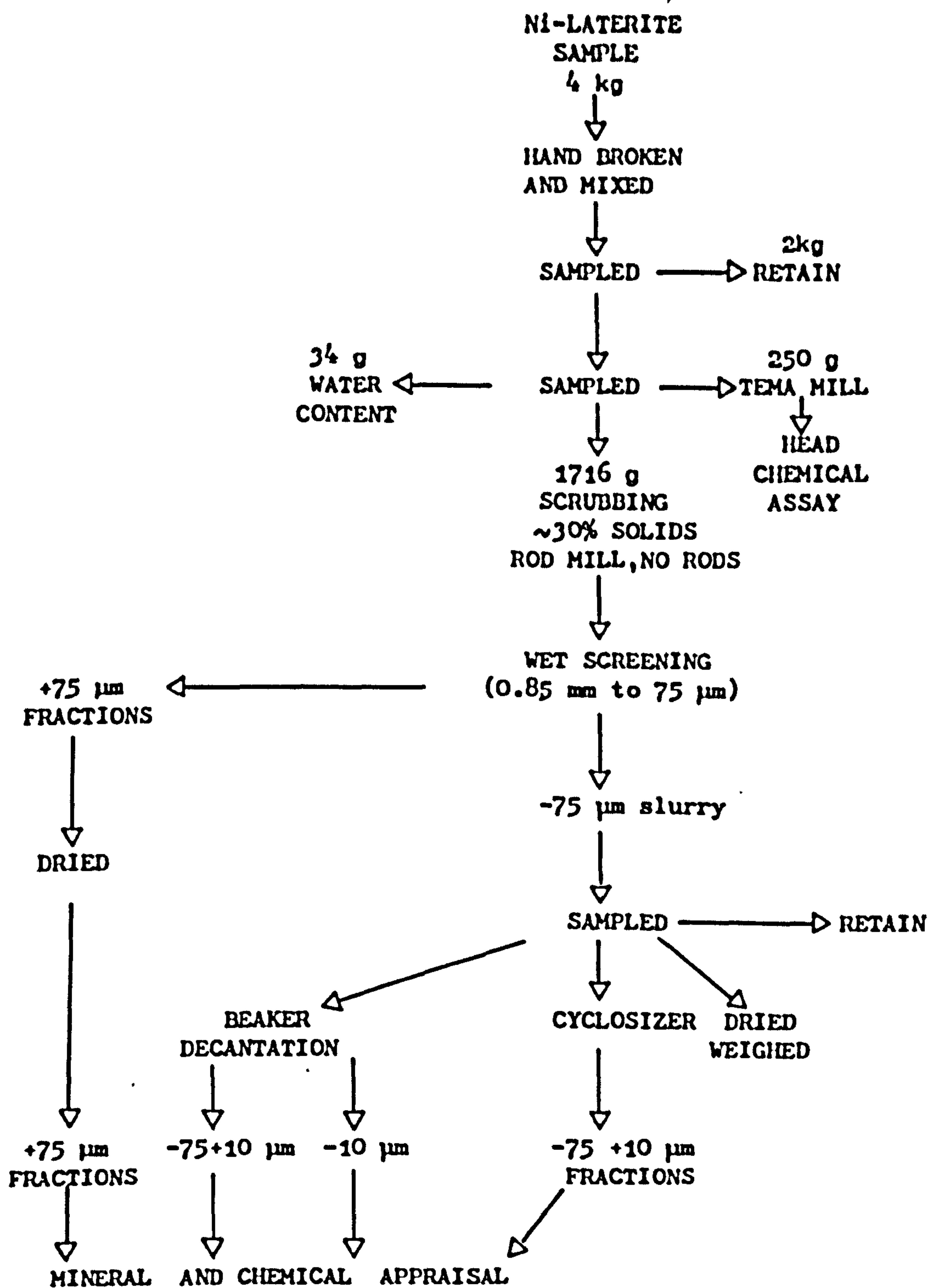
loss of weight at 110°C -	39.8
loss of weight at approx. 700°C	<u>14.4</u>
Total	54.2

It was considered that the 14.4% loss at 700°C was structural water, hence for the purpose of calculating the actual amount of material which was used for scrubbing and screening a moisture content of 39.8% was assumed and subtracted from the measured weights of humid material.

250 g of material was sampled for chemical assay. This material was dried in an oven at 110°C and then ground in a Tema mill for $\frac{1}{2}$ hour. A semiquantitative XRF scan for all elements and quantitative analysis for Fe, Ni, Cr, Mn and Si was supplied by Analytical Services, Imperial College. Additional chemical assays by Atomic Absorption Spectrophotometry (AA) were done for the elements Fe, Ni, Cr, Co, Mg, Al and Ti.

The AA assays were made by dissolving the material with hot concentrated HCl and evaporating to dryness several times. The solids left were recovered by filtration and found to contain amorphous silica and a dark mineral identified as chromite. These solids were treated in an identical manner to the ones found in the assay of the Ni-laterite from Venezuela. The solutions at appropriate dilutions were aspirated and the absorption compared with standards in the usual manner. The results of the chemical assays are shown in Table 2.12.

The material intended for screening was first scrubbed for a period of half an hour in an 8 inch rod mill without rods turning at 100 r.p.m. with a pulp density of approximately 30% solids. No dispersant was used.



Flowsheet No. 2.3 Schematic diagram showing the appraisal procedure followed with the Ni-laterite from Guatemala.

Table 2.12 Results of the chemical assay of the Ni-laterite from Guatemala.

Element	% weight	Analytical services a)
Fe_2O_3	69.6	68.0
NiO	1.7	1.4
Cr_2O_3	2.1	2.1
MnO_2	1.4	1.2
CoO	0.19	NA
SiO_2	3.95	1.86

a) Other elements reported in the XRF scan:
0.5-5%: Mg Al and K; trace: S, Zn, Ca and Ti

Screening was carried out wet in British Standard screens from B.S. 18 mesh (0.85 mm) to B.S. 200 mesh ($-75\ \mu\text{m}$). The screen fractions were dried at 110°C and weighed. The $-75\ \mu\text{m}$ slurry was thickened and several identical samples taken while stirring vigorously with a mechanical stirrer. One slurry sample was dried at 110°C and weighed. Another was used for sizing with a Cyclosizer down to $10\ \mu\text{m}$ size. In this process the $-10\ \mu\text{m}$ fraction is lost in the Cyclosizer overflow. Hence, in order to recover this $-10\ \mu\text{m}$ fraction a beaker decantation was carried out on another sample of $-75\ \mu\text{m}$ slurry.

The results of the sizing operation are shown in Table 2.13 and figure 2.13. The result of the sizing shows that 90% of the material is below $75\ \mu\text{m}$ size and 70% is below $10\ \mu\text{m}$; hence the importance of recovering a sample of the $-10\ \mu\text{m}$ fraction for mineral and chemical appraisal.

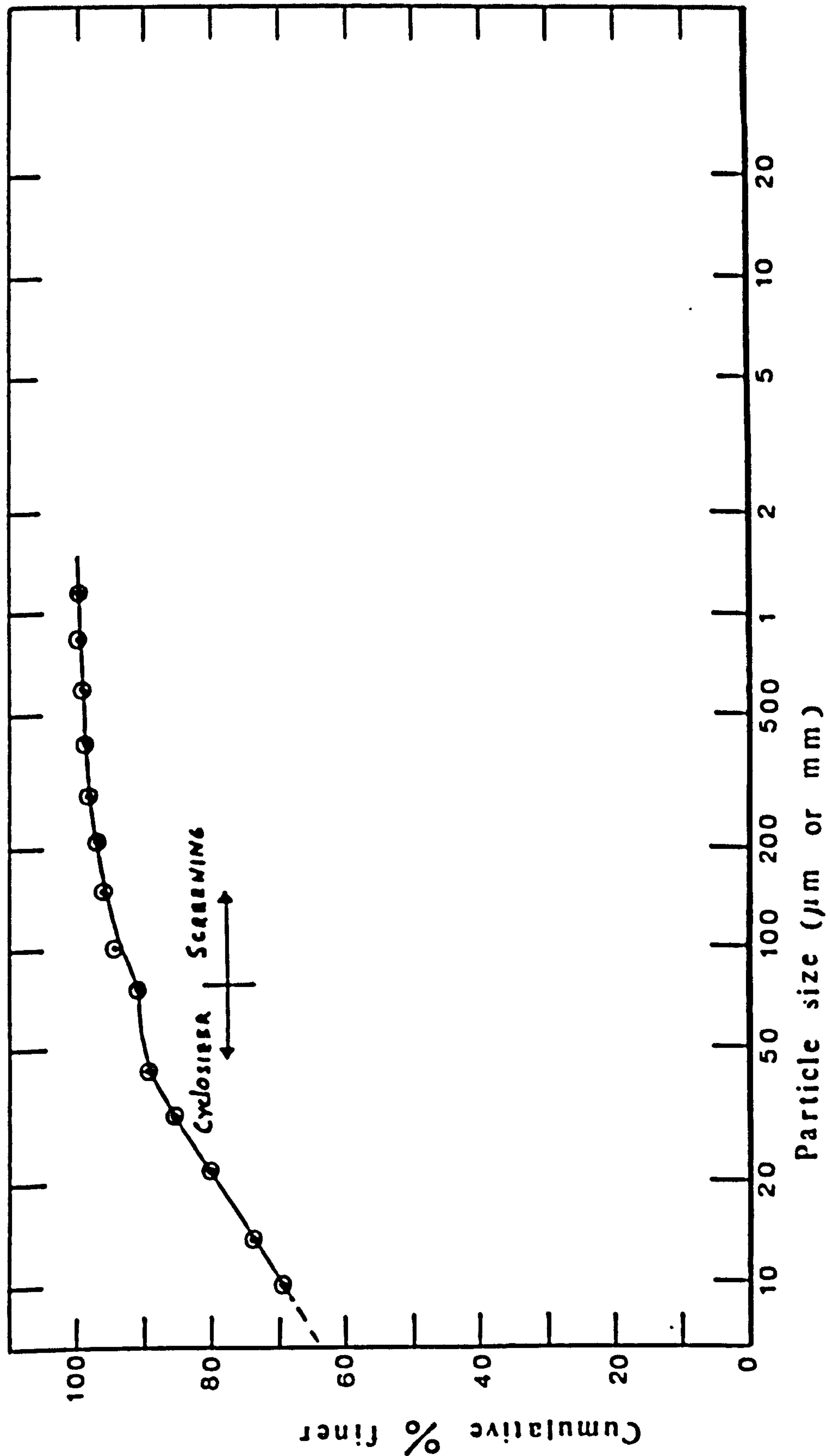


Figure 2.13 Particle size distribution of the nickel laterite from Guatemala.

Table 2.13 Particle size distribution of the Ni-laterite from Guatemala.

Size (μm)	Weight (g)	% Weight	Cumulative % finer
+850	4.28	.36	100.0
-850+590	2.95	.24	99.64
-590+420	5.84	.49	99.39
-420+290	6.06	.51	98.90
-290+210	9.73	.82	98.39
-210+150	13.72	1.15	97.57
-150+100	25.24	2.12	96.41
-100+ 76	29.77	2.51	94.28
- 76+ 43	30.68	2.58	91.77
- 43+ 32	38.74	3.26	89.18
- 32+ 22	67.36	5.68	85.92
- 22+ 14	77.70	6.55	80.24
- 14+ 10	53.76	4.53	73.69
- 10	820.14	69.15	69.15

Mineral appraisal

The large proportion of fine material in the laterite sample from Guatemala made the mineral appraisal difficult. Optical examination, that could be done with reasonable ease, is possible on only 30% of the material namely the +10 μm fraction.

Optical examination of the coarser size fractions shows that the material consists mostly of iron-bearing minerals in an advanced state of alteration that makes mineral recognition quite difficult.

In spite of the scrubbing that the mineral was subjected to, goethite in the form of yellow slime size particles, is very often found to fill the crevices or surface irregularities of most minerals.

Attempts were made to produce mineral separations by standard laboratory techniques without great success. It was found that all of the material in the coarser sizes is either highly magnetic or moderately magnetic. The nature of the material is such that practically no optical difference exists between these magnetic fractions in the coarser sizes. This is generally due to the inclusion of very fine magnetic grains in the fractions above about 40 μm . Below 40 μm there is a predominance of light yellow goethite in the less magnetic fractions, while there is a predominance of magnetite, hematite and dark coloured minerals in the more magnetic fractions.

Due to these difficulties it was necessary to rely heavily on the results of XRD for mineral identification. XRD patterns were obtained of a large number of samples taken from the different fractions. Unfortunately the XRD method is not suitable for detecting very poorly crystalline or amorphous material or minerals which occur in small proportions (less than about 5%).

Table 2.14 shows the results of the XRD analysis of different mineral fractions. It also indicates the relative proportions of the different minerals in each fraction. These proportions were derived from the relative amplitude of the most intense peaks in the pattern of each of the minerals of the given sample. Although the relative amplitude of the patterns are an indication of the relative proportions of the minerals they can not be used for quantitative purposes without first doing a series of calibrations. These calibrations are necessary because various factors such as the crystallinity of the mineral, the atomic weight of the constituent atoms and the X-ray absorption of the

Table 2.1⁴ Results of XRD on different mineral fractions of the Ni-laterite from Guatemala. The proportions indicated are estimates derived from diffraction intensities and are only very approximate (see text).

Size Fraction μm	Minerals identified in the			
	Highly magnetic %		Less magnetic %	
-420+300	Magnetite	100	Lithiophorite	70
			Goethite	25
			Magnetite	5
-100+ 76	Magnetite	70	Chromite	35
	Chromite	15	Goethite	30
	Goethite	15	Lithiophorite	20
			Hematite	15
- 43+ 32	Magnetite	70	Goethite	45
	Chromite	20	Chromite	30
	Goethite	10	Lithiophorite	15
			Hematite	10
- 14+ 10	Chromite	90	Goethite	100
	Goethite	10		
-10 μm		Goethite	65	
		Hematite	20	
		Quartz	10	
		Magnetite	5	
HCl leach residue		Magnetite	-	} 100
		Quartz	-	
		Amorphous silica	-	
HF leach residue		Chromite	100	

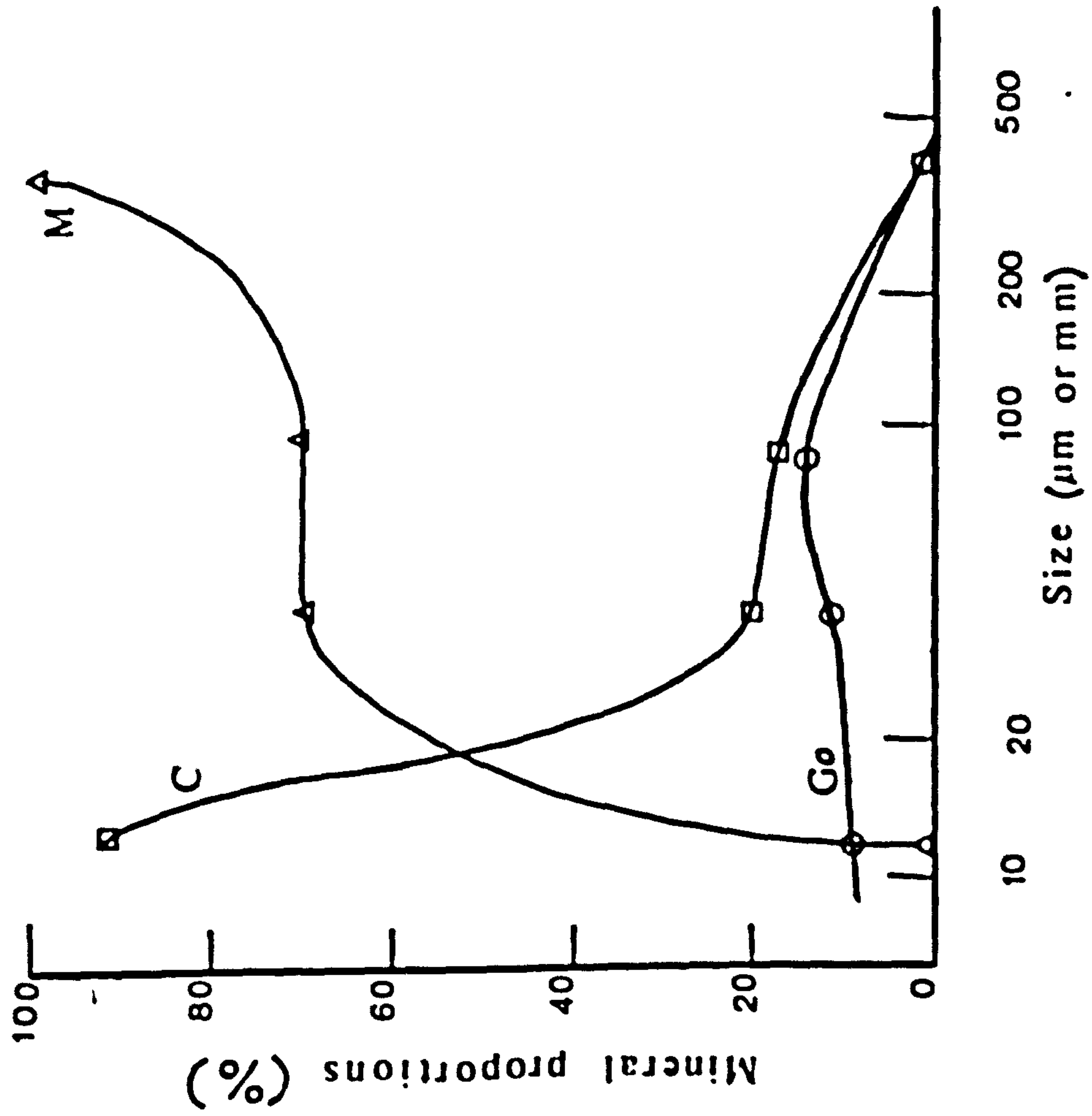
other minerals may enhance or diminish the relative intensity of the X-ray reflections. Calibrations for the XRD peak intensity in order to quantitatively determine mineral proportions require samples of pure minerals and these were not available. For this reason the method was not attempted.

The data in Table 2.14 have been plotted as a graph (figure 2.14) showing the approximate mineral proportions in the magnetic fractions as a function of size. It must be stressed that the numerical values in Table 2.14 are only very rough estimates of mineral proportions and do not show any phase that may exist in small quantities or any poorly crystalline or amorphous component that may be present.

The mineral phases that were clearly identified are goethite, hematite, magnetite, chromite and lithiophorite. No nickel minerals were found in spite of the fact that the chemical analysis showed the presence of over one percent of nickel by weight in the material. This result, in conjunction with the chemical distribution, suggests that the valuable elements Ni, Cr and Co are contained in the iron-bearing minerals.

In all patterns where goethite was identified the peaks were found to be extremely broad (figure 2.15 and 2.16). Some of these patterns were found to resemble the XRD patterns of poorly crystalline synthetic goethite prepared by ageing ferric hydroxide. The broadening of the peaks was interpreted as due not only to the average small particle size but also to a poor degree of crystallinity. It is possible that the poor crystallinity is due to the presence of Ni and other elements in the structure of goethite as is suggested in the work of Nalovic and Pinta (1972a).

Highly magnetic



Less magnetic

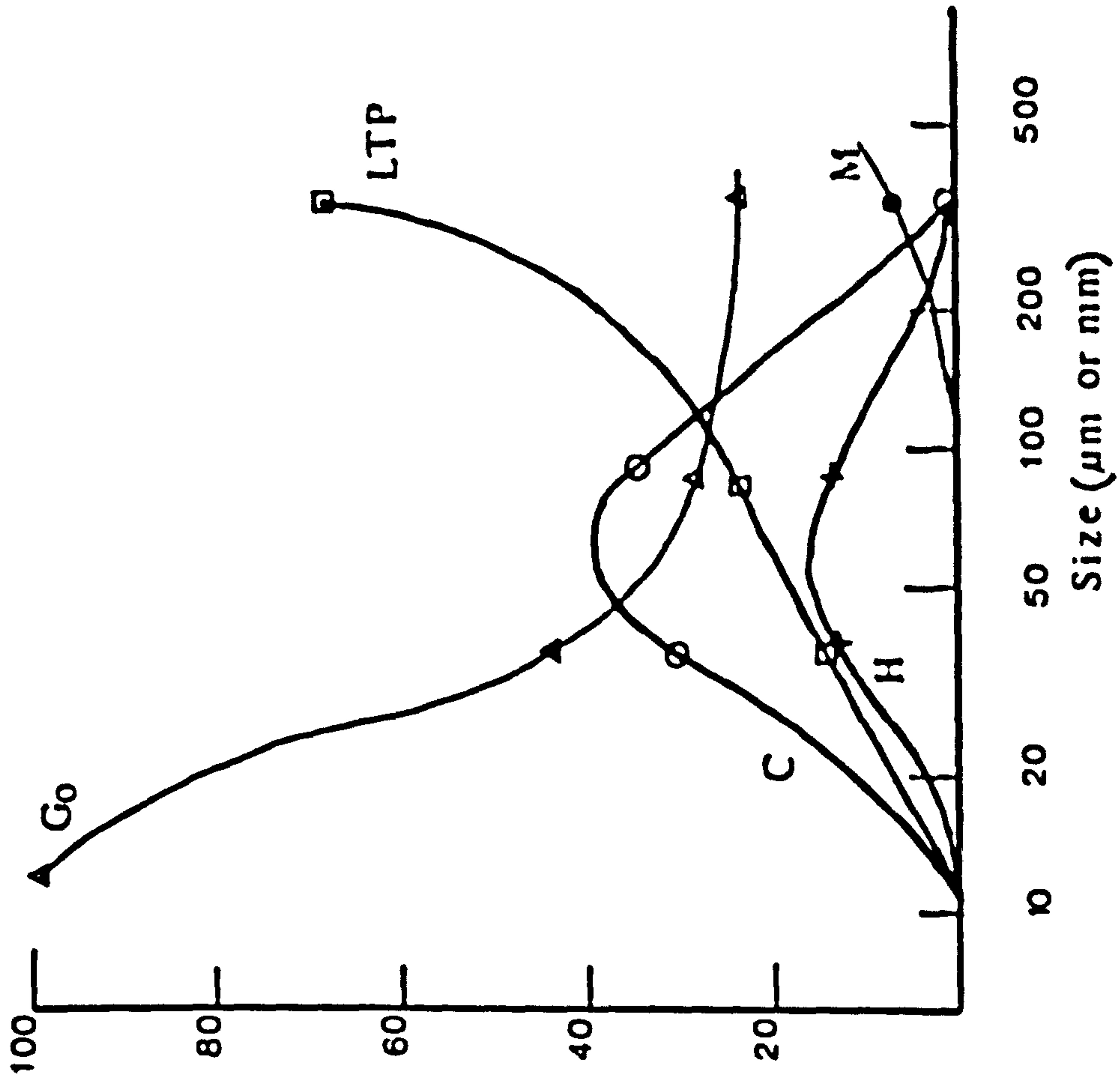


Figure 2.14 Approximate mineral proportions in the magnetic fractions of the laterite from Guatemala. Symbols as in Figure 2.15.

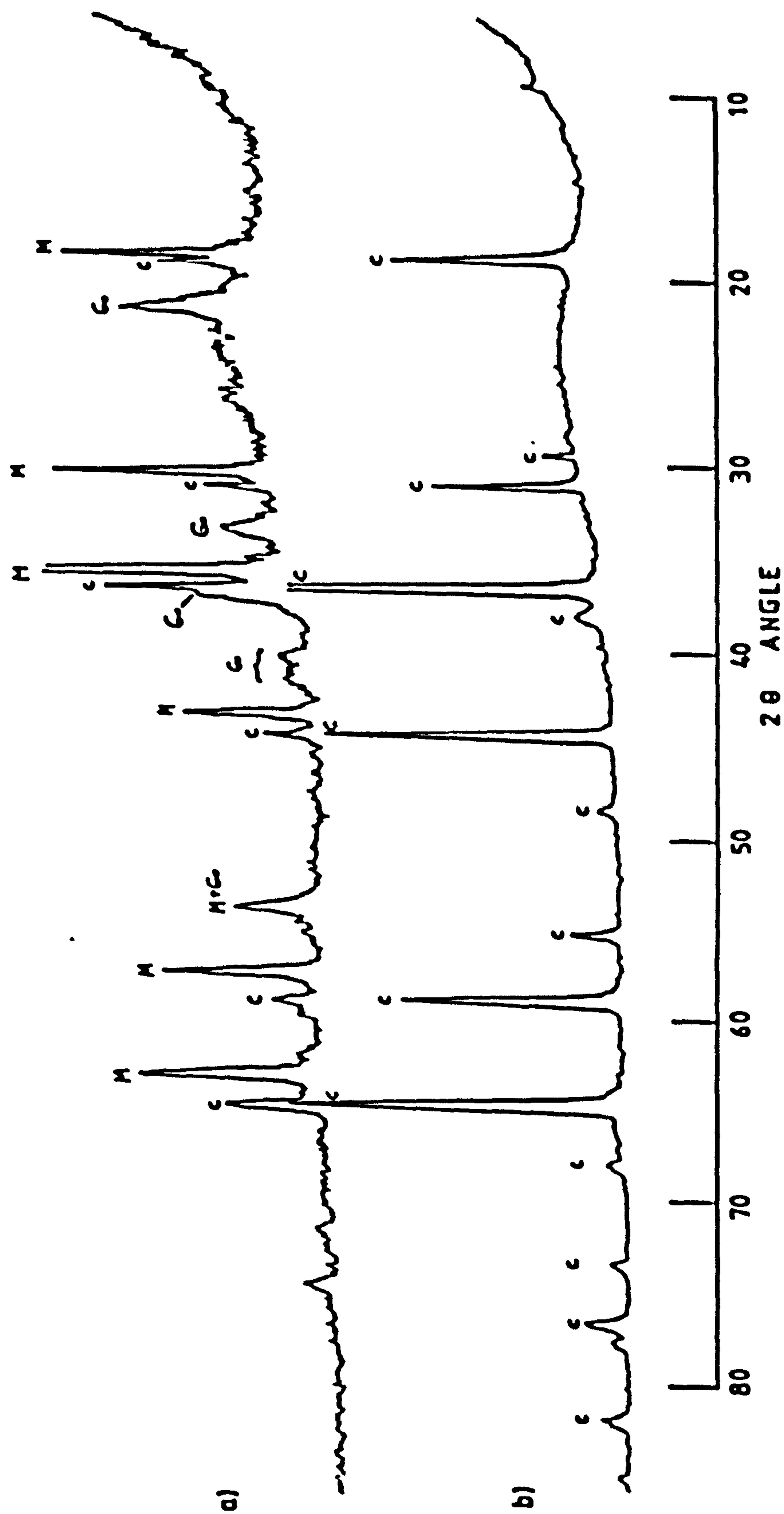


Figure 2.15 XRD patterns of mineral from the laterite from Guatemala. Cu K α radiation.

a) Highly magnetic b) Hydrochloric acid leach residue.

M = magnetite, Co = goethite, C = chromite, H = hematite,
LTP = lithiophorite, Q = quartz.

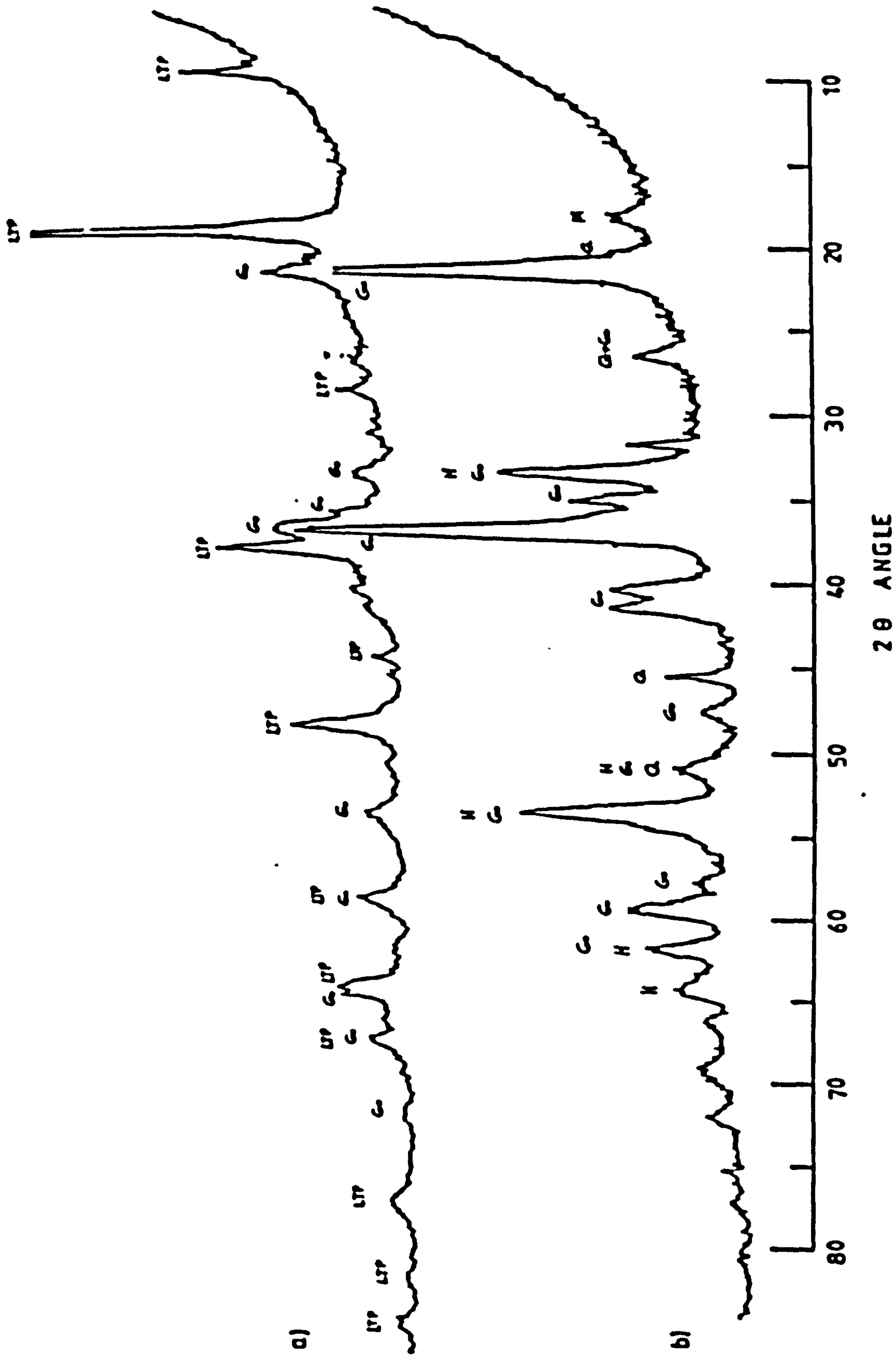


Figure 2.16 XRD patterns of minerals from the laterite from Guatemala. Cu K α radiation.
a) Moderately magnetic, b) -10 μ m material. Symbols as in Figure 2.15.

The XRD results showed the presence of two distinct spinel-type mineral phases in the laterite. One of them closely resembles the pattern of magnetite and has been identified in Table 2.1⁴ and elsewhere as magnetite. The diffractometer patterns were sufficiently good to make accurate measurements of the interplanar spacings. It was found that the measured d-spacings of the different samples agree closely with each other but had a significant disagreement with the ASTM values reported for stoichiometric magnetite. These results may be due to the presence of substitutional impurities in the structure of the magnetite in this material.

The other spinel-type mineral found in the XRD patterns was identified as chromite. This mineral has been found to be relatively inert to chemical attack. It is very slowly soluble or insoluble in hot concentrated HCl (it accounts for the majority of the residue after 24 hours of attack by hot concentrated HCl) and is very slowly soluble in hot 40% HF acid or a mixture of HF and HNO₃ acids.

Further work on these phases was carried out using Mössbauer spectroscopy. The results of those experiments are presented in Section 5.4.

Chemical distribution

Chemical analysis were carried out on several size fractions in order to establish the distribution of the main elements in the material. All the material was divided into four size fractions. Since a very large percentage of the material is of very fine size, the size fractions for assay could not be chosen to have even approximately equal weights.

The analysis was done by AA for the elements Fe, Ni, Co, Cr and Mn.

Difficulties were encountered in dissolving the coarse fractions because of the larger proportion of chemically resistant minerals in these fractions. It was found that a melt of potassium bisulphate followed by a treatment with HCl renders all, but a small silicate residue, soluble. This method of dissolution was adopted in the assay of the size fractions.

The dissolution method consisted of mixing 100 mg of material with 1 to 1.5 g of KHSO_4 . The mixture was heated in a platinum crucible (gently at first to avoid loss of material due to excessive boiling). A clear melt is usually obtained at high temperature (bright red). The crucible is allowed to cool and the light green solid dissolved in distilled water with gentle heating. Three ml of concentrated HCl are added at this stage and the solution made up to 100 ml. The solutions, or convenient dilutions, were aspirated and the absorption compared to that of standards to which proportional amounts of bisulphate had been added.

Table 2.15 shows the result of the assays and the calculated distribution of the elements in the size fractions. This information is shown graphically in figure 2.17.

The results show that there is a significant increase in the proportion of the elements Ni, Cr, Co and Mn in the coarse fractions. This suggests an easy means of upgrading the material by sizing. Unfortunately examination of the proportion of the total of each element in the size fractions (distribution in Table 2.15) shows that a very large percentage of the valuable elements are contained in the fine fractions and hence upgrading can only be done by this method at the cost of very poor recovery.

Table 2.15 Grade and distribution of various elements in the size fractions of the nickel laterite from Guatemala.

size (mm or μm)	weight (%)	GRADE %				DISTRIBUTION %				
		Ni	Cr	Mn	Co	Fe	Ni	Cr	Mn	Co
+300	1.61	4.4	6.7	5.8	1.0	28.2	5.8	7.7	11.7	13.3
-300+75	6.62	2.3	3.8	4.5	0.7	40.0	12.5	18.1	36.8	35.1
- 75+10	22.62	1.4	2.2	0.8	0.15	51.7	25.6	35.8	21.2	26.4
-10	69.15	1.0	0.8	0.3	0.05	46.5	56.1	38.4	30.3	25.2
Calculated		1.22	1.39	0.79	0.12	46.9				
Measured (AA)		1.31	1.59	0.86	0.16	49.0				

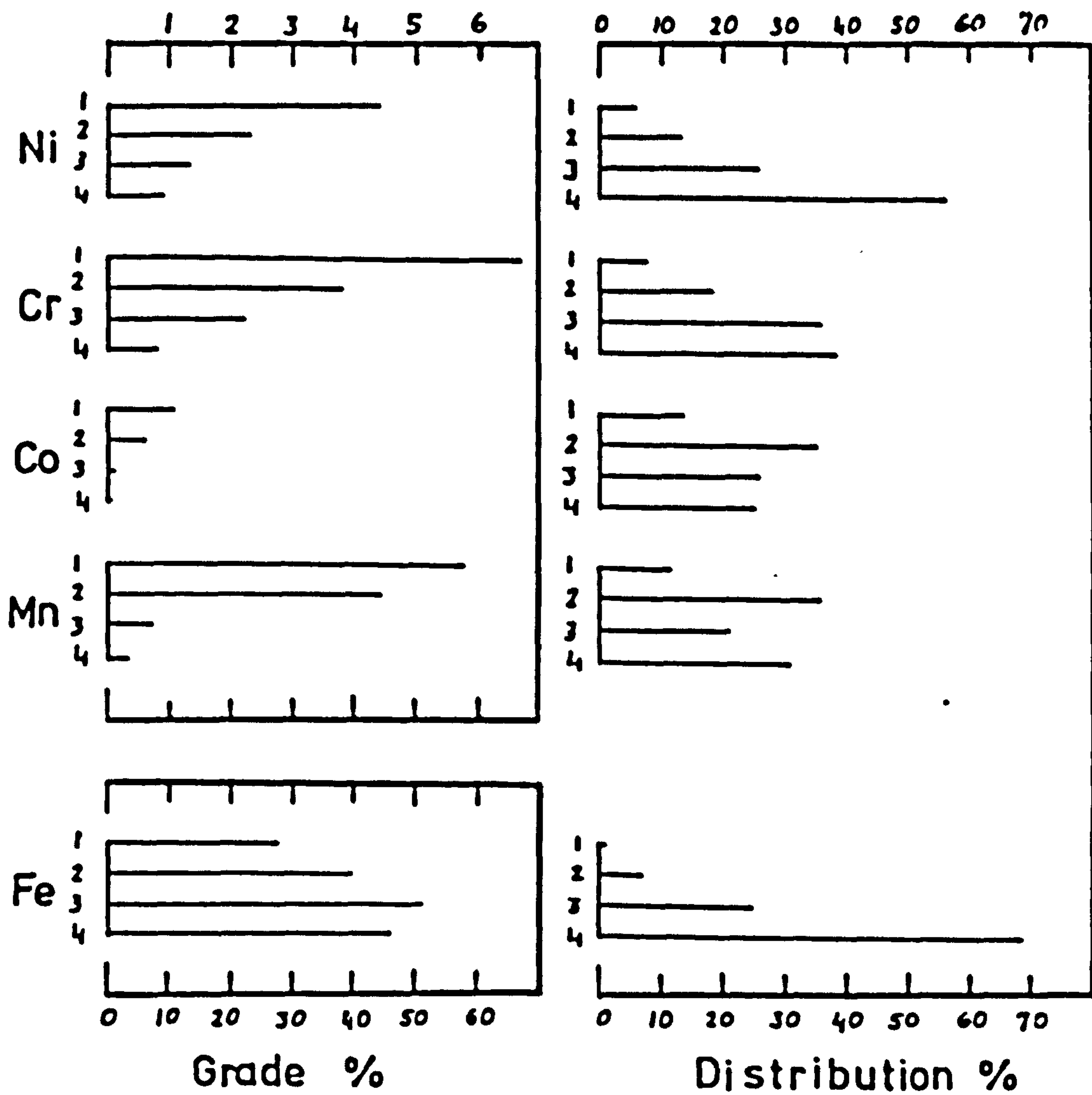


Figure 2.17 Diagram showing the grade and distribution of the main elements in the particle size fractions of the nickel laterite from Guatemala 1 = +300 μm , 2 = -300 +75 μm , 3 = -75 +10 μm , 4 = -10 μm

An experiment was conducted in order to assess the possibility of upgrading the material by wet high intensity magnetic separation. A sample of -75 μm slurry representing 91.7% of the material was treated in a magnetic separator. The treatment produced two fractions which had distinct colour differences. The less magnetic was light yellow and the more magnetic was dark brown.

The separation was achieved by passing the slurry, after suitable dispersion, through a glass tube containing fine steel wool. The tube was placed between the poles of a strong magnet while the slurry was fed. The more magnetic particles were retained and were recovered by removing the magnet and running clear water.

Chemical assays of the two fractions for the elements Ni, Cr, Mg, Co and Fe were carried out, and the results of grade and distribution are shown in Table 2.16. It can be seen that the more magnetic fraction has a grade higher than the less magnetic fraction in all the elements but the improvement in grade is marginal and the recovery is very poor.

Table 2.16 Results of magnetic separation of -75 μm material of the nickel laterite from Guatemala.

Sample	weight (%)	GRADE %				D I S T R I B U T I O N %					
		Ni	Cr	Mn	Co	Fe	Ni	Cr	Mn	Co	Fe
More Magnetic	43.6	0.9	1.5	0.6	0.12	56.0	47.1	56.0	56.6	70.4	62.1
Less Magnetic	56.4	0.8	0.9	0.4	0.045	26.1 ^{a)}	52.9	44.0	43.4	32.6	37.9

Calculated .84 1.2 0.49 0.077 39.3

Calculated^{b)} .99 1.0 0.41 0.063 43.8

- a) This result is unreasonably low and could be in error.
- b) Calculated by adding the suitably-weighed measured grades of the -75 +10 μm fraction and the -10 μm fraction in Table 2.15.

CHAPTER 3

THEORETICAL CONSIDERATIONS

This chapter presents a number of theoretical considerations that are relevant to the measurements carried out with nuclear resonance and Mössbauer effect. The experimental aspects of all the techniques used are discussed in Chapter 4 and Chapter 5 collects the results and provides a discussion of the results.

3.1 Hyperfine interactions

Introduction and general considerations

In a compound or mineral the detailed structure and the internal distribution of charges and currents determine the so-called hyperfine environment in which the nuclei of the constituent atoms are immersed.

This hyperfine environment for a given element is constant under a given set of conditions and is characteristic of a mineral or compound. Therefore it may be useful, for the mineral technologist, to probe the hyperfine fields which surround the nuclei of the atoms in minerals.

The information derived may be useful in characterising the minerals and hence aid in recognition or yield, in particular cases, information which may be of use in mineral processing.

There are various instrumental techniques which probe the hyperfine fields. Among them nuclear resonance and Mössbauer effect are prominent.

In nuclear resonance an external radio frequency wave is used to excite resonance transitions between sublevels of the nuclei in their

ground state. In Mössbauer effect spectroscopy the resonant radiation is provided by a radioactive isotope of the same element that is under study. This radiation excites transitions between levels in the ground state and an excited state in the nucleus. Mössbauer spectroscopy is limited to those elements for which there is a convenient radioactive isotope to produce the resonant radiation. In nuclear resonance it is possible, in principle, to study all elements with isotopes that possess a ground state spin different from zero. In practice various limitations reduce the number of elements in which resonance experiments are practicable.

A unique feature of these techniques, and especially of Mössbauer spectroscopy, is that they probe the hyperfine field surrounding the single element under study without regard to the presence or absence of other elements or other factors. Hence they provide a powerful tool to study the physico-chemical state of the element of interest in the particular sample studied, or to follow changes that take place to that element when the sample is subjected to a process.

These techniques of analysis have only very seldom been used in the study of mineral samples in connection with mineral processing problems. For laterite minerals other, more usual methods of mineral analysis, have very limited utility and it may result that useful information can be obtained by probing the hyperfine fields. Some particular instances are: 1) the identification of a mineral or compound, present in the laterite, by a characteristic spectrum.

- 2) the possible quantification of the minerals or compounds
- 3) the determination of physical or chemical properties which may throw some light on the problem of laterite treatment.
- 4) the determination of whether a given element which is present in a mineral is there as an essential component, a chemical substitute in solid solution, as an interstitial impurity or if it is there as an altogether different mineral phase, very finely associated with the mineral in question.

In order to put into perspective the results of the experiments carried out, a brief description of the phenomenology of the subjects is presented below. Particular emphasis is made in respect to the techniques of NMR, NQR and Mössbauer effect spectroscopy. Other techniques of probing the hyperfine fields such as electron spin resonance, electron spectroscopy, and various forms of angular correlations of radiation following nuclear reactions or natural radioactivity have been specifically excluded.

Hyperfine interactions involve the interaction between electrons and nuclei. These interactions form a bridge between the otherwise separate disciplines of solid state physics and nuclear physics. The most important hyperfine interactions are those between the effective magnetic field at the nuclear site and the nuclear magnetic dipole moment and the electrostatic interaction between the electric field gradient and the electric quadrupole moment of the nucleus.

The literature on the subject is quite extensive. There are numerous reviews and books, usually written from the point of view of one of the several techniques available. The phenomena may be described with a semiclassical approach but for quantitative calculations a full quantum mechanical treatment is usually required.

Magnetic hyperfine interactions

The magnetic hyperfine interaction is formally described by the interaction Hamiltonian. This was first derived by Fermi in 1930. Since then a very large number of papers and some review articles have appeared in print. The discussion below is based on the review article by A.J. Freeman and R.E. Watson (1965).

The Hamiltonian for the interaction of one electron, with orbital $\hat{\mathbf{L}}$ and spin $\hat{\mathbf{S}}$ angular momentum operators, with the nucleus with spin $\hat{\mathbf{I}}$ angular momentum operator, is written as

$$H = g g_N \mu_0 \mu_N \left[\underbrace{\frac{8}{3} \delta(r) \mathbf{S} \cdot \mathbf{I}}_A + \underbrace{\frac{\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}}{r^3}}_B - \underbrace{\frac{\hat{\mathbf{S}} \cdot \hat{\mathbf{I}}}{r^3} + \frac{3(\hat{\mathbf{S}} \cdot \hat{\mathbf{r}})(\hat{\mathbf{I}} \cdot \hat{\mathbf{r}})}{r^5}}_C \right] \quad 3.1$$

where g and g_N are electronic and nuclear g -factors μ_0 and μ_N are the Bohr and nuclear magnetons and $\hat{\mathbf{r}}$ is the distance between the nucleus and the electron.

Term A, which contains the delta function, is called the Fermi contact term and is non-zero only for s electrons. It accounts for the magnetic field that the s electrons in "contact" with the nucleus produce.

Term B accounts for the magnetic field that is produced at the nucleus by the electron orbiting the nucleus.

Term C accounts for the magnetic field contribution due to the intrinsic spin of the electron. Smaller contributions to the Hamiltonian such as higher order terms and additional factors of smaller magnitude such as relativistic effects, perturbations due to the mutual interaction between states and effects of finite nuclear size are not included in equation 3.1 above.

If the electron is an s electron then terms B and C in eq. 3.1 are zero. If the electron is not an s electron then term A is zero.

In a multi-electron atom each electron of the atom will interact with the nucleus with an expression of the form of eq. 3.1. Hence each electron produces a net field at the nucleus and the vector sum of the magnetic fields of all the electrons in the atom makes up the magnetic hyperfine field.

For the sake of simplicity the Hamiltonian for the magnetic interaction is usually written as

$$\mathcal{H} = - \mu \cdot \mathbf{H} \quad 3.2$$

where μ is the nuclear magnetic moment and $\mathbf{H}$ is the effective magnetic hyperfine field at the nucleus; $\mathbf{H}$ being the resultant of the various electronic contributions discussed above.

The detailed calculations of the net magnetic field $\mathbf{H}$ in any particular compound are carried out by breaking down all the electrons into groups such as core electrons, conduction electrons, etc. and calculating the contribution that each group makes to the overall magnetic field.

Detailed calculations of the hyperfine field at the nucleus of isolated ions, and for certain ions in solids have been made. (See for example W. Marshall, 1958; Portis and Gossard, 1960; Goodman and Raynor, 1970). These calculations are quite involved and in some cases can predict with reasonable accuracy the observed fields.

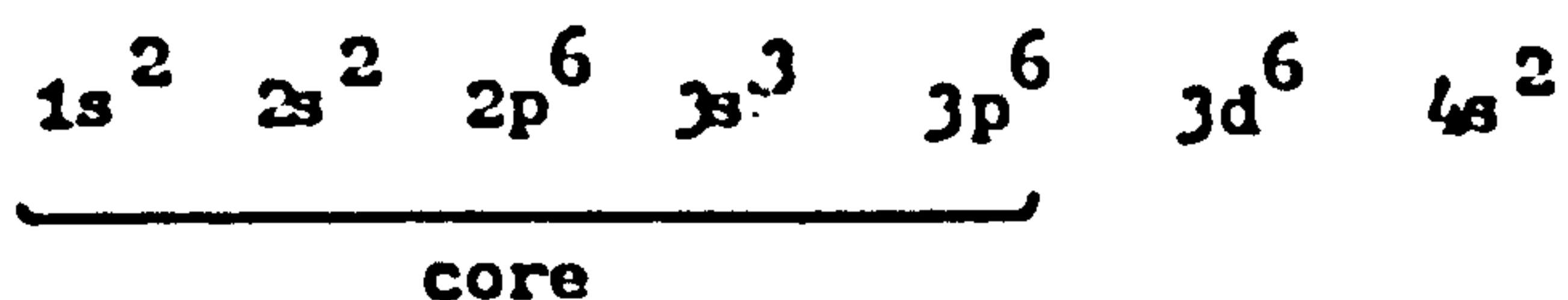
A very crude estimate of the hyperfine field, sometimes used, is obtained by a semi-empirical rule of thumb through which one calculates the field due to the polarization of the core electrons and neglects all other terms.

Unfortunately the present state of the theory is such that it is impossible, a priori, to obtain reliable values for each of the contributions that make up the magnetic hyperfine field. One cannot even guarantee that all experimentally significant terms (say to ± 1 Tesla) have been enumerated (Freeman and Watson, op. cit. P.272).

Magnetic hyperfine field at Fe ions.

The case of the Fe ions has been extensively discussed in the literature in connection with the Mössbauer effect of Fe^{57} . (See for example Danon, p.182, 1968).

The hyperfine field at the nucleus is dependent on the electronic structure which for Fe is



The atom loses the two $4s$ electrons to become the Fe^{2+} ion (represented by $3d^6$) and loses an additional $3d$ electron to become the Fe^{3+} ion (represented by $3d^5$).

The free Fe^{3+} ion is in an ${}^6S$ state with zero orbital angular momentum $L = 0$ and spin multiplicity $5/2$ (five electrons, each spin $\frac{1}{2}$, missing from the $3d$ to complete the subshell).

The effective hyperfine field at the nucleus in Fe^{3+} is primarily determined by the unpaired $3d$ electrons, although the main effect of the $3d$ electrons is produced in an indirect way.

The largest contribution to the field comes from the s electrons in the core through the Fermi contact interaction: term A in eq. 3.1. This comes about because the core s electrons are polarized by the unfilled $3d$ subshell. This polarization consists of an "attraction" of

1s, 2s and 3s electrons having spins parallel to the d-subshell spin and a "repulsion" of the electrons with opposite spin. The result of this polarization is a modification of the radial distribution of the s electrons and a net unpaired electronic spin density at the nucleus. This net unpaired spin produces in Fe a large field. Estimates by Watson and Freeman, 1961 (quoted by Danon, p.185, 1968) are

$$\text{Fe}^{2+} (3d^6) = -55.0 \text{ T and } \text{Fe}^{3+} (3d^5) = -63.0 \text{ T}$$

In Fe ions, after the core polarization contribution, the next terms in order of magnitude are the orbital and spin (so-called dipolar) contributions (terms B and C in eq. 3.1) of the 3d electrons which have been estimated at about +10 T each with the orbital contribution vanishing for Fe^{3+} .

When the ion is in a solid the electron distributions are strongly affected by the crystalline environment and the nature of the bonding of the atom in the solid. Each of the electronic contributions to the hyperfine field is affected in a major or minor way depending on the nature of the solid and the type of chemical bond that takes place. Hence the magnetic hyperfine field in Fe^{3+} salts decreases from the highly ionic compound FeF_3 to the more covalent FeO as shown in Table 3.1. This behaviour is explained as due to the 3d electrons becoming delocalised and admixed with the electrons of the surrounding ligand atoms as the compound becomes more covalent. As a result core polarization decreases and possibly also some orbital moment increases. Since these contributions have opposite signs (core polarization being the stronger) the net effect is a decrease in the effective magnetic hyperfine field.

Table 3.1 Measured magnetic hyperfine fields, extrapolated to 0°K, at the Fe nucleus in some Fe compounds. (After Forsyth, et al. 1968; Greenwood & Gibb, p.150, 1971).

Compound	H (Tesla)	Compound	H (Tesla)
Fe F ₃	62.2	α-FeO OH	50.4
Fe ₂ (SO ₄) ₃	55.0	β-FeO OH	49.0
Fe ₂ O ₃	54.0	γ-FeO OH	46.0

Electric hyperfine interactions

The theory of the electrostatic interaction between electrons and nuclei has been reviewed in the literature in connection with nuclear magnetic resonance spectroscopy (Cohen and Reif, 1957; Das and Hahn, 1958; Abragam, 1961), in connection with Mössbauer spectroscopy (Freeman and Watson, 1965; Goldanskii and Makarov, 1968; Greenwood and Gibb, 1971) and in connection with nuclear quadrupole resonance spectroscopy. (Smith, 1977). Below is a very brief summary of the subject with emphasis on the physical phenomena that take place.

Electric hyperfine interactions arise by the interactions between the charges which are located near the nucleus and the charges in the nucleus itself.

The nucleus may be considered as a spheroid of charged particles described by a particular charge and current distribution: $\rho(x)$ and $J(x)$ respectively. In a solid the nucleus is surrounded by its own atomic electrons and by the charges of electrons and other atoms in its immediate neighbourhood. All of these charges create electric

fields at the site of the nucleus. The magnitude of these electric fields over the nuclear volume are described by the electrical potential $V(x)$ which they cause over the nuclear volume. The electric hyperfine interaction is then treated as the interaction between the nuclear charge, described by $\rho(x)$, and the electrical potential created by the charges surrounding the nucleus, described by $V(x)$.

The interaction is expressed by the Hamiltonian function which here is simply an integral over the nuclear volume:

$$H = \int \rho(x) V(x) d^3x \quad 3.3$$

To evaluate this expression it is usual to express the potential $V(x)$ as a power series about the centre of mass. When this is done the Hamiltonian is expressed as a series of terms which correspond to the classical multipolar expansion of an electric charge. It can be shown (Cohen and Reif P.328, 1957) that, of all the terms in the expansion, the only non-vanishing term of sufficiently large magnitude is the quadrupolar term. This term represents the interaction between the nuclear electric quadrupole moment and the gradient of the electric field.

In physical terms, the nuclear electric quadrupole moment measures the departure of the nuclear charge distribution from spherical symmetry; and the electric quadrupolar interaction measures the interaction between this asymmetrical charge distribution and the electric field gradient (EFG).

The electric field gradient is a tensor quantity which, by a suitable choice of coordinate system, can be represented by its principal three components: V_{xx} , V_{yy} and V_{zz} which satisfy

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad 3.4$$

and

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$$

With this choice of coordinate system the EFG can be completely specified by two independent parameters: the maximum value of the field gradient $eq = -V_{zz}$ and by an asymmetry parameter η defined by

$$\eta = \frac{(V_{xx} - V_{yy})}{V_{zz}} \quad 3.5$$

which measures the degree of asymmetry or the departure from symmetry of the EFG. If $V_{xx} = V_{yy}$ the field gradient has axial symmetry and $\eta = 0$. For cubic or spherical symmetry around the nucleus all components of the EFG are zero and the quadrupole interaction is zero.

The condition for a nucleus to possess an electric quadrupole moment is that its spin quantum number I be greater or equal to one.

With the conventions mentioned above the electric quadrupole Hamiltonian is usually written as

$$\mathcal{H} = \frac{e^2 q Q}{4I(2I-1)} \left[3m^2 - I(I+1) + \frac{1}{2} \eta (I_+^2 + I_-^2) \right] \quad 3.6$$

where eQ is the quadrupole moment, I and m are the spin and magnetic quantum numbers and I_+ and I_- are spin raising and lowering operators.

With the use of relation 3.6 it is possible to determine the positions of the nuclear energy levels in the presence of an EFG and to derive the energy and frequency which are obtained with spectroscopic techniques that probe the electric hyperfine fields.

The calculation from first principles of the EFG acting over the nucleus in any particular case is quite an involved problem. The EFG is the result of two main contributions: 1) the EFG produced at the nuclear site by neighbouring charges called the local field (or crystalline field) and 2) the field produced at the nuclear site by the atom's own electrons. This latter field is not the same as the field that would be obtained in an isolated atom because the local field interacts and "polarizes" the atom's own electrons producing induced field gradients which are proportional to the local field. The extent of polarization is taken into account by the use of proportionality factors which are called Sternheimer antishielding factors.

The local field at a site reflects strongly the symmetry of that site. Some examples are: 1) any n -fold rotation or rotation-reflection axis for which $n > 2$ requires that $\eta = 0$ (an axially symmetric EFG). 2) Two or more rotation axes each having $n > 2$ cause the field gradient to vanish as is the case of cubic or tetragonal symmetry.

The EFG at a site can also be affected by the presence of crystal imperfections such as dislocations, point defects, vacancies and impurity atoms. Symmetry considerations can usually give a clue to the type of EFG that can be expected in any given site.

From the practical point of view it is found that, contrary to the case of magnetic interactions, no appreciable EFG can be externally generated. Since the quadrupole moment and the EFG appear as products in the Hamiltonian it is impossible to separate these quantities in a single experiment and therefore nuclear quadrupole moments are not known to as high accuracy as magnetic moments. For this reason, results are

often quoted in terms of the "quadrupole coupling constant" i.e. the product (e^2qQ/h) of EFG and quadrupole moment.

Hyperfine splitting of nuclear levels

In order to predict the results of NMR, NQR or Mössbauer experiments or to interpret the results obtained, it is necessary to know the effect that the various possible hyperfine fields will have on the nuclear energy levels. The calculations involve writing down the Hamiltonian appropriate to the system, solving the eigen value problem and determining the energy levels. This is generally quite an involved calculation, but fortunately, the problem has been solved for a large number of possible combinations of hyperfine fields and nuclear spin values, and the majority of cases encountered in practice can be elucidated by reference to the literature. (Kundig, 1967).

In figure 3.1 are shown the energy levels that arise with some hyperfine field and spin combinations. This figure does not, by any means, show all the possible cases, and neither are the splittings indicated unique, as the relative magnitudes of the fields and the size and signs of the nuclear moments will change the relative positions of the energy levels.

The simplest case of all is that of a pure magnetic field H acting on the nuclear site. The interaction of the magnetic field with the magnetic dipole moment totally lifts the degeneracy of a spin I level and produces $(2I + 1)$ equally spaced sublevels. (Fig. 3.1 column 3). Splittings of this nature are expected in cubic crystals (so that the effective EFG is zero) when there is an externally applied magnetic field or the material is intrinsically magnetic. This type of splitting is always present in NMR experiments due to the externally applied

magnetic field superimposed on, or otherwise modified by, electric quadrupolar effects that may also be present in the specimen.

A symmetric EFG with zero magnetic field also produces simple splittings. In this case the degeneracy of the energy levels is not completely lifted leaving all sublevels either with spin 0 or ± 1 (Figure 3.1 column 4), the so-called Kramers degeneracy.

Non-symmetric EFG ($\eta \neq 0$) or simultaneous magnetic and electric interactions produce more complex splittings. In some cases the calculations are straight-forward and analytical solutions are found, while in other instances the calculations may be lengthy and no solutions in closed form exist. In this last instance, numerical calculations are usually done. Figure 3.1 columns 5 and 6 show the simplest cases of a non-symmetric EFG and simultaneous electric and magnetic interaction.

When an external magnetic field is applied, the angles between the external field and the internal field or the principal axis of the internal EFG will enter into the relations for the position of some of the energy levels. In this case the outcome of the experiment depends on whether the sample is a single crystal or a polycrystalline powder, and on the relative orientation of the sample when placed in the external field. Particular attention to this consideration must be given when attempting experiments with specimens which are all polycrystalline such as the study of lateritic minerals.

Figure 3.1 Splitting of the nuclear energy levels under certain hyperfine fields for spin values from $I = \frac{1}{2}$ to $I = \frac{5}{2}$. H = magnetic field, EFG = Electric field gradient, η = asymmetry parameter. The splittings shown are non-unique as the relative positions of the sublevels depend on the sign and magnitude of the nuclear moments. Only first order quadrupolar interactions considered.

1 Spin I	2 $H = 0$ EFG = 0 $\eta = 0$	3 $H \neq 0$ EFG = 0 $\eta = 0$	4 $H = 0$ EFG $\neq 0$ $\eta = 0$	5 $H = 0$ EFG $\neq 0$ $\eta \neq 0$ a)	6 $H \neq 0$ EFG $\neq 0$ $\eta = 0$ b)
$\frac{1}{2}$	—	— $+\frac{1}{2}$ — $-\frac{1}{2}$	— $\pm\frac{1}{2}$	— $\pm\frac{1}{2}$	— $+\frac{1}{2}$ — $-\frac{1}{2}$
1	—	— $+1$ — 0 — -1	— ± 1 — 0	— $+1$ — -1 — 0	
$\frac{3}{2}$	—	— $\frac{3}{2}$ — $\frac{1}{2}$ — $-\frac{1}{2}$ — $-\frac{3}{2}$	— $\pm\frac{3}{2}$ — $\pm\frac{1}{2}$	— $\pm\frac{3}{2}$ — $\pm\frac{1}{2}$	— $\pm\frac{3}{2}$ — $+\frac{1}{2}$ — $-\frac{1}{2}$ — $-\frac{3}{2}$
2	—	— 2 — 1 — 0 — -1 — -2	— ± 2 — ± 1 — 0	— ± 2 — $+1$ — -1 — 0	
$\frac{5}{2}$	—	— $\frac{5}{2}$ — $\frac{3}{2}$ — $\frac{1}{2}$ — $-\frac{1}{2}$ — $-\frac{3}{2}$ — $-\frac{5}{2}$	— $\pm\frac{5}{2}$ — $\pm\frac{3}{2}$ — $\pm\frac{1}{2}$	— $\pm\frac{5}{2}$ — $\pm\frac{3}{2}$ — $\pm\frac{1}{2}$	— $\pm\frac{5}{2}$ — $\pm\frac{3}{2}$ — $+\frac{1}{2}$ — $-\frac{1}{2}$ — $-\frac{3}{2}$ — $-\frac{5}{2}$

a) Only cases of small asymmetry parameter

b) Electric interaction small compared to magnetic

3.2 Magnetic materials - Macroscopic considerations

In the following are summarized some concepts and relationships of magnetism relevant to the measurements of magnetic susceptibility, nuclear resonance and Mössbauer effect. The material presented has been drawn from a number of references including Kittel (1962), Schieber (1967), Cullity (1972), Stacey and Banerjee (1974) and Crangle (1977).

Additionally, a table of units and conversion factors taken partly from Crangle (1977) has been added due to the confusion in the literature in the use of magnetic quantities and units. (Table 3.2).

Table 3.2 Units, dimensions and conversion factors of some magnetic quantities (T = Tesla, J = Joule, G = Gauss, Oe = Oersted).

Quantity Symbol	Name	Conversion factor			Reduced to elementary units
		SI	C*	CGS ⁺	
B	Magnetic induction	T	10^4	G	$\frac{\text{mass}}{\text{charge time}}$
μ	magnetic dipole moment	$\frac{\text{J}}{\text{T}}$	10^3	$\frac{\text{erg}}{\text{Oe}}$	$\frac{\text{charge length}^2}{\text{time}}$
σ	specific(mass) magnetization	$\frac{\text{J}}{\text{T}} \frac{1}{\text{Kg}}$	1	$\frac{\text{erg}}{\text{Oe}} \frac{1}{\text{g}}$	$\frac{\text{charge length}^2}{\text{time mass}}$
M	magnetization (volume)	$\frac{\text{J}}{\text{T}} \frac{1}{\text{m}^3}$	10^{-3}	$\frac{\text{erg}}{\text{Oe}} \frac{1}{\text{cm}^3}$	$\frac{\text{charge}}{\text{time length}}$
χ_m	specific(mass) susceptibility	$\frac{\text{J}}{\text{T}^2} \frac{1}{\text{Kg}}$	10^{-4}	$\frac{\text{erg}}{\text{Oe}^2} \frac{1}{\text{g}}$	$\text{length time} \left(\frac{\text{charge}}{\text{mass}} \right)^2$
K	volume susceptibility	$\frac{\text{J}}{\text{T}^2} \frac{1}{\text{m}^3}$	10^{-7}	$\frac{\text{erg}}{\text{Oe}^2} \frac{1}{\text{cm}^3}$	$\text{time} \left(\frac{\text{charge}}{\text{mass length}} \right)^2$
M	molar susceptibility	$\frac{\text{J}}{\text{T}^2} \frac{1}{\text{mole}}$	10^{-1}	$\frac{\text{erg}}{\text{Oe}^2} \frac{1}{\text{mole}}$	$\text{length time} \left(\frac{\text{charge}}{\text{mass}} \right)^2$

* SI = C x CGS. C is a "numerical equivalence" factor.

⁺ The unit (emu/g) for magnetization and/or susceptibility is used by some authors to signify the use of CGS units.

The magnetic moment $\underline{\mu}$ of a sample of material is produced by the vector sum of all the elementary magnetic dipole moments in the material. (Spin and orbital magnetic moments of the electrons, and magnetic moments of nuclei which add up vectorally in a complex way to give a bulk magnetic moment).

The magnetic moment $\underline{\mu}$ (either, an elementary dipole moment, or the bulk magnetic moment of a sample) is defined in terms of the torque that acts on it when placed in an external magnetic induction field $\underline{B}$ by means of the relation

$$\underline{T} = \underline{\mu} \times \underline{B} \quad 3.7$$

The magnetization $\underline{M}$ of a sample is defined as the magnetic moment of the sample $\underline{\mu}$, in a specific spacial direction, per unit volume v or

$$\underline{M} = \underline{\mu}/v$$

The magnetization measures the extent to which the elementary magnetic dipoles in the material are aligned so that they add up to make the bulk magnetic dipole moment.

The specific magnetization $\underline{\sigma}$ (magnetization per unit mass) is defined as magnetic dipole moment per unit mass

$$\underline{\sigma} = \underline{\mu}/m \quad 3.8$$

The relationship between magnetization $\underline{M}$ and specific magnetization is

$$\underline{\sigma} = \underline{M}/\rho \quad 3.9$$

where

ρ = density of the specimen.

The magnetization of a specimen depends on the nature of the material, the externally applied field and on the temperature. The previous magnetic history of a specimen can also influence its magnetization. It is customary to quote values of spontaneous magnetization which is the magnetization that exists in a sample under zero applied field. Otherwise the magnitude of the applied field must be specified.

The magnetic susceptibility of a material is a quantity which measures the ability of the elementary spin moments in the material to align themselves along an externally applied field. Hence the susceptibility measures the ease with which a material becomes magnetized when placed in a magnetic induction field B . The susceptibility χ is defined as the induced magnetic moment divided by the externally applied field.

$$\chi = \frac{\mu}{B} \quad 3.10$$

Susceptibility may be expressed as specific susceptibility, volume susceptibility or molecular susceptibility depending on whether the quantity is defined in terms of mass, volume, or molar induced magnetization.

The defining relations are

$$\chi_m \text{ specific (mass) susceptibility} = \frac{\mu}{B} \frac{1}{m} = \frac{\text{susceptibility}}{\text{mass}} \quad 3.11$$

$$K \text{ volume susceptibility} = \frac{\mu}{B} \frac{1}{v} = \frac{\text{susceptibility}}{\text{volume}} \quad 3.12$$

$$\chi_m \text{ molecular (or molar) susceptibility} = \frac{\mu}{B} \frac{1}{\text{mol.wt.}} = \frac{\text{susceptibility}}{\text{mass}} \quad 3.13$$

These susceptibilities are related by

$$\chi_m = K/\rho \quad 3.14$$

and

$$\chi_m = \text{mol.wt.} \times K/\rho = \text{mol.wt.} \times \chi_m \quad 3.15$$

Specific susceptibility χ_m and specific magnetization σ are related by

$$\chi_m = \sigma/B \quad 3.16$$

Volume susceptibility K and volume magnetization M are related by

$$K = M/B \quad 3.17$$

The susceptibility of a material is often field and temperature dependent. The form of the dependence is different for different classes of magnetic materials. The susceptibility of a particular specimen may also be a function of the particle size or of its previous magnetic thermal or mechanical history.

Additionally, in magnetically anisotropic substances, a distinction must be made between the bulk magnetic susceptibility of polycrystalline specimens and the susceptibility of single crystals. In single crystals the susceptibility of magnetically anisotropic materials depends on the crystal orientation.*

The susceptibility of ferromagnetic and ferrimagnetic materials have a characteristic dependence on externally applied fields. The susceptibility is very large for weak applied fields and decreases to a low constant value at high fields. Due to this strong dependence on field it is customary to quote for these materials χ_∞ which is the specific susceptibility extrapolated to infinite field.

The susceptibility in antiferromagnetic materials is very much lower and is only weakly dependent on magnetic field. It is also customary to quote χ_∞ .

*This is a consequence of the tensor nature of the magnetic susceptibility.

The magnetic force F exerted by a magnetic field B on a sample of mass m and specific susceptibility χ_m is given by

$$F = m \chi_m B (dB/dx) \quad 3.18$$

where dB/dx is the magnetic field gradient over the sample.

Using relation 3.16 one gets

$$F = m \sigma dB/dx \quad 3.19$$

Relations 3.18 and 3.19 are the basis for the measurements of magnetic susceptibility by the Faraday method. In this method the force F is measured with a balance. The value of χ_m of an unknown may then be obtained either by comparison with the susceptibility of a known standard or by independently measuring the magnetic induction B and the induction gradient dB/dx .

The temperature dependence of various types of magnetic materials is shown graphically in figure 3.2.

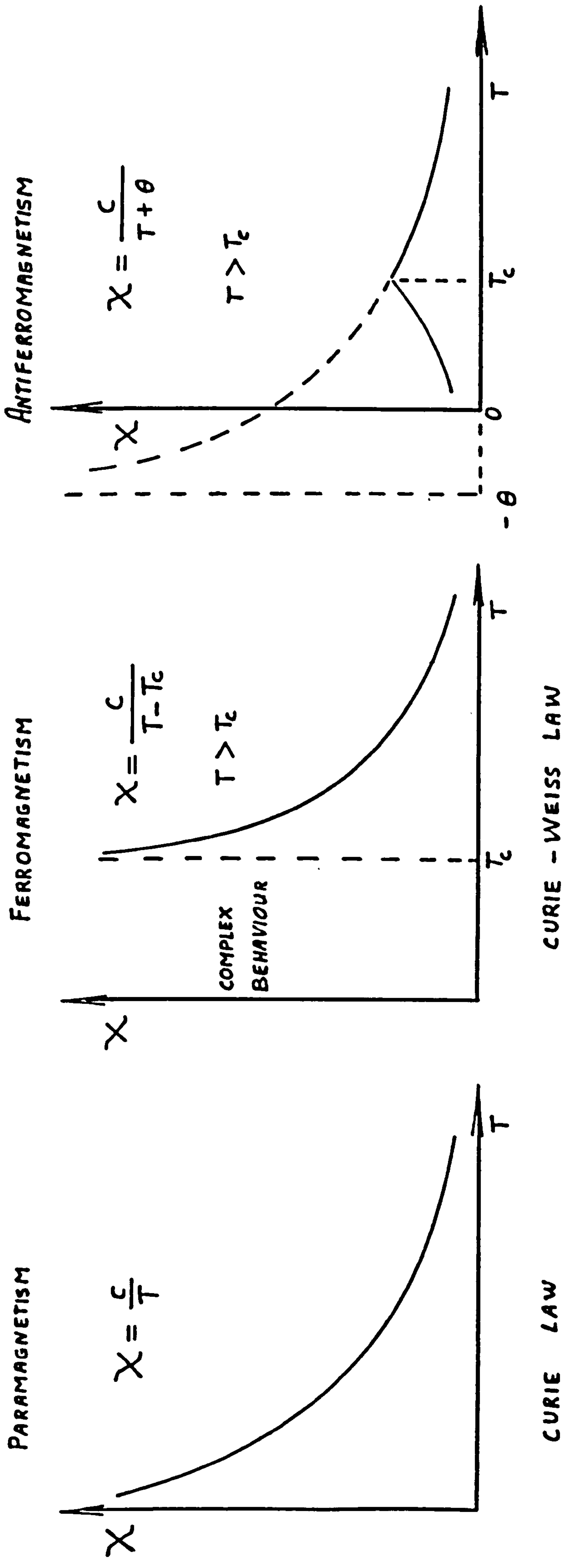


Figure 3.2 Behaviour of the magnetic susceptibility as a function of temperature of paramagnetic, ferromagnetic and antiferromagnetic materials (after Kittel P.292 (1962)).
 χ = magnetic susceptibility, T = absolute temperature, T_c = Curie temperature (or Neel temperature) C and θ constants

Magnetic materials. Microscopic considerations

A large number of the observed phenomena in magnetic materials can be explained in terms of the Heisenberg exchange energy between the magnetic spin moments present in these materials.

The interaction between electrons which is responsible for ferromagnetic and antiferromagnetic behaviour in solids is not the magnetostatic interaction. (Stacey and Banerjee, P.10, 1974).

The magnetostatic interaction E_m between the magnetic spin moments of two electrons located in neighbouring atoms and separated by a distance a is of the order of

$$E_m = \mu_B H \quad 3.20$$

where μ_B is the magnetic moment of the electron and H the static magnetic field produced by one electron at the site of the other. The temperature, above which, this energy is lower than the thermal energy (the Curie temperature) can be calculated approximately by equating the thermal energy with the magnetostatic energy:

$$k T_c \simeq \mu_B H \quad 3.21$$

hence

$$T_c = \mu_B H/k \quad 3.22$$

where k is Boltzmann's constant. From eq. 3.22 the temperature T_c obtained is of the order of 0.3°K. If ferromagnetism depended on magnetostatic interactions, observed Curie points would all be lower than 1°K. In fact Curie points observed are several hundred degrees Kelvin as shown in Table 3.3. It is now generally recognised that the interactions responsible for ferromagnetic behaviour are of electrostatic nature. These interactions between electrons that give rise to ferromagnetic phenomena are called exchange interactions. They are spin-dependent electrostatic interactions which makes them similar to

magnetostatic interactions but with much greater magnitudes.

The energy of the interaction may be calculated by the so-called exchange integral A .

$$A = \iint V \psi_1 \psi_2 dv_1 dv_2 \quad 3.23$$

where V is the coulomb potential energy between charges $\psi_1 dv_1$ and $\psi_2 dv_2$, ψ_1 and ψ_2 are wavefunctions which represent the charge clouds of the electrons and dv_1 and dv_2 are differential volume elements.

If electrons i and j are represented by spin vectors $\underline{S}_i$ and $\underline{S}_j$; the exchange energy of the two spin vectors is given by (Stacey and Banerjee P.13, 1974)

$$E_e = -4 A \underline{S}_i \cdot \underline{S}_j \quad 3.24$$

where A is the exchange integral.

Eq. 3.24 refers to direct exchange interactions between spin moments. The interaction may take place through a third intermediate spin giving rise to indirect exchange, superexchange and other interaction mechanisms that have been proposed in the literature. (Scheiber P.43-50, 1967).

If the exchange energy is greater than the thermal energy, the spins in the material tend to align parallel or antiparallel depending on the sign of the exchange integral (positive produces parallel alignment, negative antiparallel alignment) as shown in Fig. 3.3.

If the exchange energy is smaller than the thermal energy the thermal fluctuations in the material prevent alignment of the spins and the material exhibits paramagnetic behaviour. The critical temperature above which the material becomes paramagnetic is called the Curie temperature T_c . Below the Curie temperature the coupling

* This formula is also written as

$$E_e = -2A \bar{S}_i \cdot \bar{S}_j \quad (\text{Kittel P.273, 1962; Cullity P.133, 1972}).$$

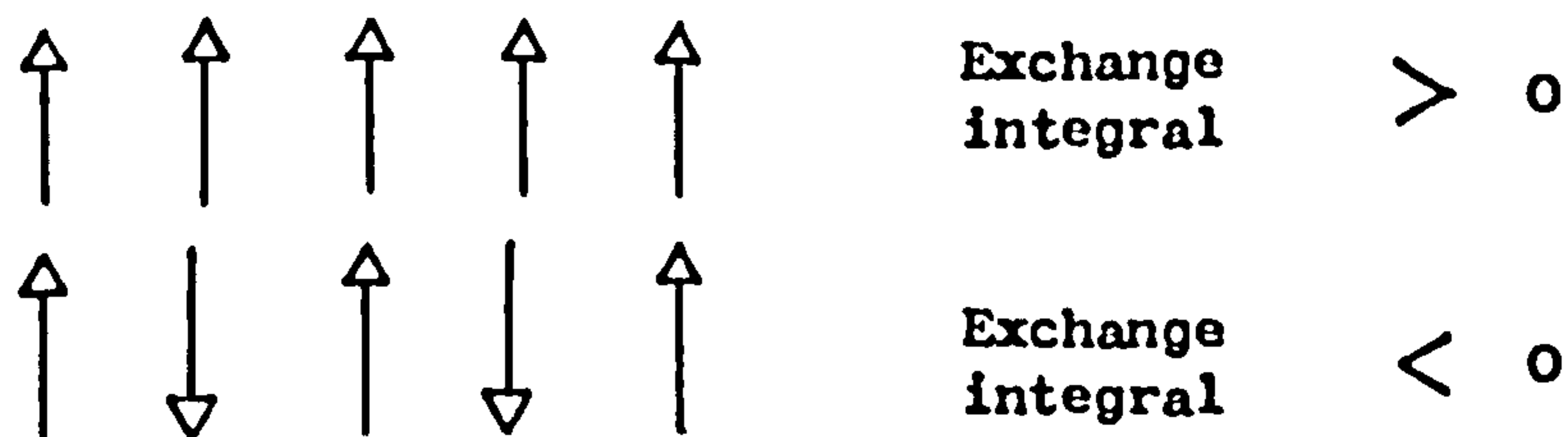


Fig. 3.3 Spin ordering according to the sign of the exchange integral A .

of the spin moments in neighbouring atoms becomes stronger with a decrease in the temperatures.

Magnetic Ordering

In ferromagnetic materials the spin moments align parallel to each other. In antiferromagnetic materials the exchange integral is negative and the spins align antiparallel. In this case the net magnetic moment of the material is zero. Ferrimagnetic materials are a special case of antiferromagnetism: the magnitude of the spin moments of the atoms are not all identical and, although antiparallel alignment exists, the material exhibits a net spontaneous magnetization. Figure 3.4 shows schematically the orientation of the magnetic moments in some of the various types of magnetic materials that exist.

As in the case of ferromagnetism, the magnetic ordering of antiferromagnetic and ferromagnetic materials decreases with increasing temperature up to a critical value above which the materials behaves paramagnetically. The critical temperature in this case is called the Neel point (or Neel temperature). Representative values of Neel points are shown in Table 3.3. At the Curie and Neel points the order-disorder magnetic transition gives rise to specific heat and other anomalies (electrical conductivity, crystallographic, etc.).

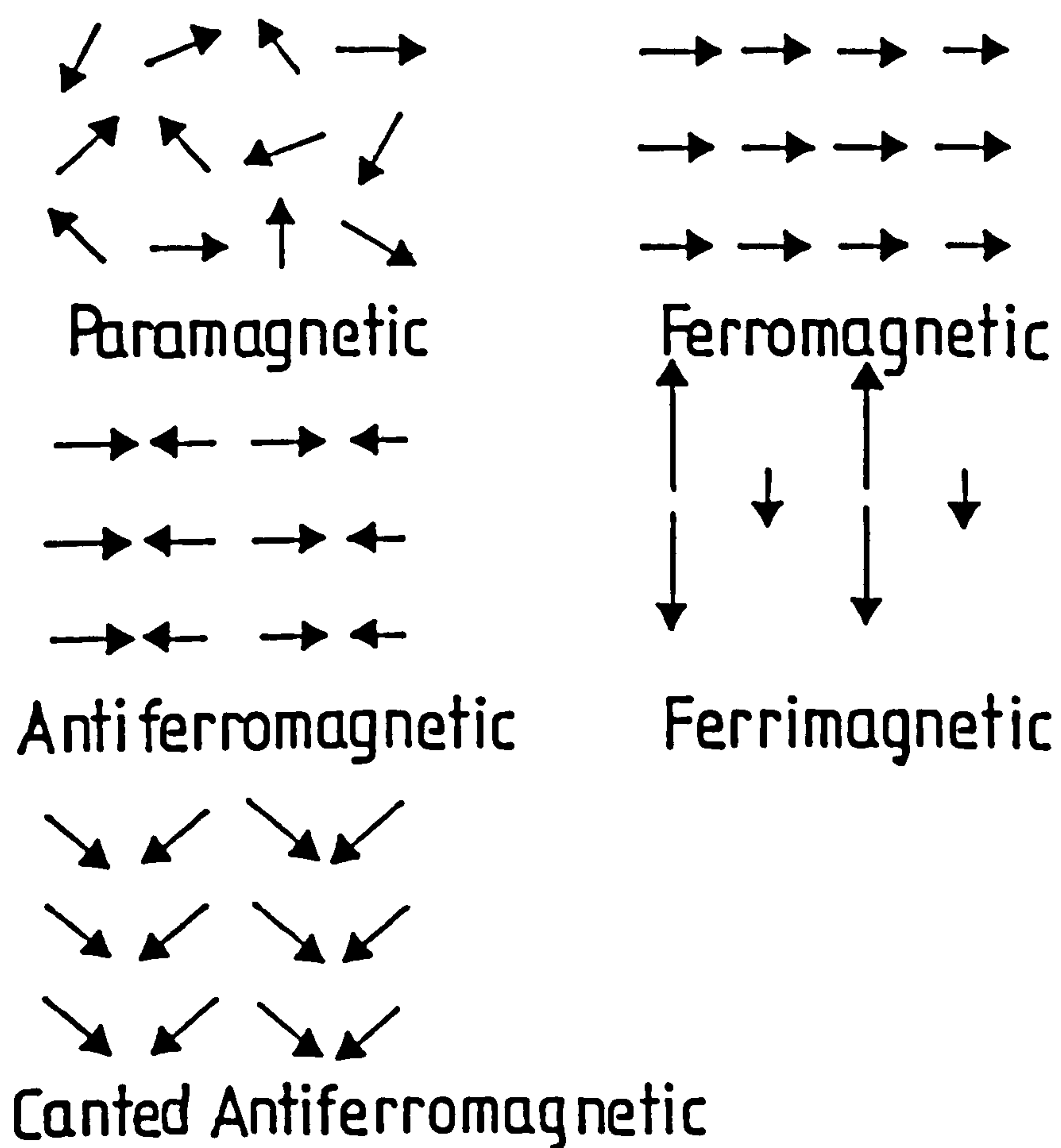


Fig. 3.4 Schematic diagram showing some of the different types of ordering of the spin moments of neighbouring atoms leading to magnetic behaviour (After Scheiber P.35, 1967).

Table 3.3 Magnetic ordering temperatures in some materials (Curie point in ferromagnets (F); Neel points in antiferromagnets (AF)) (FI ferrimagnet)

Material	Temperature (K)	Magnetic Structure
Fe (metal)	1043	F
Co "	1400	F
Ni "	631	F
Gd "	289	F
Magnetite(Fe_3O_4)	853	FI
Hematite (Fe_2O_3)	956	AF*
Goethite (FeO OH)	403	AF

* canted antiferromagnetic material

Anisotropy Energy

As we have seen, a magnetic material below the Curie temperature is composed, on a microscopic scale, of magnetic moments all aligned in a parallel or antiparallel manner. This tendency for parallel alignment is described by equation 3.24 as follows

$$E_e = -4A \underline{S}_i \cdot \underline{S}_j = -4A S_i S_j \cos \theta$$

where θ is the angle between spin vectors $\underline{S}_i$ and $\underline{S}_j$. If θ is assumed small, then $\cos \theta$ can be expanded in a power series as

$$\cos \theta = 1 - \frac{\theta^2}{2!} + \frac{\theta^4}{4!} - + \dots$$

With substitution into the previous relation and retention of up to the quadratic term one obtains

$$E_e = -4A S^2 + 2A S^2 \theta^2$$

$$\text{or } E_e = E_o + 2A S^2 \theta^2$$

3.25

where two identical spins $S_i = S_j = S$ are assumed and E_0 is the minimum exchange energy corresponding to $\theta = 0$.

Relation 3.25 shows that the minimum energy is obtained for $\theta = 0$ i.e. for spin alignment, but the exchange energy tells nothing about which spacial direction the alignment assumes with respect to the crystal axes. This is determined by the crystalline anisotropy energy.

The anisotropy energy tends to make the magnetization of a domain line up with certain crystallographic axes. These special axes are called axes of easy magnetization. Some examples of easy magnetization axes are shown in Table 3.4.

Table 3.4 Axes of easy magnetization for some magnetic materials

Material	Easy Axis
Hexagonal cobalt	(0001) hexagonal axis
Cubic iron	(100) cube edges
Cubic nickel	(111) body diagonals
Cubic magnetite	(111) " "

Under the influence of an applied magnetic field spins may be deflected out of the easy direction but the field must do work against the anisotropy constant thus producing anisotropy energy.

The physical origin of the anisotropy energy lies in the coupling of the spin magnetic moment of the electron to the orbital magnetic moment of the same electron. Since the electron orbits are an integral part of the lattice and the orbital angular momenta are fixed to lattice directions, then this spin-orbit interaction couples the electron spin

angular momentum through the electron's orbital angular momentum to the crystal lattice.

The energy of the spin-orbit coupling is expressed in terms of the scalar product of the orbital and spin angular momenta $\underline{L}$ and $\underline{S}$ by

$$E_c = \alpha \underline{L} \cdot \underline{S} = \alpha LS \cos \beta$$

where β is the angle between $\underline{L}$ and $\underline{S}$ and α is a coupling constant.

Macroscopically the anisotropy energy is represented by empirical anisotropy constants K whose units are energy/volume (Cullity, P.207, 1972).

Anisotropy constants are characteristic of each material and are temperature dependent. They decrease with increasing temperature and have minimum values at magnetic disordering temperatures (Curie or Neel points) see Table 3.5.

Magnetic Domains and Bloch wall

Whereas on a microscopic level the spins in a magnetic material all tend to align parallel, on a macroscopic level a saturated material with perfectly aligned spins has higher energy than an imperfectly aligned one. Hence a saturated configuration tends to break up into smaller saturated sections in order to decrease the total energy of the system. These saturated sections are called magnetic domains and are separated from each other by domain walls sometimes called Bloch walls.

With N domains the magnetic energy of a given sample is decreased approximately by $1/N$ of the magnetic energy that the sample would have in the saturated configuration. The breakup into smaller and smaller domains continues until the energy required to establish an additional

Bloch domain wall, separating two oppositely magnetized domains, is greater than the energy reduction achieved by the greater subdivision. The energy associated with a Bloch wall results from the tendency of adjacent spins to align themselves according to the exchange interaction forces and to minimise the exchange energy given by equation 3.25.

This explanation of the origin of magnetic domains is really a simplified picture. It leads to some problems such as the prediction that there should not be any antiferromagnetic domains* whereas these are well documented (Roth, 1960). A more complete description, as shown by Newnham (1974), must consider not only magnetic energy but all other forms of energy contained in the solid. This description starts with a consideration of the free energy function and the tensor properties of the orientation states. These considerations then lead to a general formulation in which magnetic domains are but one example of a wider class of orientation states which arise as a result of minimising the total mechanical, electrical and magnetic energy of the crystal.

The Bloch walls are not a discontinuous jump from one spin orientation to another. They are an extensive transition layer that separates adjacent domains magnetized in different directions (Figure 3.5).

This wall structure is due to the fact that the total exchange energy for a wall E_w composed of N atoms given by

$$E_w = + 2A S^2 \theta^2 / N \quad 3.26$$

is smaller than the exchange energy of a wall composed of only one

*Since the net magnetization of a perfect antiferromagnet is zero, no decrease in the energy of a single-domain "saturated" crystal would be achieved by its breakup into smaller domain sections.

Table 3.5 Anisotropy constants for some materials (data from Cullity P.234, 1972 unless otherwise indicated)

Structure	Substance	K_1 ($\times 10^4$ J/m ³)	K_2	source
cubic	Fe	4.8	± 0.5	
	Ni	-0.5	-0.2	
	Fe ₃ O ₄	-1.1		
	Fe ₃ O ₄	-1.36	-0.44	(1)
	MnO.Fe ₂ O ₃	-0.3		
	NiO.Fe ₂ O ₃	-0.62		
	MgO.Fe ₂ O ₃	-0.25		
	CoO.Fe ₂ O ₃	20		
hexagonal	Co	45		
	BaO.6Fe ₂ O ₃	33		
	Y CO ₅	550		
	Mn Bi	89		
	Fe ₂ O ₃	.41(21) at 205 K		(2)
	Fe ₂ O ₃	.47(11) at 300 K		(2)

(1) Stacey and Banerjee P.47, 1974

(2) Kundig, et al. 1966

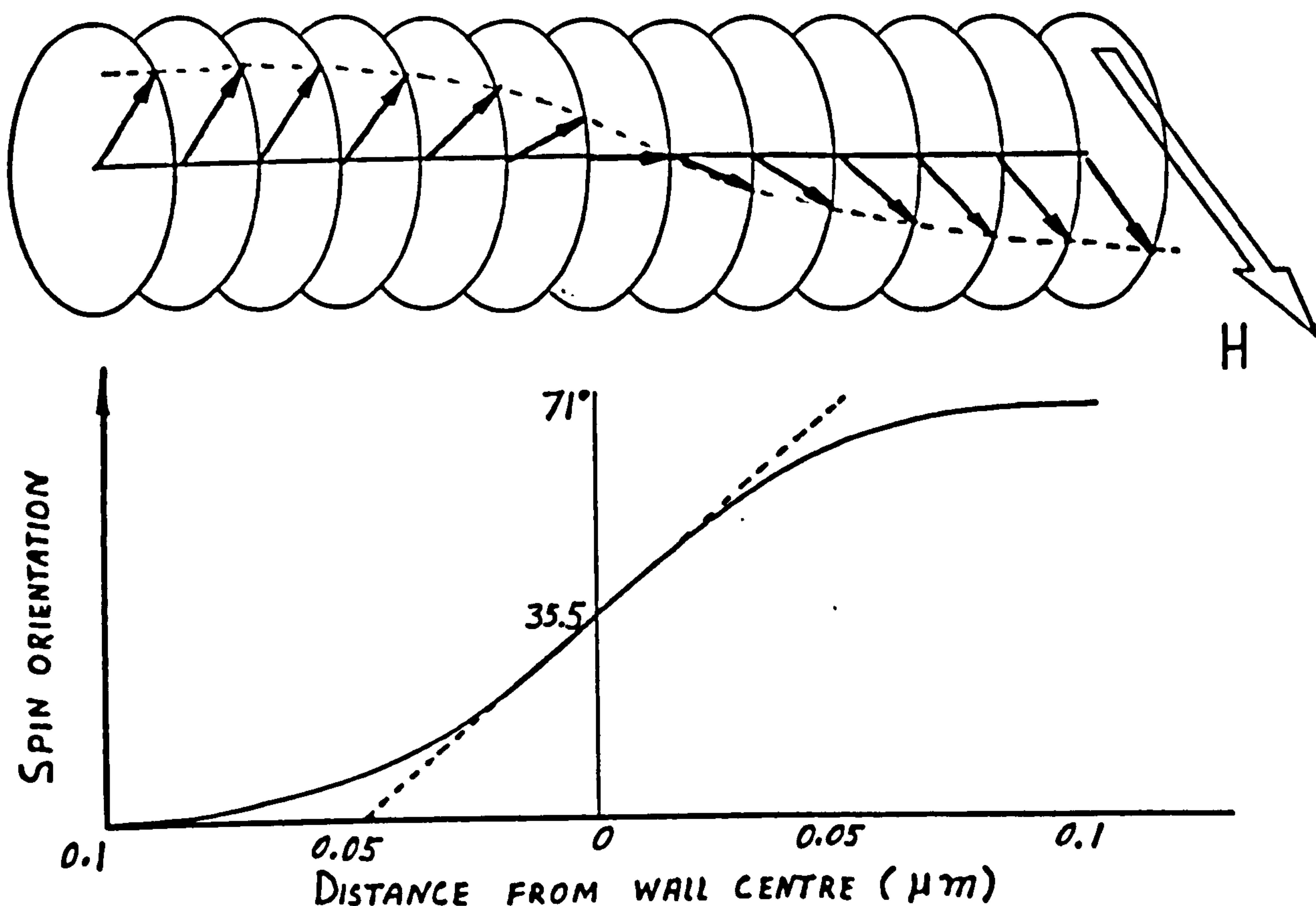


Fig. 3.5 The Bloch wall. Variation of spin orientation through a 71° domain wall in magnetite (Data from Stacey and Banerjee, 1974). An externally applied field H would tend to move the wall to the left.

discontinuous transition given by

$$E_w^1 = + 2A S^2 \cos \theta \quad 3.27$$

The form of equation 3.26 for the exchange energy of a line of N atoms across a wall shows that the energy is inversely proportional to the wall thickness. Hence the wall tends to spread out until it fills a sizable proportion of the crystal. This spreading out of the wall does not continue indefinitely because of the restraining effect of the anisotropy energy which acts to limit the wall thickness. Hence the thickness of the transition layer from one domain direction to the other domain direction is the result of the competing claims of exchange energy (tending to increase the wall size) and the anisotropy energy (tending to decrease the wall size).

The order of magnitude of domains and domain walls are (in iron) (Scheiber P.40, 1967)

Domains - 100 - 10 μm

Domain walls - 0.1 μm ; 300 lattice constants.

An important feature of the properties of domain walls is that their energies are functions of their positions by virtue of their interactions with crystal defects that may be present. In this connection important defects are inclusions, holes and dislocations. These defects have been shown to pin down domain walls to particular locations in the crystal (Roth, 1960).

The size of domains and of domain walls becomes particularly important in finely divided magnetic materials. As the particle size approaches the domain size, the volume occupied by the domain boundaries becomes an increasingly greater proportion of the particle volume and an increasing number of particles become single domain particles. These effects in turn change the magnetic behaviour of the material in the microscopic as well as the macroscopic scale.

Changes in the magnetic behaviour of the material with particle size are important in laterite minerals where a large proportion of the material is present in very small sizes and the bulk of the material is composed of iron minerals which are magnetic.

Superparamagnetic behaviour

A particle ensemble in the superparamagnetic state is characterised by particles which are below the domain size for the material and by a magnetization curve which shows no hysteresis as in Figure 3.6 (in a material which normally does show hysteresis.)

Superparamagnetic (SPM) behaviour is one of the phenomena that occurs in magnetic materials when the particle sizes are very small. The subject of superparamagnetism has been reviewed by Bean and Livingstone (1959); Neel (1962), Kneller, P.393 (1959) and Cullity P.410 (1972).

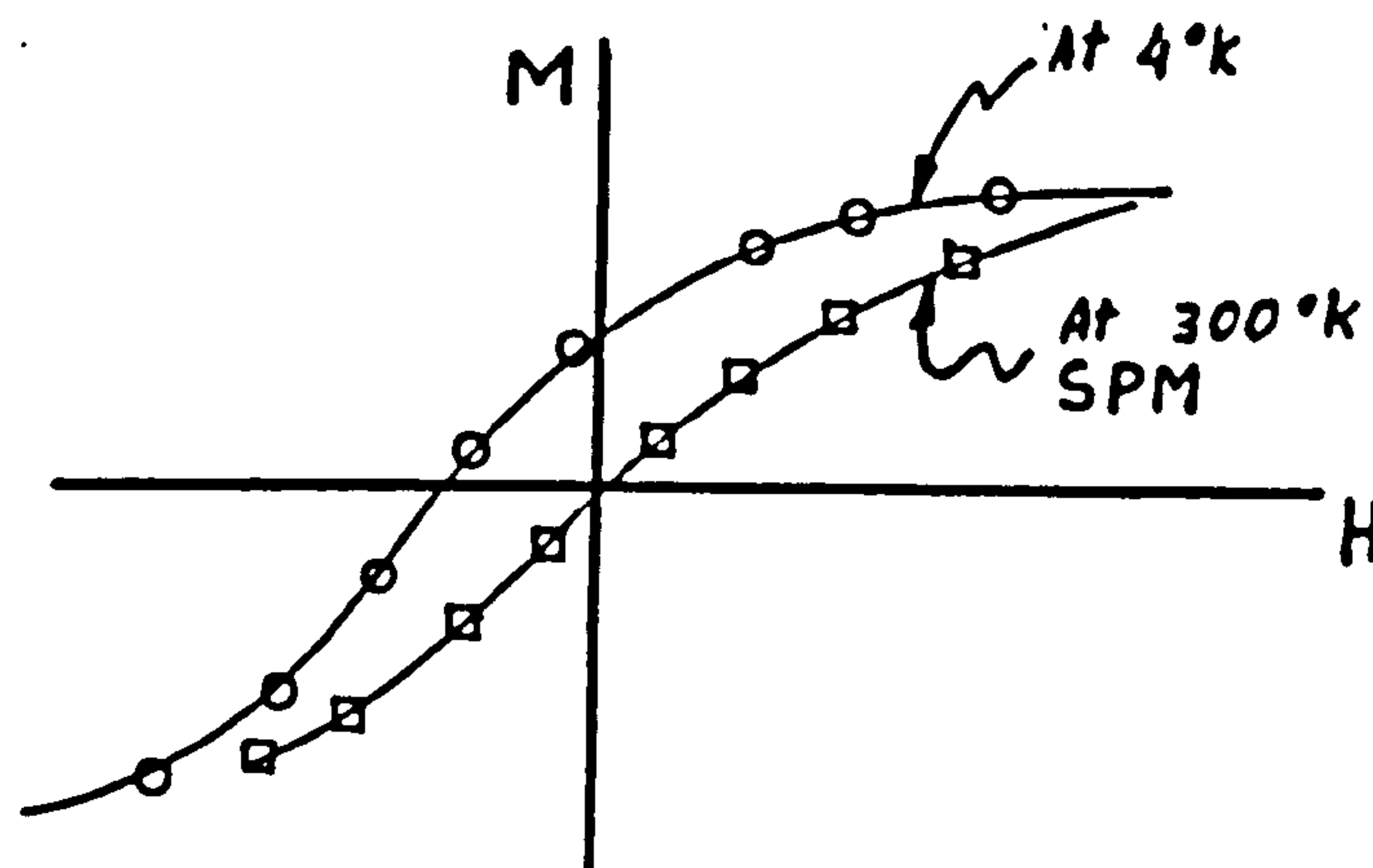


Figure 3.6 Typical macroscopic behaviour of superparamagnetic particles. Magnetization curves of α -Fe particles of 4.4 nm diameter.

If the particles of a material are small enough to be below the domain size, then all the particles will be single-domain. In this instance the energy barrier that a particle must overcome to change (reverse) its magnetization is KV Joules, where K is the anisotropy constant (J/m^3) and V is the particle volume. In any material, fluctuations of thermal energy are continually occurring on a microscopic scale. If single domain particles are small enough, then the energy to reverse the magnetization, KV , is so small that the thermal energy fluctuations can overcome the anisotropy forces and

spontaneously reverse the magnetization of the particle. In this case the direction of magnetization of the particles flips randomly from one easy direction to another even in the absence of an applied field.

If an external magnetic field is applied to an assemblage of SPM particles, the field will align the magnetic moments of the particles without much difficulty. Upon removal of the field thermal fluctuations randomise the magnetic moments of the particles and the sample does not show hysteresis.

If SPM particles of a certain size are cooled, then at a certain temperature the thermal fluctuations become smaller than the energy required for magnetization reversal. At this temperature the SPM behaviour disappears and the material begins to show magnetic hysteresis. Hence the critical diameter below which a certain material behaves as SPM is a function of the temperature and of the anisotropy constant for the material.

Critical particle diameter for SPM behaviour

Suppose a material composed of uniaxial particles has been brought to some initial state of magnetization M_i by an applied field. The field is then turned off at a time $t = 0$. Some particles in the assemblage will immediately reverse their magnetization because their thermal energy is larger than the average. The magnetization of the assemblage will therefore begin to decrease. The rate of decrease at any time will be proportional to the magnetization existing at that time and to the Boltzmann factor $e^{-KV/kT}$. The Boltzmann factor gives the probability that a

particle of volume V at an absolute temperature T has enough thermal energy to overcome the energy gap, KV , required for reversal (k = Boltzmann's constant = 1.38×10^{-23} J/°K.) Hence one can write for the rate of decrease of magnetization M (Cullity P.413, 1972).

$$dM/dt = (M/\tau_0) \exp -(KV/kT) \quad 3.28$$

where τ_0 is a proportionality factor.

If we make the rate of decrease of magnetization equal to M/τ , where τ is some characteristic relaxation time

$$dM/dt = M/\tau \quad 3.29$$

Substitution of this relation in 3.28 results in

$$\tau = \tau_0 \exp (KV/kT) \quad 3.30$$

which relates the relaxation time of the assemblage of particles to the particle volume and the absolute temperature.

τ is strongly dependent on V and T as these quantities are in the exponent. For example in a specimen of cobalt particles, if the diameter of the particles is increased from 6.8 nm to 9 nm the relaxation time increases from 1 second to 3.2×10^9 s = 100 years. Hence it is possible to define an upper limit (in volume) V_p for SPM behaviour by arbitrarily letting a value of $\tau = 100$ s mark the transition from superparamagnetic to normal behaviour.

Examination of equation 3.30 shows that in the limit of high temperature $\tau = \tau_0$, and it is seen that τ_0 is the relaxation time in the limit of high temperatures. (In the literature the inverse of τ_0 , called the frequency factor, is sometimes quoted). τ_0 does not greatly affect the calculations with equation 3.30 so that it is usually sufficient to know its value to within an order

of magnitude. A value of 3.6×10^{-10} S is used as an estimate for calculations with iron (Kneller P.382, 1969; Cullity, P.413, 1972).

Relation 3.30 may be used to calculate the critical particle volume below which a material behaves superparamagnetically at a given temperature. To do this a value of $\tau = 100$ S is chosen and an estimate must be made of the relaxation time τ_0 and the anisotropy constant K for the material in question.

Using estimates of Kündig, et al. (1966) and of Shinjo (1966), Syzdalev (1970) has proposed relations between the critical particle volume and temperature for hematite and goethite. Assuming spherical particles these relations can be written as

$$\begin{aligned} d_{cr} &= 2.2 \times 10^{-9} T^{\frac{1}{3}} \text{ metre (for } \alpha\text{-Fe}_2\text{O}_3\text{)} \\ d_{cr} &= 2.73 \times 10^{-9} T^{\frac{1}{3}} \text{ metre (for } \alpha\text{-FeO OH)} \end{aligned} \quad 3.31$$

These relationships may be used to deduce the particle size of goethite and hematite specimens by detecting the superparamagnetic behaviour with the Mössbauer effect. This method has been used in the present work to estimate the particle size distribution in laterite mineral samples (Section 5.2).

It is important to consider the assumptions which have been made in the deduction of Syzdalev's formulae, 3.31, because they determine the accuracy of calculated critical particle diameters.

Solving equation 3.30 for the particle volume gives

$$V = (kT/K) \ln (f_0 \tau) \quad 3.32$$

In order to determine a particle diameter a particle shape has to be assumed. Syzdalev quotes a "mean particle dimension" so that spherical particles are assumed. The formula also uses a value of K the anisotropy constant for the material. Usually the anisotropy constant is a function of temperature and hence a value of K at the appropriate temperature should be used to calculate the particle diameter.

Coarse particles of hematite show a variation of K with temperature, particularly as the direction of magnetization changes upon cooling through the Morin transition at 260°K . Nevertheless, it has been shown (Nakamura, et al, 1964) that fine particles of hematite do not show a Morin transition and that the magnetization direction remains constant upon cooling to 10°K (Kündig, et al, 1966). It is on the basis of these results that the room temperature anisotropy constant is used to deduce relation 3.31 applicable to hematite.

For goethite the anisotropy constant also depends on temperature. Shinjo (1966) has used relation 3.30 to calculate the value of K in very fine particles of synthetic goethite at two different temperatures. The particle sizes were measured with electron micrographs and by the broadening of XRD lines. The values of the anisotropy constant reported at 210°K and 298°K were, $1.0 \times 10^3 \text{ J/m}^3$ and $1.5 \times 10^3 \text{ J/m}^3$ respectively. Relationship 3.31 for goethite reported by Syzdalev (1970) is based on the value of K at the lower temperature.

These considerations throw some light on the accuracy of the particle size measurements which are obtained with relations 3.31.

It is clear that measurements of the absolute value of particle sizes in these small size ranges are very difficult. Therefore, the detection of superparamagnetic behaviour, although limited by the available data, provides a useful means of estimating particle sizes.

Superparamagnetic behaviour is not restricted to the minerals hematite and goethite discussed here. The behaviour is also expected to occur in all magnetically ordered minerals and therefore formulae

similar to the ones used for hematite and goethite can be written for other minerals and could be used in conjunction with some means of detection of superparamagnetic behaviour to estimate particle sizes.

3.3 Nuclear resonance

In nuclear resonance experiments the nuclei contained in the sample are subjected to a magnetic field or an electric field gradient (EFG) with the result that the ground state energy level of the nucleus is split into two or more sublevels (section 3.1). Normally these sublevels will be occupied according to the Boltzmann distribution law which at room temperature predicts a small difference in the populations of the energy sublevels with the lower one being more densely populated.

An electromagnetic wave of frequency ω (rad/s) is applied externally to the sample and when the frequency satisfies the resonant condition energy is absorbed and transitions take place between the sublevels. The resonance condition is

$$\Delta E = \omega \hbar \quad 3.33$$

where ΔE is the energy difference between the sublevels and $\hbar$ is Planck's constant h divided by 2π . While the frequency is at resonance, energy is absorbed until the saturation condition is attained. In this condition all sublevels have equal populations and as much energy is absorbed as is re-emitted. Normally experiments are carried out below saturation and the existence of a sufficiently fast relaxation process for spontaneous decay to the lower sublevel is required for resonance to be detected.

Nuclear resonance frequencies lie in the radiofrequency region of the electromagnetic spectrum, between a few KHz and several thousand MHz, depending on the magnitude of the splitting of the sublevels.

Nuclear magnetic resonance

In nuclear magnetic resonance (NMR) the splitting of the levels, between which resonance is to take place, is accomplished by applying an external magnetic field to the sample or relying on the existence of an internal magnetic field within the sample itself.

For a nucleus of spin $\underline{I}$ characterised by total angular momentum $\hbar \underline{I}$ and nuclear magnetic dipole moment $\hat{\underline{\mu}}$, the interaction between the magnetic moment of the nucleus and the magnetic field $\hat{\underline{B}}$ (Tesla) is given by the interaction Hamiltonian : (Slichter, 1963).

$$\mathcal{H} = - \hat{\underline{\mu}} \cdot \hat{\underline{B}} \quad 3.34$$

This magnetic interaction splits the spin I level into $2I + 1$ equidistant sublevels (Figure 3.7) each one characterised by a magnetic quantum number m and an energy given by

$$E = -\gamma \hbar B m \quad 3.35$$

where m can take the values $I, I-1, I-2, \dots -I+1, -I$ and γ , called the gyromagnetic ratio, is the ratio of the magnetic moment to the total angular momentum:

$$\gamma = \underline{\mu} / \underline{I} \quad 3.36$$

Quantum mechanical selection rules limit transitions between sublevels to those in which $m = \pm 1$, that is to transitions between adjacent sublevels. The energy separation between adjacent sublevels ΔE is given by

$$\Delta E = \gamma \hbar B \quad 3.37$$

When an external electromagnetic field of frequency ω is at resonance it satisfies relation 3.33 and 3.37, hence the resonant frequency ω ($\frac{\text{rad}}{\text{sec}}$) and the magnetic field are related by

$$\omega = \gamma B \quad 3.38$$

$$f(\text{Hz}) = \frac{\omega}{2\pi} = \frac{\gamma B}{2\pi}$$

This last relation can be used to calculate the resonant frequency for any nucleus in which the magnetic moment has been previously measured*.

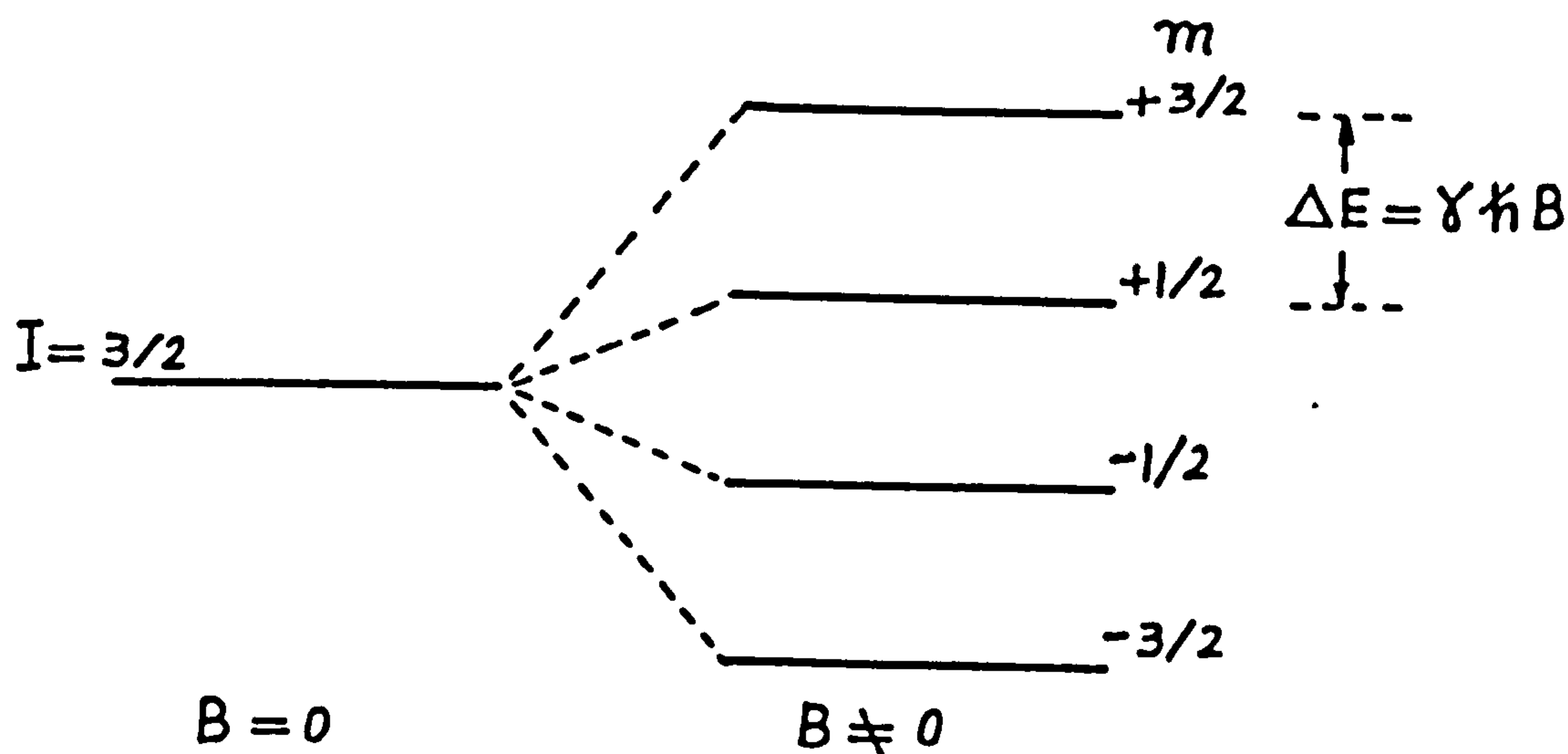


Figure 3.7 Splitting of a spin $I = 3/2$ energy level into four magnetic sublevels by the application of a magnetic field B .

Resonant frequencies for most isotopes with nuclear spins different from zero have been measured and are tabulated (Emsley, et al. Appendix A, 1966). In a 1.0 Tesla magnetic field the resonance frequencies range from about 0.3 MHz to about 45 MHz ($f(\text{Hz}) = \omega(\text{rad/s})/2\pi$).

*Relation 3.38 can be written in terms of the magnetic moment with the use of 3.36 as $f(\text{Hz}) = \mu B / \hbar$ so that tabulated values of the magnetic moments in nuclear magnetons ($\text{nm} = e\hbar/2Mc = 5.04929 \times 10^{-27} \text{ J/T}$) can be used to calculate resonant frequencies.

Therefore if a magnetic field is externally applied it is a straightforward matter to calculate with the use of the tabulated values the frequency at which resonance should be observed in any given isotope.

The experiment consists in observing the absorption of a continuous external radio frequency wave which is tuned to the particular resonance either by varying the frequency in a fixed magnetic field or more usually by varying the field and keeping the exciting radio frequency constant.

From the experimental point of view a distinction is made between instrumentation which is devoted to detecting very sharp resonance lines as in liquids and relatively wide resonance lines as in solids. The former are called high resolution NMR instruments and are largely concerned with $I = \frac{1}{2}$ nuclei such as H^1 , F^{19} , P^{31} etc. in liquids or solutions. The instrumentation devoted to detecting relatively wide resonance lines is called wide-line NMR and is the most appropriate technique to study resonances in solid materials.

As seen above in NMR experiments in which an external magnetic field is applied, the resonance frequency is dependent on the magnitude of the external field. The characteristics of the particular specimen often manifest themselves by modifications of the resonant frequency brought about by the internal fields in the material.

Examination of the Hamiltonian for the interaction shows (Cohen and Reif, P.338, 1957) that the magnitude of the angle between the direction of the applied field and the direction of the internal fields, determine the positions of some, and in certain cases of all, of the energy levels. This creates no problems in the study of single crystals

but if the specimen is a polycrystalline powder with a random orientation of crystallites then the resonance frequency is shifted randomly and the expected spectrum consists of a very broad line. Sometimes, with fine structures, this is an unfortunate fact which limits the usefulness of wide-line NMR in the study of solids. The broad lines become difficult to detect and much of the information which would otherwise be available about the internal fields is lost.

Zero-field nuclear resonance

In the absence of an externally applied magnetic field it is still possible in some cases to observe nuclear resonance. The necessary condition is that the ground state level of the isotope in question be already split due to the existence within the specimen of an effective magnetic field or an electric field gradient produced by the hyperfine environment surrounding the nucleus. When the splitting of the level is due to magnetic fields within the specimen the technique is called zero-field NMR. If the splitting is due to an electric field gradient the technique is called nuclear quadrupole resonance (NQR).

Zero-field nuclear resonance experiments, in addition to providing the magnitude of the hyperfine fields in single crystals, can yield information on polycrystalline samples that is not available in experiments in which an external magnetic field is applied. Experiments of this nature were until recently only seldom carried out due to experimental difficulties. This situation is now changing with the relatively recent commercial availability of NQR spectrometers,

(Smith, 1977), with more sophisticated methods of data analysis due to the generalization of computer averaging techniques, and with the introduction of new techniques such as nuclear double resonance (Schmied, 1973; Edmonds, 1977).

The main difficulty in the use of zero-field NMR and NQR spectroscopy is the problem of locating the resonance frequencies. This is due to a lack of prior knowledge of the magnitude of the internal fields and to the inherent weakness of the resonant signals. If the magnitude of the fields is unknown it implies that a very wide frequency range has to be scanned at high sensitivity to determine the resonant frequency. It is therefore necessary to make use of any information that can narrow down the range of frequencies to be searched. In the event that no resonances are detected in any particular frequency range, this may still be due to insufficient spectrometer sensitivity.

Another difficulty is that once a resonance signal is found it is not immediately known which of the many atoms in the specimen is producing the resonance. This may be resolved without undue difficulty in a simple compound, but in a complex mixture as one would expect in natural minerals, it may be difficult to establish which element corresponds to the observed resonance.

In all of the techniques discussed above the radio frequency signal which is used to excite resonance is assumed to consist of a continuous radio frequency field. Such experiments are called continuous wave (CW) methods as opposed to pulse resonance methods.

Pulse NMR Qualitative

While in CW resonance methods the specimen is placed in a continuous radio frequency field, in pulse experiments the sample is placed in a coil and a very high burst of radio frequency (RF) power is applied during a very short time. If the RF pulse is at or near the resonant frequency of nuclei in the specimen these will absorb energy from the RF field and subsequently will "decay" or relax back to their original state. The pulse spectrometer picks up the decay signal in a coil around the sample and, after suitable amplification and filtering, displays it on an oscilloscope or other display device. This decay signal is called the free induction decay (FID). Provided the RF pulse is short compared to the signal decay the FID approximates to the Fourier transform of the absorption line. Observation and recording of the FID signal in the time domain then allows reconstruction of the absorption line in the frequency (energy) domain. (Farrar and Becker, 1971).

Pulse NMR experiments therefore provide, in addition to the resonance frequency, information about the mechanisms by which the nuclear spins excited by the RF pulses return to thermal equilibrium. The time constant which is characteristic of the establishment of equilibrium with the crystal lattice is called the spin-lattice relaxation time (T_1). The time constant which is characteristic of the establishment of equilibrium between the nuclear spins themselves is called the spin-spin relaxation time (T_2). Both T_1 and T_2 may be measured by suitable sequences of RF pulses. In most solids $T_1 \gg T_2$.

Pulse NMR, Quantitative

Assume a specimen with nuclear spin I and nuclear magnetic dipole moment μ . If this specimen is placed in an external magnetic field B_0 which we assume coincides with the z -axis, the nuclear spins will precess around the field axis at the Larmor precession frequency ω_0 (Radians/sec) given by relation 3.38:

$$\omega_0 = \gamma B_0$$

The vector summation of the precessing nuclear moments results in a macroscopic magnetization (M) in the specimen along the z -axis.

If an RF pulse with field B_1 , oriented along the y -axis and oscillating at the Larmor precession frequency is applied for a short time; it will turn the magnetization in the x - z plane with a precession frequency ω_1 about the y -axis given by

$$\omega_1 = \gamma B_1 \quad 3.39$$

The angle of rotation of the magnetization achieved during the short time t_p (sec.) that the field is applied is α (radians) where

$$\omega_1 = \alpha / t_p \text{ radian/sec} \quad 3.40$$

From relations 3.39 and 3.40, provided B_1 is constant, it follows that the angle α of rotation of the magnetization is related to the duration of the RF pulse t_p by

$$\alpha = \gamma B_1 t_p \quad 3.41$$

If the pulse duration t_p is such that the angle of rotation of the magnetization is $\alpha = \pi/2$ or $\alpha = \pi$; the pulses are called, respectively, 90 degree pulse or 180 degree pulse. Relation 3.41 is used to determine the magnitude of the RF field and pulse duration which produces a 90 degree pulse when searching for resonances in a pulse spectrometer.

3.4 Nuclear resonance in magnetic materials

To understand the phenomenon of zero field nuclear resonance of Fe^{57} in magnetic materials it is necessary to pay special considerations to the magnetic structure of the materials. The first reason is that the ground state of Fe^{57} has spin $\frac{1}{2}$ and as such has a magnetic dipole moment but zero nuclear quadrupole moment. Hence zero-field nuclear resonance experiments on this isotope can only be carried out in magnetically ordered materials which, under the conditions of the experiment, provide a net effective magnetic field at the Fe site.

The second reason is that the radio frequency (RF) field which induces the transitions between the nuclear sublevels in magnetic materials is not the externally applied RF field. In magnetic materials the nuclei are "shielded" from external fields by the magnetic structure of the material itself. Hence the RF field seen by the resonant nuclei is the consequence of the interaction of the external RF fields with the internal fields. The mechanisms through which nuclei respond to the externally applied RF field have been the subject of a number of papers since the discovery of nuclear resonance in ferromagnetic materials. (Gossard and Portis, 1959; Portis and Gossard, 1960, Jaccarino, 1965; Portis and Lindquist, 1965).

Resonance mechanism in magnetic materials

The first detection of a resonance signal in a ferromagnetic material was Co^{59} in metallic cobalt (Portis and Gossard 1959).

Soon afterwards (1960 to 1963) resonance of Fe^{57} and Ni^{61} were reported in a number of magnetic materials. The following notes

summarise the mechanism proposed in these papers to explain the observed results. They have been taken mainly from Portis and Gossard (1960), Streever and Bennett, (1963) and from the review article by Portis and Lindquist (1965).

Nuclear resonance excitation in magnetic materials takes place indirectly through the response of the sample magnetization to the RF field rather than by the radio frequency field acting directly over the nuclear moments. For these reasons the resonance response of any magnetic material depends on the magnetic structure and magnetization processes in the material. Other factors which affect the magnetic structure such as lattice defects, crystallinity and particle size may have a profound effect on the nuclear resonance response through modifications that they produce on the character of the magnetic structure of the material.

In metals or materials with high electrical conductivity the electron conduction limits the penetration of the RF field to the skin depth. In this case the material can be subdivided into small particles in order to increase the proportion of the material which is penetrated by the RF field. The usual practice is to use fine metal powders produced either by hydrogen reduction of the oxide or by grinding the material. These fine particles are then placed in the RF coil diluted by an inert insulating powder or suspended in cotton or glass wool to reduce the "loading".

The effect of a transverse field H_x provided by the applied RF is to turn the electron magnetization M through an angle H_x/H_a , where H_a is the static anisotropy field acting on the electrons. (Portis and Lindquist, 1965). This establishes a transverse magnetization M_x given by

$$M_x = M (H_x/H_a)$$

The nuclei, which are subject to an effective magnetic field H_n , will see a transverse field H given by

$$H = H_x + (M_x/M)H_n = H_x + (H_N/H_a)H_x$$

or

$$H = H_x (1 + H_N/H_a)$$

Thus the field seen by the nuclei is enhanced by a factor $(1 + H_N/H_a)$ which affects the transition probability and the energy absorption rate. H_N the effective magnetic field at the nucleus is much greater than H_a the anisotropy field and the enhancement factor has been found to be extremely large; up to several orders of magnitude in some substances.

Some examples of magnetic materials which show large enhancements in their nuclear magnetic resonance signals are Co^{59} in metallic cobalt (Portis and Gossard, 1960), Co^{59} in ferromagnetic alloys made with Co and Fe, Ni, Cu, Cr, Mn and Al (Kushida, et al. 1962), Fe^{57} in metallic iron (Budnick, et al, 1961), Fe^{57} in the iron oxides hematite and magnetite (Matsuura, et al. 1962; Ogawa and Morimoto, 1962; Boyd and Slonczewski, 1962; Boyd, 1963) and Ni^{61} in nickel metal (Bruner, et al. 1961; Streever and Bennett, 1963).

It is important to consider the enhancement mechanism since its presence may determine whether resonance absorption can be observed. When the RF is applied to a magnetic sample its magnetization can change either by domain rotation or by domain wall displacement. Hence the enhancement mechanism occurs through one or the other of these two phenomena.

Domain rotation

Domain rotation can occur in multidomain and in single domain particles. For single domain particles or for large particles magnetically saturated by a static applied field the sample response can be described by a small displacement of the uniform magnetization produced by the applied RF field, as shown above. This occurs if the RF field is incapable of true domain rotation. This case has been considered by Portis and Lindquist (1965) who derived expressions for the rate of energy absorption in terms of the electronic and nuclear susceptibility.

Magnetic domain reversal or domain rotation from one easy direction to another easy direction as a response to the applied RF field is unlikely in multidomain particles. This is because of the anisotropy energy. However, it would seem that this process may take place in small single domain particles where the field required for switching between magnetization direction is small enough for the available RF fields. In this case the effective magnetic field over the nuclei will experience large variations in magnitude, of the order of the full hyperfine field. No resonance absorption in the conventional sense can be experienced in this case as there is no steady B field to produce the splitting of the nuclear sublevels.

Domain wall motion

In multidomain particles with a weak applied RF field the principal magnetization process is domain wall motion. With an applied field the domain walls shift in such a way as to increase the size of favourably oriented domains. Nuclei located inside

domains experience a strong constant magnetic field and they are "shielded" from the RF excitation, (Portis and Lindquist, P.360, 1965) while nuclei which are located within domain walls will experience variations in the strong internal field due to local rotation of the magnetization as the domain walls shift back and forth following the applied RF field.* This mechanism results in an enhanced RF field being experienced by nuclei within domain walls which has been estimated to be of the order of 10^3 times the applied RF field (Portis and Gossard, 1960; Streever and Bennett, 1963).

In addition to accounting for the magnitude of the driving field at the nuclear site the domain wall motion mechanism can account for the rate of energy absorption. This mechanism is reported to consist of a modulation of the wall losses by the nuclear precession. Estimates of the energy absorption expected are in good agreement with observations and the observed dispersion shape of the resonance signals are also adequately explained.

Other effects well explained by the domain wall motion mechanism are the results of "zero-field" resonance experiments in the presence of externally applied DC magnetic fields or pulsed magnetic fields.

*It would seem that the domain displacements produced by the applied RF field, which are effective in exciting nuclear transitions, must be limited to displacements which are a small fraction of the domain wall dimensions. For larger displacements the fields seen by nuclei are similar to those in domain rotation. Therefore the arguments for non-observation of nuclear resonance of that case would apply.

It is found that the application of a weak external DC magnetic field (up to 1 T) decreases slightly the intensity of the resonance signal. At higher values of magnetic field the signal intensity decreases until it disappears into the noise. The resonance frequency during this time is not shifted, as would be expected if the external field added to the hyperfine field at the nucleus, but rather remains constant within the measurement uncertainty. The decrease of the signal amplitude is due to the decrease in the number of domain walls present as the sample is magnetized. When the sample nears saturation the majority of the walls have disappeared and the resonance signal becomes undetectably small.

From the foregoing discussion it is clear that observation of zero-field nuclear magnetic resonance in magnetic materials depends not only on the intrinsic magnetic factors such as the magnetic structure and its temperature dependence, but also on the state of sub-division of the compound due to the effects that result from whether the particles are multidomain, single domain or subdomain size. In laterite minerals it is a common occurrence that a large proportion of the material is found to be of very small size. Hence the influence of particle size is important in experiments with these materials.

If the mechanism of enhancement which permits observation of the resonance signals is domain wall motion, then a necessary requirement is that the average particle size be large enough so that particles are multidomain. This means sizes not less than 10 - 100 μm (domain sizes of metallic Fe).

On the other hand, if the mechanism of resonance is by domain rotation, the size requirement is not so stringent and sizes down to single domain particles might be tolerated. It is doubtful that even in this case it would be possible to observe resonance in very small subdomain particle sizes. If the particles are so small that they behave superparamagnetically, the magnetization direction is not fixed in any one direction, but oscillates randomly due to the thermal fluctuations. The behaviour of the system is therefore as if the effective magnetic field at the nuclear site is zero (as observed in Mössbauer spectroscopy). It is clear that under these conditions, it is impossible to observe magnetic resonance.

3.5 Mössbauer effect

The physical nature of the Mössbauer effect

The Mössbauer effect is the name given to the phenomenon of recoil-free emission and absorption of gamma rays from nuclei in solids. The phenomenon was discovered by R. Mössbauer (1957) and its use as a tool of research is called Mössbauer spectroscopy.

For nuclei which are relatively free in space such as in liquids or gases, the phenomena of emission and absorption of quanta of electromagnetic radiation (gamma rays) are accompanied by recoil of the absorbing or emitting nucleus. When a nucleus emits a gamma ray in a transition from an excited to a ground state, the nucleus recoils and part of the energy of the transition is taken up by the recoiling nucleus and part is taken up by the gamma ray. The magnitude of the recoil energy is such that the gamma ray now has insufficient energy to resonantly excite another identical nuclei from its ground state to the excited state.

When a gamma ray is emitted in a solid the recoil energy of the nucleus is smaller than the bonding energy between atoms in a crystal; therefore rather than recoiling as in a free nucleus, the atom remains in the lattice and the recoil energy and momentum must be taken by the whole crystal lattice. Since the crystal lattice is so much more massive than the emitting atom, a calculation shows that the whole crystal recoil energy is negligible in comparison with the single nucleus recoil energy.

In solids the atoms are not rigidly fixed in the lattice, but rather oscillate about equilibrium positions. The recoil energy, after a gamma ray is emitted, may therefore be taken up in the lattice by exciting oscillations in the crystal, or in the language of solid state, by creating phonons. Phonons are quantised and therefore can be created only in integral numbers. Thus if the lattice is to absorb the recoil energy a discrete number of phonons must be created. If the recoil energy is large in comparison with the energy of the phonons then there is a large probability of excitation of a number of phonon energy levels. If, on the other hand, the recoil energy is of the order of or smaller than the phonon energy levels, the probability of the recoil energy being taken up by the creation of phonons is much reduced. Recoil-free emission or absorption occurs when no phonons are created by the emission or absorption process so that all oscillators in the lattice remain in the same energy levels. Then the lattice absorbs the momentum as a whole and the gamma ray is emitted with the full energy of the nuclear transition.

The recoil-free fraction f is the fraction of emission or absorption events that take place without the lattice changing state, i.e. without the creation of phonons.

The energy spectrum of gamma rays emitted and absorbed without recoil have the natural energy distribution and the full energy of the nuclear transition; therefore the emission and absorption bands completely superimpose and it becomes possible to observe the nuclear resonance fluorescence phenomenon. The unique feature of recoillessly emitted gamma radiation is that it is monochromatic electromagnetic radiation with a very narrowly defined energy spectrum (1 in 10^{12}). It is this feature, which allows resolution of minute energy differences, which is used to study the physico-chemical environment of resonating nuclei and to deduce physical and chemical properties of materials.

The Mössbauer spectrum

In order to use the Mössbauer effect the effective energy of the gamma rays E_γ from a radioactive source with a substantial recoil-free fraction are Doppler shifted by a relative motion between the source and an absorber containing resonating nuclei. The gamma rays going through the absorber are detected with a radiation detector and are recorded as a function of the instantaneous relative velocity between source and absorber. A Mössbauer spectrum consists of a graph of absorption as a function of relative velocity which by use of the Doppler relation $E = (v/c) E_\gamma$ may be expressed as absorption as a function of energy E (v = relative velocity, c = speed of light E_γ = gamma ray energy).

Any shifts, broadening or splitting of the energy levels of the resonating nuclei in the source and/or absorber are reflected in corresponding variations in the absorption observed in a Mössbauer spectrum.

In order to observe the Mössbauer effect in any particular isotope a number of conditions must be satisfied by the physical properties of the isotope in question. These conditions are reviewed in detail by Greenwood and Gibb P.30 (1971).

The Mössbauer effect has been detected in 72 isotopes of 42 different elements but experimental difficulties restrict to a much smaller number the ones that can be used for the study of material properties. At present only Fe^{57} and Sn^{119} can be run on a routine basis.

The Mössbauer effect in Fe^{57}

The parent radioactive isotope used as a source of the radiation of Fe^{57} is Co^{57} which has a half life of 270 days. This isotope is produced by the $\text{Fe}^{56}(\text{d}, \text{n})\text{Co}^{57}$ reaction. Figure 3.8 shows the decay scheme of Co^{57} . The 14.4 KeV transition is the one commonly used. The lifetime of this first excited state determines the minimum observable energy linewidth of the radiation of 0.192 mm s^{-1} .

If the specimen to be studied contains sufficient iron (more than a few percent) it is usual to use a single-line Co^{57} source and to use the specimen under study as absorber; any shifts or splitting observed in the spectrum will then be produced by the absorber.

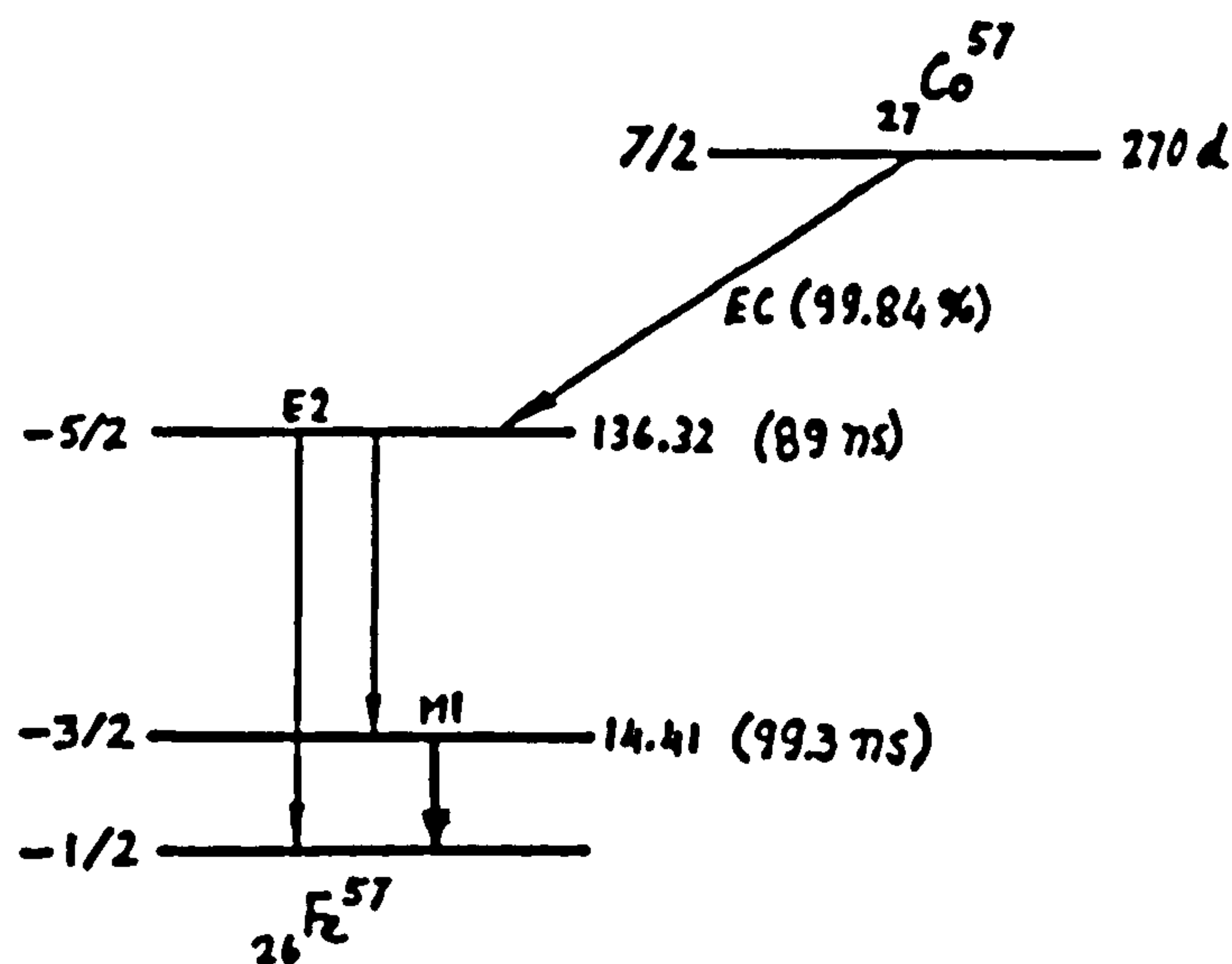


Figure 3.8 Decay scheme of Co^{57} showing the 14.41 KeV transition commonly used in Mössbauer experiments with iron.

Single-line sources are produced by incorporating the Co^{57} activity into a solid matrix that provides a high recoilless fraction and that minimises any hyperfine interaction. Cubic non-magnetic metals such as chromium, copper, platinum and palladium are used as matrices. The single-line Co^{57} sources which are commonly used are available commercially.

Fe^{57} hyperfine splittings

There are three hyperfine interactions which are important in Mössbauer spectroscopy. These are the electric monopole interaction, the electric quadrupole interaction and the magnetic dipole interaction. The splittings of Fe^{57} levels and the shape of spectra produced by these interactions are shown in Figure 3.9. A very brief discussion of these three interactions is presented below.

1) The electric monopole interaction

The electric monopole interaction between the nucleus and the electrons slightly alters the energy separation between the ground state and excited state of the nucleus. This interaction causes a slight shift in the position of the resonance which depends on the nature of the chemical compound or oxidation state of the atom. For this reason it is called the chemical isomer shift.

With Fe^{57} Mössbauer spectroscopy it is usual to consider the isomer shift of pure metallic iron as reference (zero) and to quote the isomer shifts of all other compounds with reference to iron.

2) The electric quadrupole interaction

The electric quadrupole interaction between the nuclear quadrupole moment and the electric field gradient (EFG) produces a splitting of energy levels which have a spin greater than $\frac{1}{2}$.

In the case of Fe^{57} the Mössbauer transition is from spin $3/2$ to spin $\frac{1}{2}$. Hence, if the EFG is not zero, the only level affected is the spin $3/2$ level which splits into two sublevels. The spectrum observed of a polycrystalline absorber is a simple doublet in which the separation of the lines is given by

$$\Delta = \frac{e^2 q Q}{2} (1 + \eta^2/3)^{\frac{1}{2}}$$

where eq is the electric field gradient.

eQ is the nuclear quadrupole moment of the $3/2$ excited level and η , called the asymmetry parameter, is a measure of the symmetry of the electric field gradient (See Section 3.1).

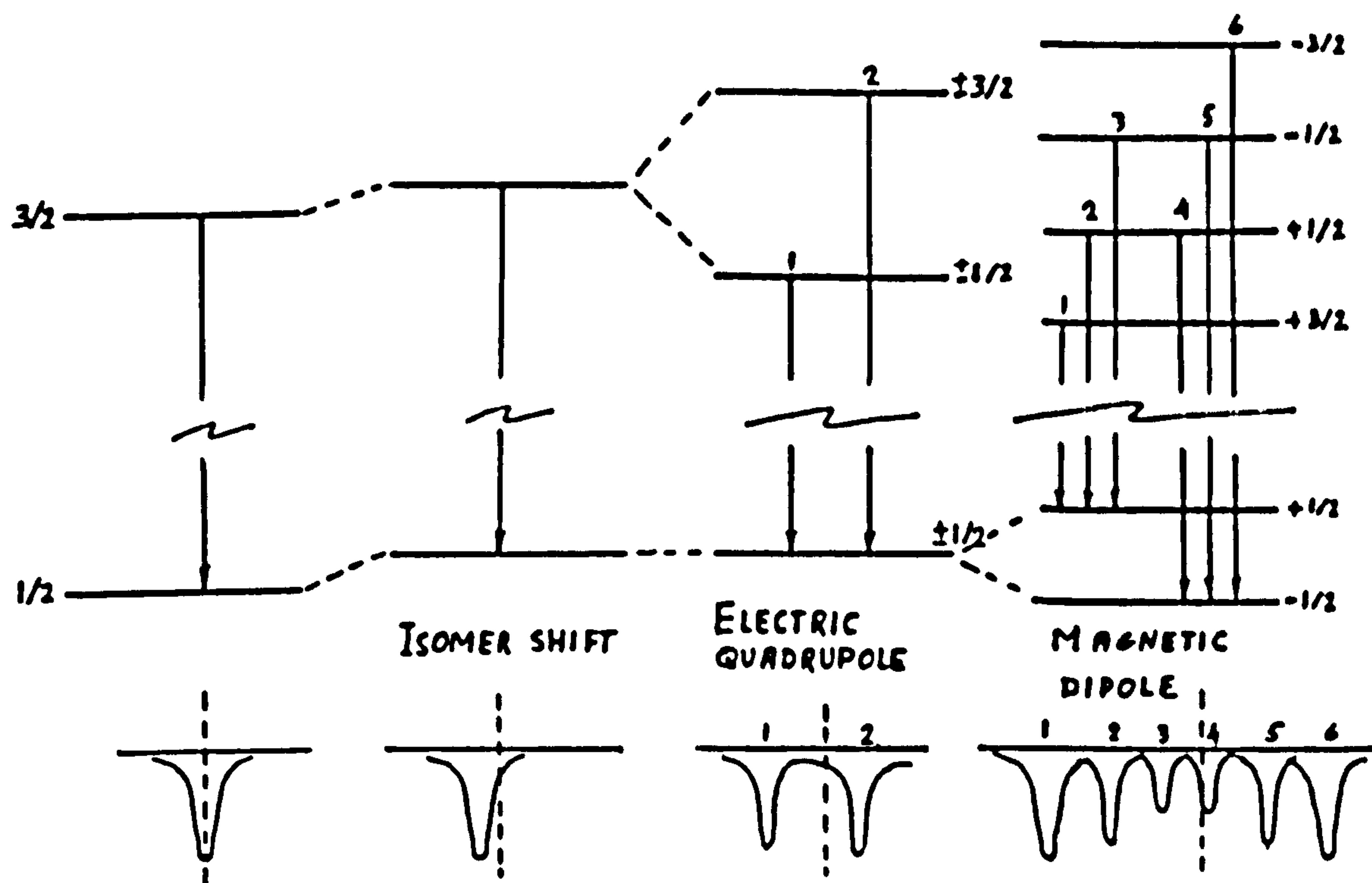


Figure 3.9 The diagram shows the most common splittings of the energy levels of Fe^{57} and the absorption spectra which are obtained from a polycrystalline absorber and a single line source.

In the absence of a magnetic field the asymmetry parameter η and e^2qQ can only be determined from spectra of single crystals. Hence in spectra of polycrystalline powders it is impossible to separate the EFG, the quadrupole moment and the asymmetry parameter. Therefore in the majority of compounds only the "quadrupole splitting", in mm/s equal to the separation between the doublet peaks is measured.

3) The magnetic dipole interaction

The magnetic dipole interaction takes place when there is a net magnetic field at the nucleus. In Fe^{57} nuclei it affects the ground state and the excited state producing splitting of the levels as shown in Figure 3.9. The energy E of each sublevel with magnetic quantum number m is given by equation 3.35

$$E = -\gamma \hbar B_m$$

In Fe^{57} the dipole moment of the ground state and excited states have been accurately measured so that a measurement of the magnetic

splitting in an unknown compound yields directly the magnitude of the effective magnetic field.

In practice magnetic fields are usually obtained by comparing the splitting obtained in an unknown compound with the splitting obtained in a standard material. The usual standard material is metallic iron in which accurate measurements of the magnetic field have been made. Since the isomer shift scale is also based on the metallic iron spectrum, Mössbauer spectrometer calibrations are performed with standard metallic iron foils from which the zero position and velocity scale are derived.

Figure 3.10 shows schematically the Mössbauer spectrum of metallic iron with the splitting used for calibration.

Spectra of Fine Particles

The splittings discussed above and the expected spectra shown in Fig. 3.9 are applicable to bulk material composed of relatively coarse particles. When magnetically ordered materials fall below a certain critical particle size, they behave superparamagnetically (Section 3.2). This behaviour alters magnetic spectra in a drastic manner and instead of the six lines expected from a magnetically ordered material, a single line or a doublet is obtained.

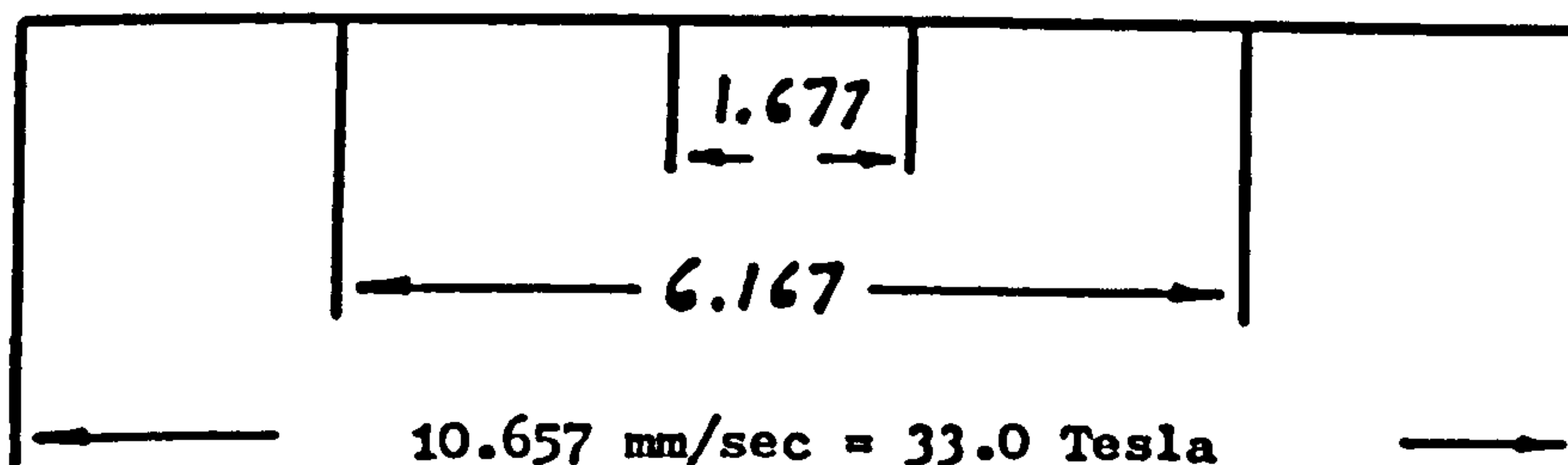


Figure 3.10 Schematic diagram of the Mössbauer spectrum of metallic iron used for spectrometer calibration. Magnetic hyperfine fields may be derived with the use of $1 \text{ mm/sec} = 3.09618 \text{ Tesla}$. (After Muir, et al. MED I, 1966).

The reason why superparamagnetic (SPM) particles show a non-magnetic spectrum is as follows:

In very small magnetically-ordered particles which behave superparamagnetically, the magnetic field orientation changes direction at a high random frequency following perturbations of thermal origin. If by some means the magnetic field is measured during a time significantly longer than the time that the magnetic field remains in a given direction, the field observed averages to zero. This is what happens in the Mössbauer effect measurement. When the magnetic field acting over the Fe nucleus remains constant for a period longer than the lifetime of the Fe^{57} excited level, the nucleus experiences a net magnetic field and a magnetic spectrum is observed. When, on the contrary, the magnetic field fluctuates during the lifetime of the Fe^{57} excited level, the nucleus instantaneously experiences the field, but the measured value averages to zero and the observed spectrum is that of a non-magnetic material.

A measure of the time duration of the thermal fluctuations is given by the constant τ_0 in equation 3.30 Section 3.2. This time is of the order of 10^{-10} s, while the lifetime of the Fe^{57} excited level is 993×10^{-10} s. These values show that for a magnetic particle which behaves SPM, the magnetic field fluctuations are very fast compared with the lifetime of the Fe^{57} level and a non-magnetic spectrum is expected.

Spectra of mixtures

When more than one phase is present in a specimen the Mössbauer spectrum of the specimen consists of the superposition of the spectra of each of the phases contained. (Lerman, et al, 1967). This superposition can be used to determine the proportions of each phase in the specimen.

In a mixture the resonant absorption produced by each phase is proportional to the total number of Fe^{57} nuclei contained and to the recoil-free fraction of each phase. The proportion of Fe^{57} nuclei in each phase can be assumed to be directly proportional to the number of Fe atoms in minerals with natural isotopic composition.

The recoil-free fraction of each phase, at the temperature of the experiment, can be calculated for each of the components with the Debye temperature of the material. This calculation is done with formulae which are derived by assuming a model for the material. Hence their accuracy depends on whether the model is applicable to the compounds in question. Simple formulae for the recoil-free fraction are available which have been calculated with the Debye model of a solid (Greenwood and Gibb, p.11, 1971). These formulae are only valid for cubic monoatomic crystals. Nevertheless, the Debye model gives a reasonable estimate of the recoil-free fraction for materials in which it is not strictly applicable, and hence, for want of a better method, recoil-free fractions are very often calculated using this model.

The problem of using Mössbauer spectra of mixtures for mineral recognition and quantification has been discussed in a number of papers. (Herzenberg, 1970; Bancroft P.155, 1973). Nevertheless it seems that the potential of the method has not been fully developed and that further work is needed. In Appendix C a method is proposed for quantifying the proportions of mineral phases in a specimen, on the basis of its Mössbauer spectrum.

Mössbauer effect in Ni^{61}

This section reviews the possibility of performing Mössbauer effect measurements on Ni^{61} for the purpose of studying lateritic minerals. It also examines the possible usefulness of such experiments in characterising Ni-bearing laterites.

The literature dealing with the Mössbauer effect of Ni^{61} has been reviewed up to about 1970 by Greenwood and Gibb, P.493 (1970). Additional bibliographical listing and basic extracted data of published papers dealing with this isotope can be found in the various issues of the Mössbauer effect Data Index (MEDI) edited by Muir, Ando and Coogan (1966) and Stevens and Stevens (1969-1975). The information presented here has been extracted from these sources.

There are five stable nickel isotopes. Of these only Ni^{61} with a natural abundance of 1.2% is suitable for Mössbauer effect. Figure 3.11 and Table 3.6 taken from Stevens and Stevens, MEDI (1975) shows the energy level diagram of Ni^{61} and basic data as well as derived parameters useful for Mössbauer effect of this isotope. The spins of the ground and excited states of Ni^{61} are 3/2 and 5/2 respectively, therefore both levels will be split in the presence of magnetic fields or electric field gradients. Figure 3.12 shows the splittings in a pure magnetic field and in a pure EFG. Also indicated by line-bar diagrams are the shape of spectra expected in experiments with a single line source and a split absorber. Twelve lines are expected with a pure magnetic field and three lines with a pure EFG.

As can be seen in Figure 3.11, the radioactive sources for Ni^{61} are either Co^{61} or Cu^{61} . Both of these isotopes have short halflives (1.65 h and 3.41 h respectively) which restrict the performance of experiments to locations which have a quick access to the irradiation

Table 3.6 Measured properties and derived parameters useful for Mössbauer effect of Ni⁶¹ (from Stevens and Stevens MEDI, 1975)

Property	Value	Property	Value
Gamma ray energy KeV	67.403(10)	cross section σ_b	71.2(3)
Lifetime ns	5.27(9)	min.linewidth Γ eV	$8.66(15) \times 10^{-8}$
Conversion coefficient α_T	0.135	" mm/s	0.77(13)
Natural abundance %	1.19	Recoil energy eV	.039984(6)
Magn. d. mom.(ground)n.m.	0.7498(1)		
(excited/ground)Mag.d.mom.	-0.637(11)	1 mm/s =	54.368(6) MHz
Elect.q.mom.(ground) b	+0.162(15)	1 mm/s =	$2.24849(23) \times 10^{-7}$ eV
(excited/ground)Elect.q.mom.	-1.21(13)		

b = barn (10^{-28} m²)

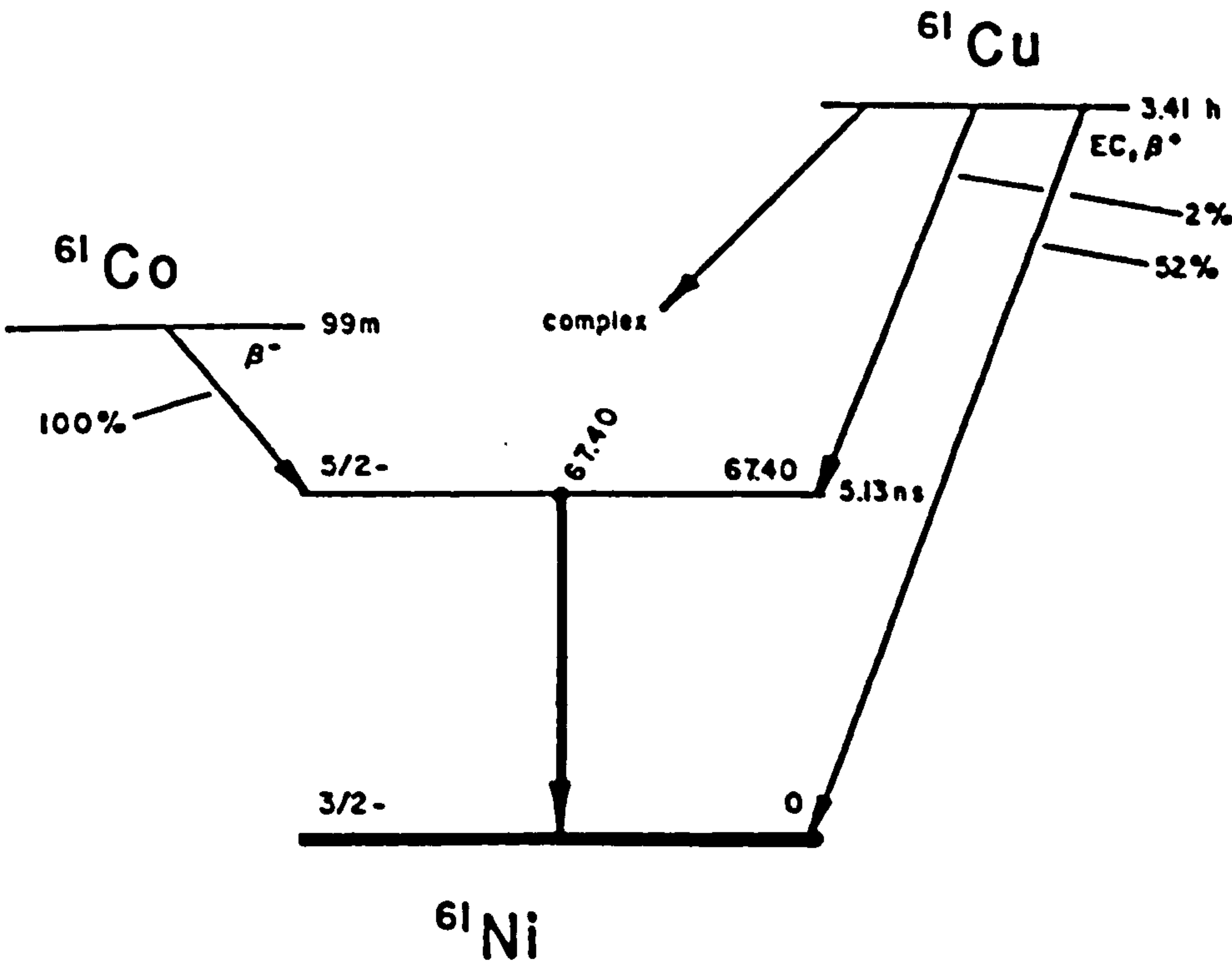


Figure 3.11 Energy level diagram for Ni⁶¹ showing the radioactive sources for this isotope.

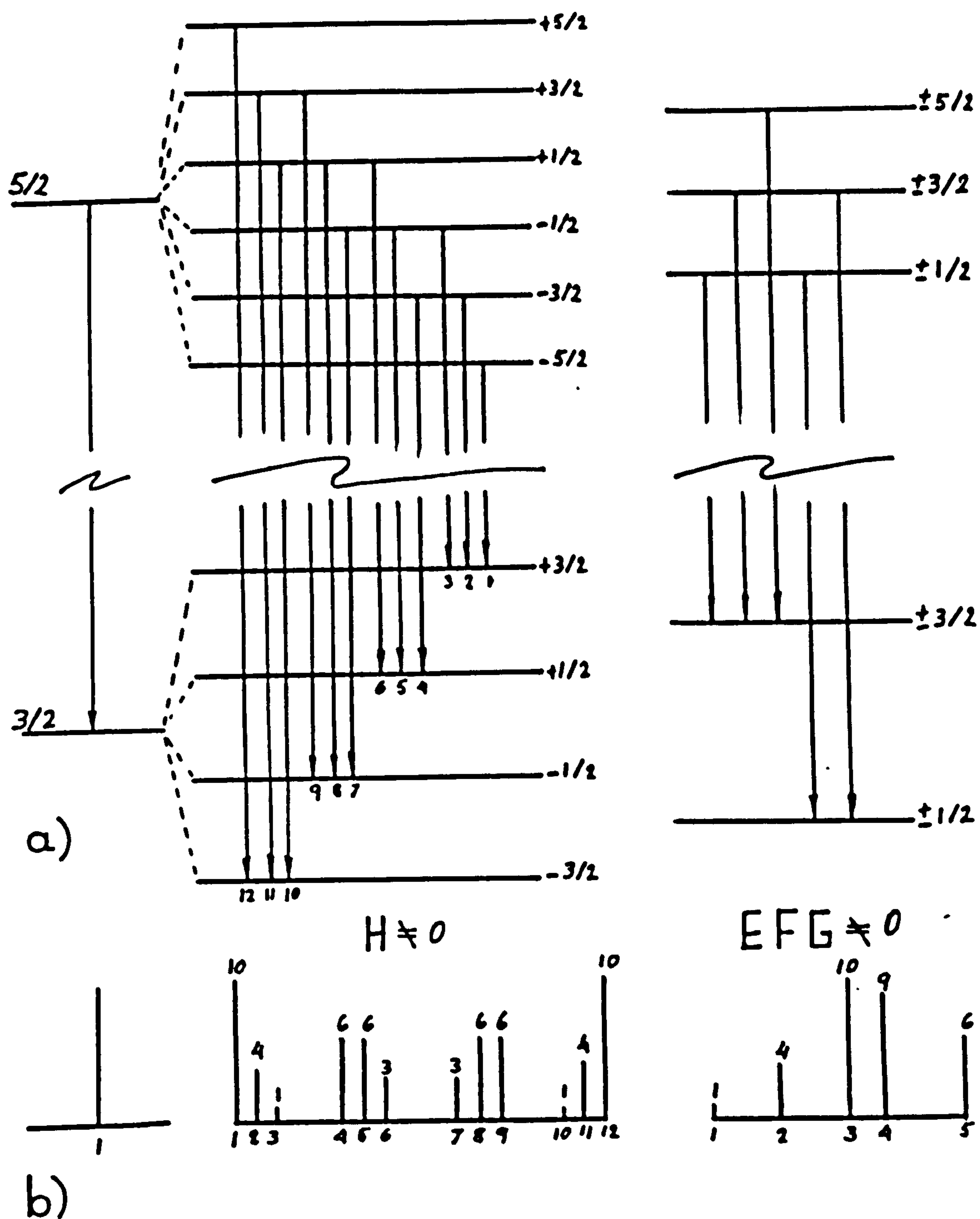
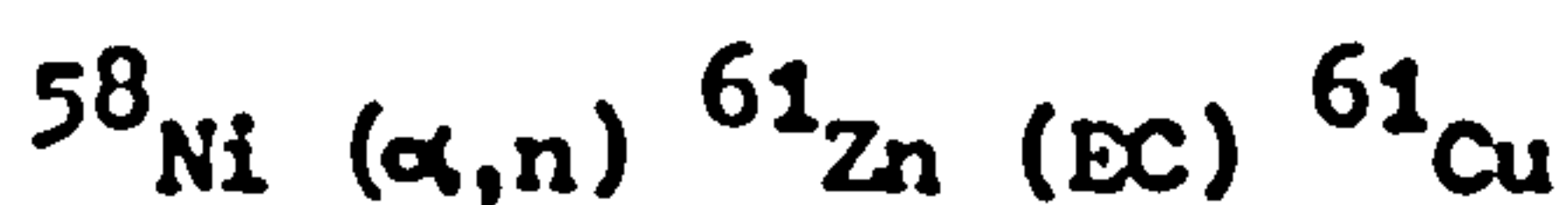
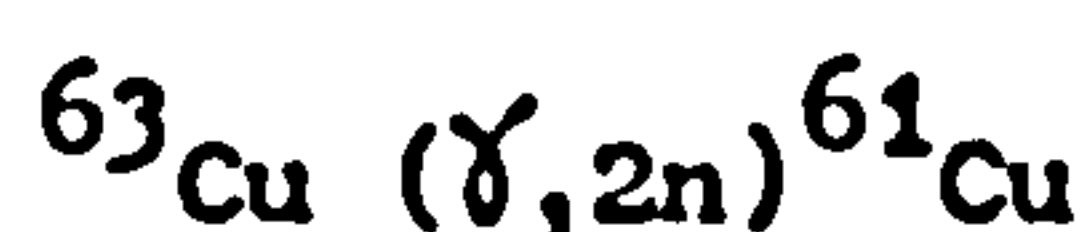


Figure 3.12 a) Splitting of the excited and ground state energy levels of Ni^{61} in a magnetic field, ($H \neq 0$) and in a symmetric electric field gradient ($EFG \neq 0$). b) Expected line positions and intensities of Mössbauer effect spectra of a polycrystalline absorber with a single line source.

machines required for producing the sources. Both Co^{61} and Cu^{61} sources have been used. The reactions that have been used for the production of these sources require the use of charged particle accelerators. Possible reactions are:



The gamma ray energy of the Mössbauer transition is 67.40 KeV. This energy is relatively large and produces a recoil energy in the Ni nucleus of 39.9×10^{-3} eV which is much larger than, for instance, the 1.9×10^{-3} eV of Fe^{57} . This means that the recoil-free fraction expected is much smaller than that of iron and that the use of liquid nitrogen or liquid helium temperatures is required.

For example the recoil-free fraction of a hypothetical compound with a Debye temperature of about 350°K would be 0.08% at 300°K , 1.6% at 77°K and 12.6% at 4.2°K .

The relatively large value of the gamma ray energy results in a value of the resonant absorption cross section of $71 \times 10^{-24} \text{ m}^2$ which is smaller than the $256 \times 10^{-24} \text{ m}^2$ of Fe^{57} .

Another difficulty with this isotope is the low natural abundance of Ni^{61} . The natural abundance of 1.2% of Ni^{61} , coupled with a relatively low value of the gamma ray resonant absorption cross section, means that materials enriched in Ni^{61} should be used. If the materials

to be studied have the natural isotopic composition and a low total nickel content as with lateritic mineral, then to have sufficient Ni^{61} for an optimum absorber would require very thick absorbers which would attenuate the gamma rays in a very significant amount. This difficulty would not be so severe with pure Ni-bearing minerals which contain from 22 to 45 percent nickel.

Assuming that spectra could be obtained, it is of interest to examine how useful these spectra would be. The minimum absorption linewidth observable can be calculated on the basis of the lifetime of the excited level. This value has to be compared with the expected magnitudes of hyperfine shifts or splittings to determine whether spectra will be resolved and capable of yielding accurate measurements of hyperfine field parameters. The minimum observable linewidth is 0.77 mm/s. The magnetically split compound with the highest reported magnetic field at Ni^{61} is 1.5% Ni-Fe alloy where $H = 24.1$ Tesla. In this alloy the absorption spectrum was a pattern about 6 mm/s wide in which the 12 lines expected were only partially resolved. (See Greenwood and Gibb P.494, 1971).

Examination of the splittings reported in the literature of a number of compounds and alloys of Ni shows that the minimum absorption linewidth is of the same order or slightly smaller than the splittings. All of the spectra that have been reported have consisted of only partially resolved peaks. These results establish a fundamental limitation on the accuracy with which the hyperfine fields can be measured by this method in a given compound.

In summary, the short lifetime of the sources, the high energy of the gamma ray and the low natural abundance of Ni^{61} make Mössbauer effect experiments difficult with this isotope. In addition the low proportion of nickel contained in lateritic minerals make the use of Ni^{61} Mössbauer effect a poor prospect as a technique for characterising Ni-bearing laterites.

CHAPTER 4

EXPERIMENTAL METHODS

4.1 Wide line NMR Experimental

It was intended originally to attempt NMR on Al, Ni, Co and Cr present in the laterite samples. These elements all have isotopes in which NMR is possible (Al^{27} , Ni^{61} , Co^{59} , Cr^{53}).

Al was chosen for the first set of experiments as a large, easily detected signal was expected. Natural aluminium consists of 100% Al^{27} , and the sensitivity for this element relative to that for H^1 is reasonably high at 0.2. (Emsley, et al. Appendix A, 1966). In addition the aluminium content in the Al-laterite studied (see Sect. 4.1) is much higher than the other elements considered and suitable samples of reasonably pure natural minerals could be obtained by hand picking. Also available were some synthetic Al-minerals which had previously been prepared.

Only a limited number of experiments were carried out to establish the feasibility of the technique and to evaluate the possible usefulness of the observed spectra in the study of laterite minerals. In view of the results obtained with the Al^{27} experiments and the distant location of the spectrometer no experiments were carried out on the other elements.

Apparatus description

The experiments were carried out in the Nuclear Magnetic Resonance laboratories of the Department of Physics, University of Warwick by courtesy and with the help of Dr. G.A. Styles. The measurements were made in a Varian Associates Ltd.* magnet and wide-line NMR spectrometer.

Figure 4.1 shows a block diagram of the spectrometer. In this instrument both the resonance frequency and the magnetic field can be varied over a wide range either manually or automatically. The frequency ranges allow selection of any value between 3 MHz and 35 MHz using a

*Varian Associates Ltd. 28 Manor Road, Walton-on-Thames, Surrey KT12 2QF (98)43741.

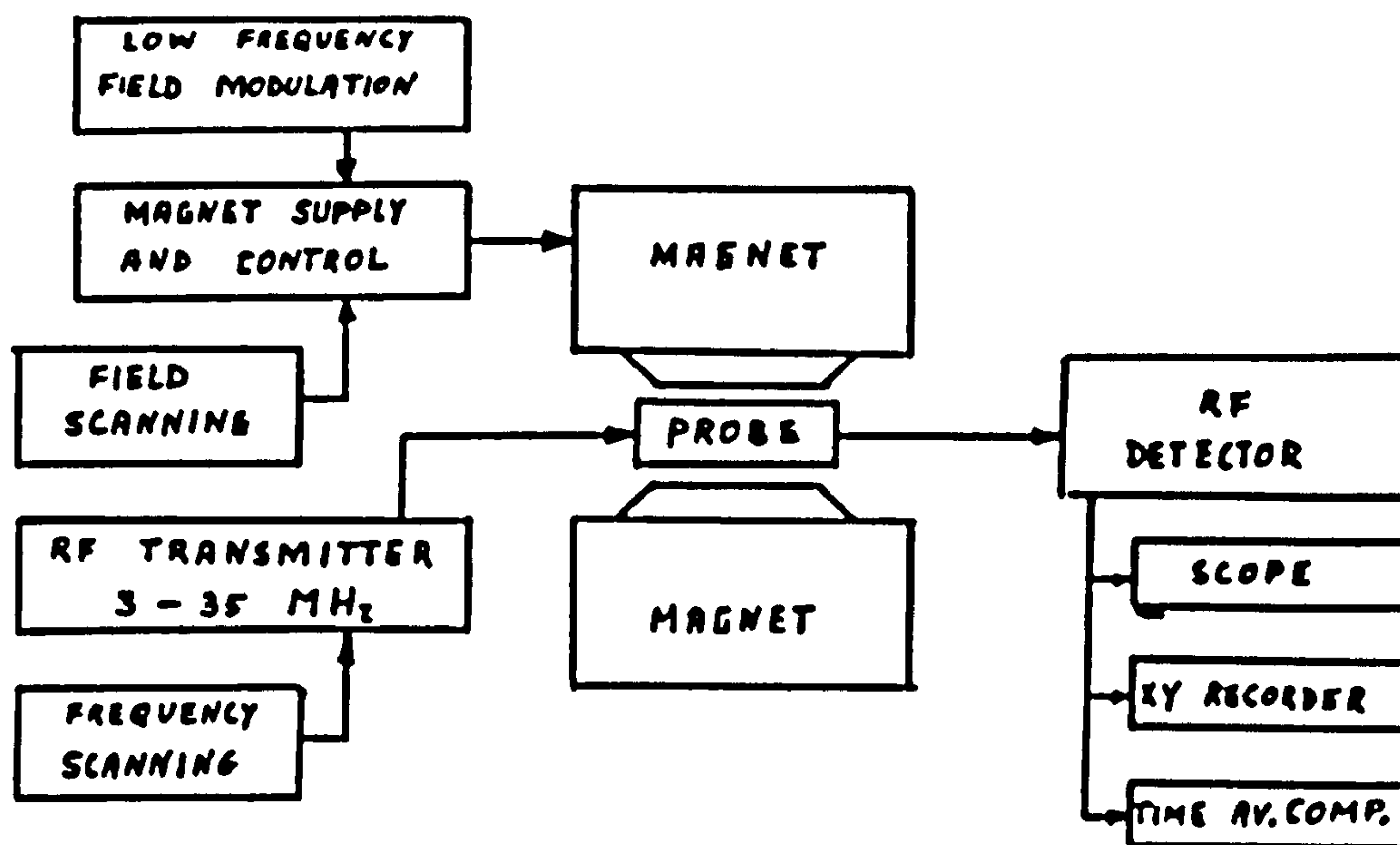


Figure 4.1 Block diagram of the Varian wide-line NMR spectrometer indicating the main functions in the instrument.

range selector switch with three ranges. An automatic frequency scan in each of the ranges is possible with a number of scanning speeds. The magnetic field range allows selection of the field up to about 2.0 Tesla. The field scanning facility allows the full range to be scanned in a number of steps.

Output of the resonance signals is through an oscilloscope, a chart recorder or a time-averaging computer.

When searching for a resonance signal either frequency or field scanning may be used. When recording a spectrum the frequency is kept constant at a predetermined value and the field is automatically scanned over a preset interval about the manually set field. Hence, resonance spectra are not presented as absorption (or dispersion) curves as a function of frequency, but as a function of magnetic field.

All the specimens studied consisted of 1-3 cm³ of polycrystalline powder. These were contained in glass specimen tubes of 17 mm diameter and placed at room temperature inside the sample coil.

Most spectra obtained resulted from relatively fast sweep rates varying from 2 minutes to 30 minutes. The sweep range varied from ± 500 Gauss to ± 50 Gauss. No attempts were made to improve the signals with the time-averaging computer.

4.2 Zero-field NMR and NQR

Zero-field nuclear resonance experiments were done in a number of natural pure minerals, in a number of natural laterite samples and in some synthetic minerals.

The experiments were done to establish the value of the technique as a method of appraising laterite minerals and in order to study the structure of particular minerals.

In this section the main features of the instrumentation and particular details of the experiments are described.

NQR Spectrometer

All of the experiments were done on a Decca Radar Ltd* NQR spectrometer. This instrument was developed in the laboratories of

*Decca Radar Ltd., Instrument Division, Lyon Road, Walton-on-Thames, Surrey, England. Walton-on-Thames 28 851.

Dr. J.A.S. Smith and has been described in the literature (Smith and Tong, 1968; Smith, 1977).

The spectrometer consists of a super-regenerative oscillator (SRO) as the resonance exciting and detecting circuit with its associated control electronics. This design provides high sensitivity and the ability to operate at high RF levels over a wide frequency range. Some of the features of the instrument are: automatic frequency scanning over the range of approximately 10 to 100 MHz, automatic gain control, a high accuracy automatic frequency measuring system and the possibility of using magnetic or frequency modulation for the phase-sensitive detector. The whole of the frequency range is covered in several ranges by changing sample coils. Within each range, frequency scanning is accomplished with a motor-driven tuning capacitor.

The super-regenerative oscillator works in the so-called logarithmic mode. It is externally quenched by a signal that is controlled manually or automatically. This allows automatic gain control through a control of the level of coherence of the quenched RF signal. It is also possible to vary automatically the quenching pulse repetition frequency. This last feature permits the suppression of sidebands which are obtained from a resonance signal with a quenched oscillator.

The instrument is specifically designed for the detection of nuclear quadrupole resonance, but it may be used as an extremely sensitive wide-band NMR spectrometer by using frequency modulation in an externally applied magnetic field or by using magnetic or frequency modulation in specimens that provide an internal magnetic field at the nuclei of interest.

The possibility of automatic frequency scanning makes the instrument particularly useful when searching for nuclear resonances when the exact resonance signal is unknown, but the expected frequency range is known.

The output of the spectrometer is a chart recorder in which resonance signals are plotted as a function of time in synchronism with the automatic frequency scanning of the spectrometer. The plots thus produced are absorption or dispersion signals as a function of frequency. It is possible to observe limited frequency regions either in an oscilloscope or to use a time averaging computer, but neither of these facilities were used.

Coils

Specimens consisting of 3-5 g of material were placed in 12 mm diameter glass tubes inside a coil which is part of the tank circuit of the SRO. Decca coils as well as specially designed coils were used. Specially designed coils improved the sensitivity and signal to noise ratio of the resonance signal. Figure 4.2 shows the geometry of typical coils.

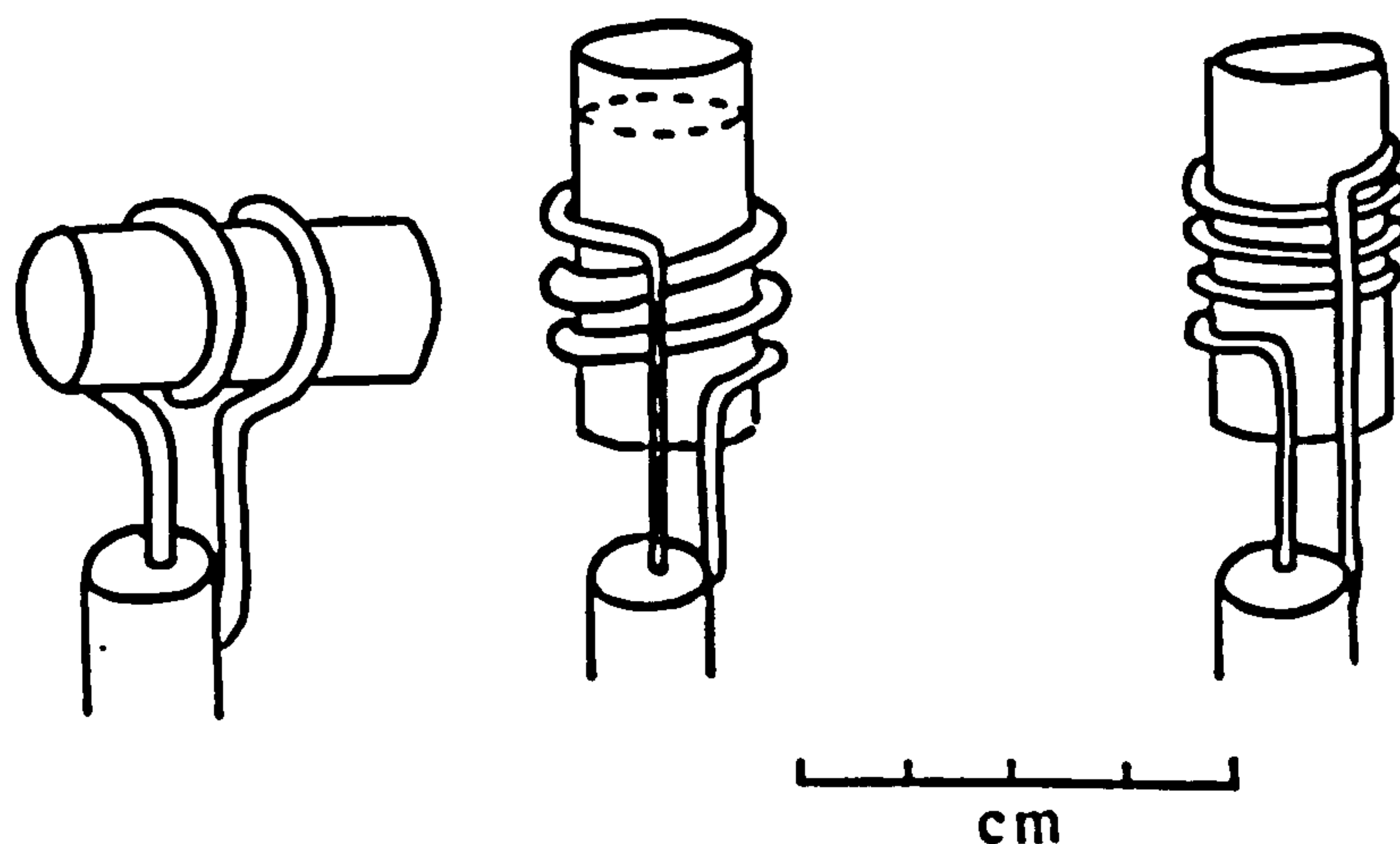


Figure 4.2 Geometry of typical sample coils used with the Decca NQR spectrometer.

The winding of successful special coils depends on closely following recommended practice for RF coil design. (Terman, P30-40, 1955; Luznick and Trontelj, 1978). In making special coils for this instrument the design objective is to produce a coil with the highest possible Q factor in the frequency range that the resonance signals are found. Q values of successful coils were typically in the range of 140 to 200 at their design frequency.

The coils were connected at the end of a short shielded probe which was located inside a small Dewar and surrounded by the magnetic modulation coils.

In order to use the Decca NQR spectrometer as a wide-band NMR spectrometer in an externally applied field, a long probe was constructed capable of reaching the gap of a large magnet. This probe was intended for the detection of proton resonances and hence only proton-free materials were used in its construction. Figure 4.3 shows the geometry of the long probe.

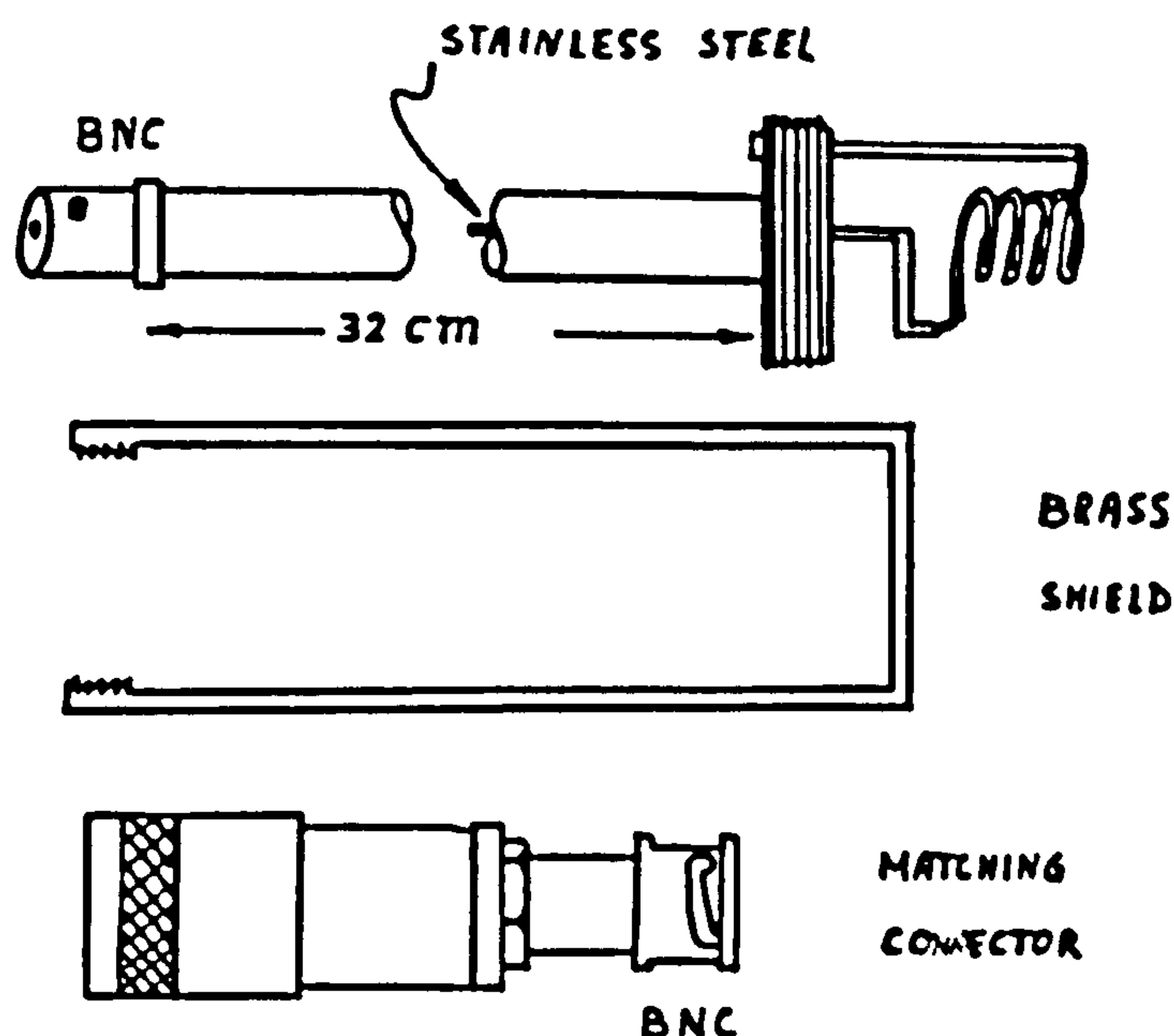


Figure 4.3 Geometry of the long probe used for proton resonances in an external magnetic field.

Cryostat

In order to study the resonant frequency as a function of temperature in some specimens, use was made of a general purpose cryostat modified for resonance work.

The cryostat was an Oxford Instruments cryostat and associated control instrumentation. It consists of a cold finger cooled by a controlled flow of N_2 gas. In order to adapt it to the Decca NQR spectrometer a low temperature probe was designed and built to match the cold end of the cryostat. In this arrangement the specimen tube and RF coil are enclosed in the cryostat vacuum chamber and in intimate contact with the cold finger (figure 4.4). With this arrangement it was possible to lower the temperature in a controlled and reproducible manner to about $100^{\circ}K$ with the use of liquid nitrogen. Temperature stability was $\pm 0.2^{\circ}K$ at any temperature reached. Figure 4.5 shows a block diagram of the cryostat and control instrumentation.

The lower limit of $100^{\circ}K$ achieved is due to the high heat leak into the cryostat produced by the conflicting requirement of having short leads and high electrical conductivity between the cold sample coil and the SRO held at room temperature.

The $77^{\circ}K$ experiments were carried out by immersing the Decca probe with coil and sample in liquid nitrogen.

In order to increase sensitivity and improve the signal to noise ratio of some low temperature resonance signals, experiments were conducted with special coils enclosed inside the sample container. (As opposed to the usual arrangement of the coil surrounding the sample container). The sample container was constructed of metal thereby restricting the RF field to the inside of the container.

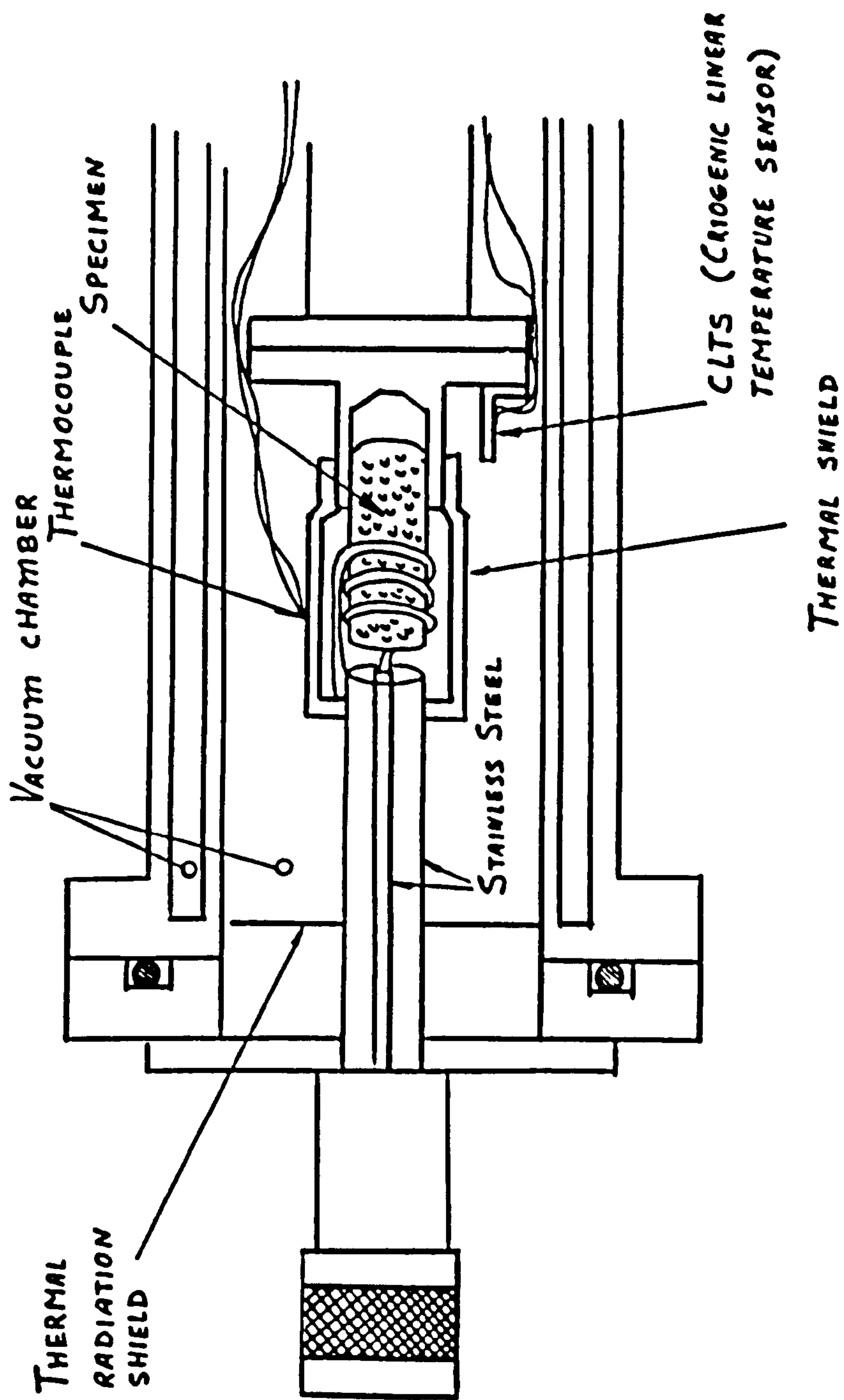


Figure 4.4 Diagram showing the low temperature probe at the cold end of the cryostat. Attachment to the spectrometer is via the connector on the left.

This geometry produces the maximum possible filling factor and it was found that an improved signal/noise ratio was achieved with some samples. Figure 4.6 shows the arrangement. A drawback of this arrangement was that it made the spectrometer operation strongly dependent on the electrical characteristics of the specimen. In particular it was found that the arrangement could not be used with highly magnetic specimens (magnetite) or with metallic powders, probably due to the specimen electrically shorting the coil.

Sample treatment

Samples consisted of 3-5 g of specimen powder although as little as 0.5 g was used when strong signals were found. All specimens had been previously characterised by optical examination, X-ray diffraction and sometimes chemical assay in order to establish the phases present, the purity of the material and degree of crystallinity.

With minerals that showed piezomagnetic or piezoelectric resonances (Section 5.1) it was necessary to grind to fine powder and sieve ($\sim 63 \mu\text{m}$) in order to avoid interference of these resonances. In experiments with fine metal powders (Fe and Ni) the material in the form of fine dust was dispersed by suspending it in cotton or glass wool and filling the specimen tube with the impregnated material.

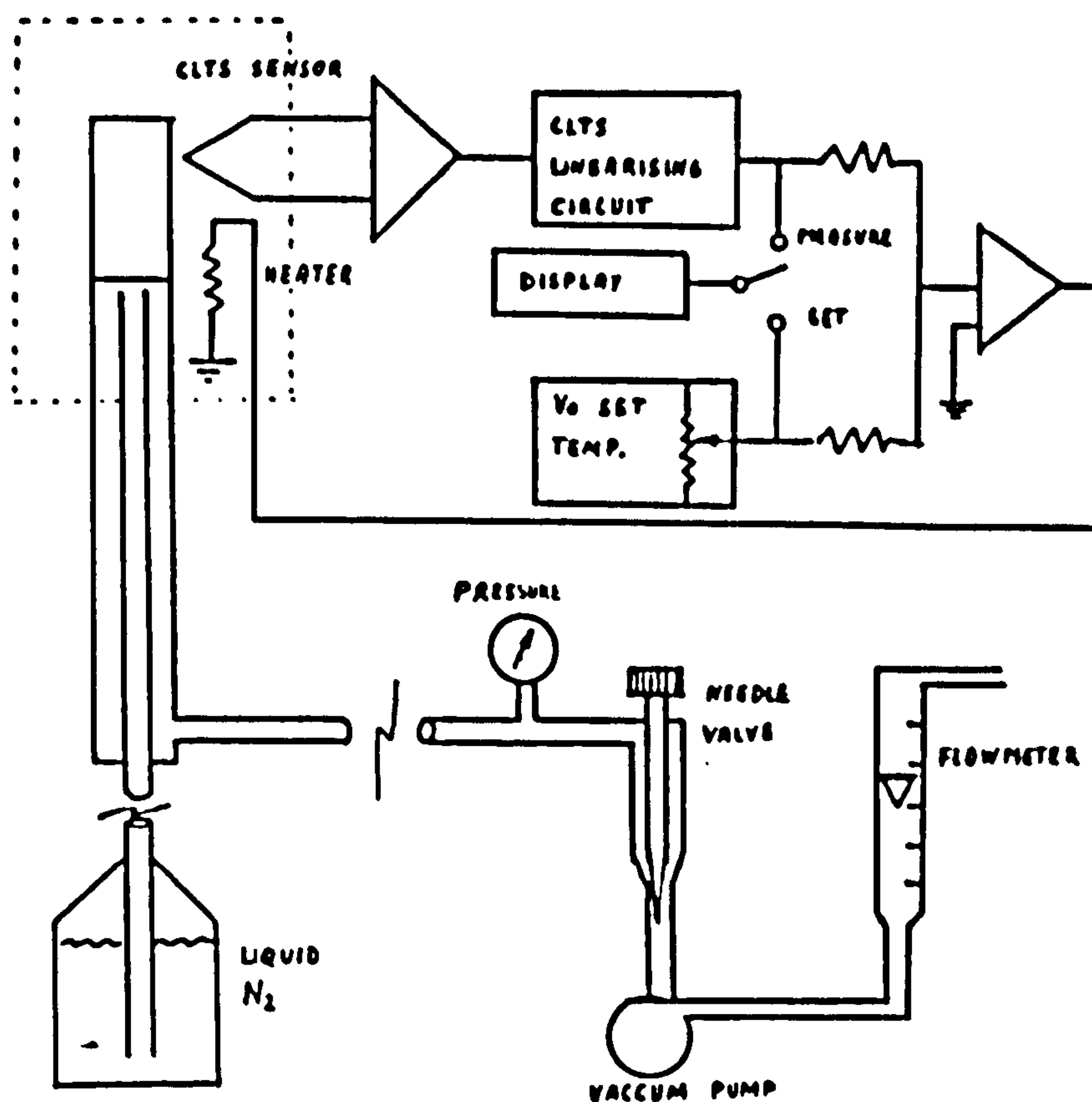


Figure 4.5 Diagram of cryostat control. Coarse temperature setting was achieved by adjusting the N_2 flow with the needle valve to a temperature just below the value required. Then the required temperature is set and maintained by the electronic control.

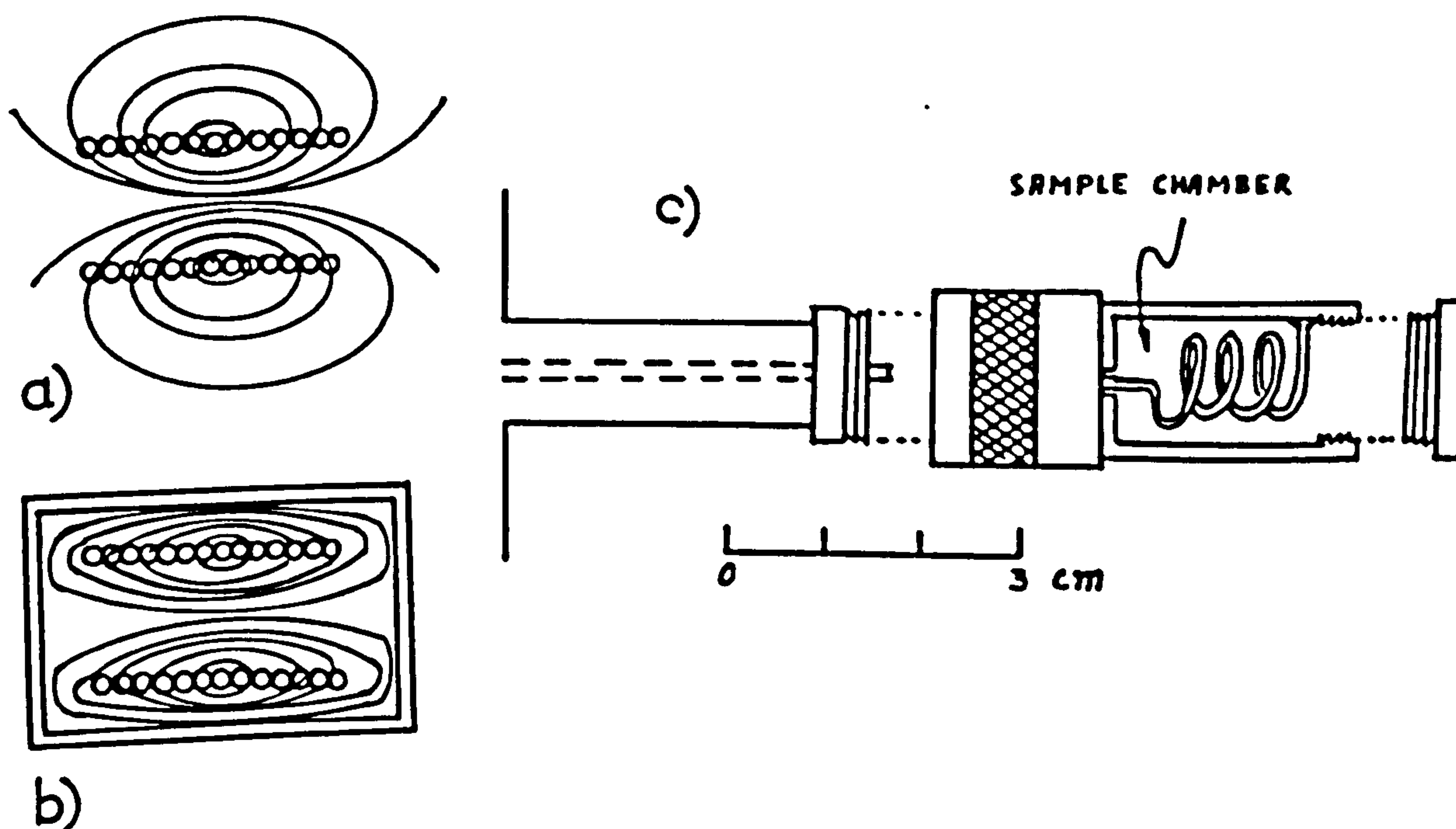


Figure 4.6 a) Magnetic induction field in an unshielded coil.
 b) Induction in a coil with a conductive, non-magnetic shield.
 c) Actual arrangement: modified type N high frequency connector.

4.3 Pulse NMR

Pulse experiments were carried out because this method might provide resonance signals in compounds for which signals had not been obtained by the CW method, particularly in the goethite samples. If the hydrogen resonance in goethite could be detected by pulse techniques and the free induction decay signal was long enough it would show the feasibility of carrying out double resonance experiments in this mineral. The technique of double resonance (Schmiedt, 1974; Edmonds, 1977) allows the study of very weak resonances and it was hoped that it could allow the detection of Fe^{57} resonances or possibly the resonance of Ni^{61} contained in goethite.

Apparatus description

The apparatus used was a Bruker Pulsed NMR spectrometer B-KR-322S. This is a variable frequency instrument capable of pulse spectroscopy in the frequency range of 4 MHz to 65 MHz. (Figure 4.7). It consists of a RF signal generator which provides a low power, CW, RF signal source for the program pulse generator.

The program pulse generator produces a repetitive train of one to four pulses of RF power arranged according to preset programs. All common program sequences are available with variable pulse width and delays between pulses. The pulse programs are then amplified by a tuned power amplifier in the transmitter which delivers the RF pulses to the sample probe.

The nuclear signals which result from the pick-up coil go through a preamplifier and amplifier before display in an oscilloscope. Diode or phase-sensitive detection are available.

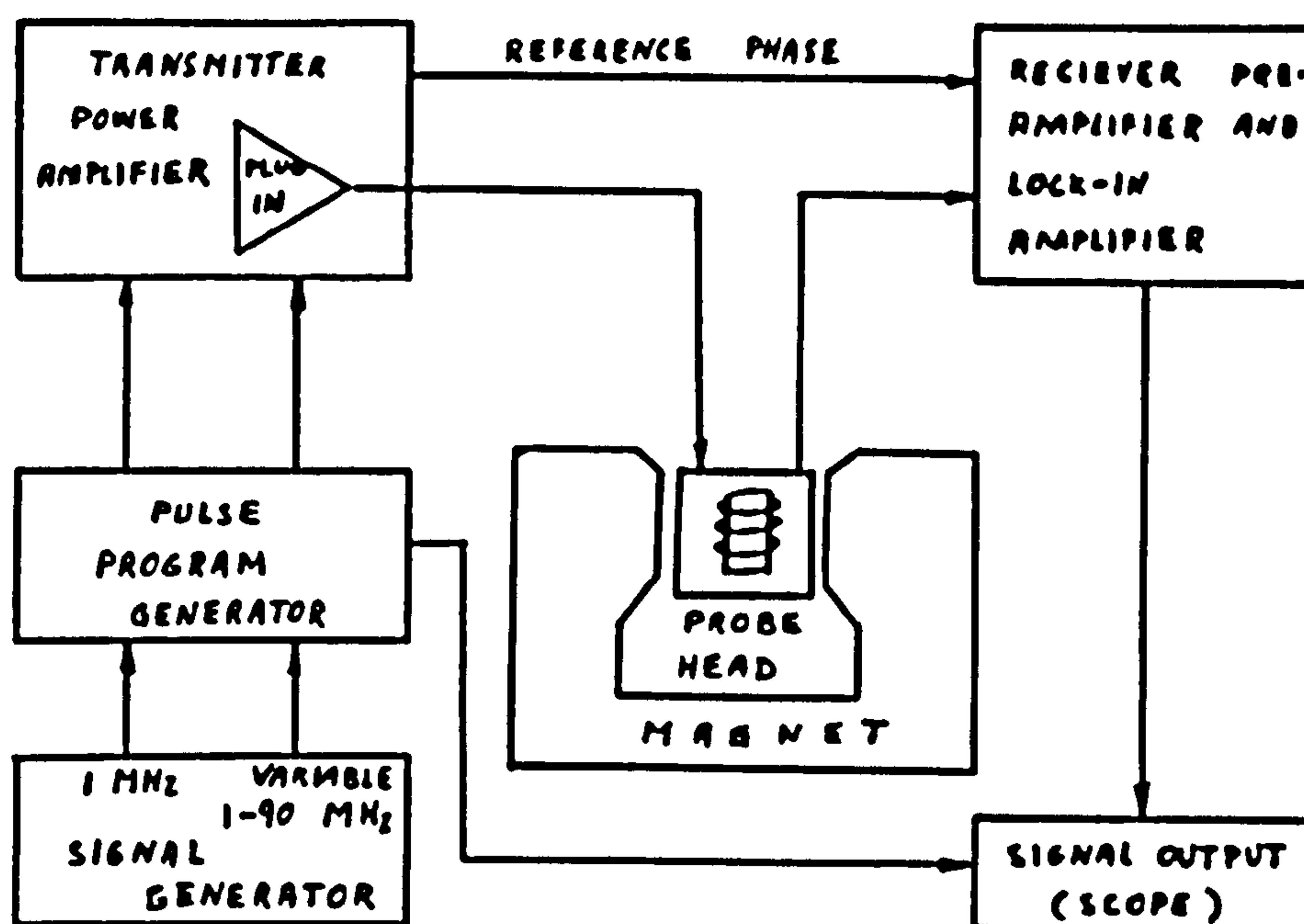


Figure 4.7 Simplified block diagram of the Bruker pulse NMR spectrometer.

The wide frequency span of the spectrometer is achieved with a number of tuned elements which span smaller frequency ranges. This involves two plug-in power amplifiers (4 to 16 MHz range and 16 to 65 MHz range) and a number of plug-in tuned circuits for a 2.5 kW power amplifier. With careful tuning to the operating RF frequency of the transmitter, sample probe and receiving circuits, great sensitivity is achieved. The instrument is particularly suited for standard NMR work in which the resonance frequency is known to be within a narrow frequency range. This is the case of all isotopes that have a known ground state nuclear dipole moment, when they are present in a paramagnetic compound and are placed in a known external magnetic field.

The instrument is not particularly suited for searching for resonant signals over a frequency range wider than a few tens of kHz. This is because all the tuned elements in the spectrometer have to be re-adjusted when the frequency is changed.

Some operating characteristics of the pulse spectrometer are shown below.

Transmitter

Output power	1 - 3 kW	(Depending on frequency)
RF output volts	0 - 800 Vpp	" " "
RF pulse rise time	200 - 300 nsec	" " "
RF pulse duration	0.5 μ s to 1 ms	

Receiver

Amplification	Approx. 110 dB
RF band width	0.8 - 2 MHz
Receiver dead time	Approx. 5 μ sec

Figure 4.8 shows the geometry of the pick-up and transmitter coils in the probe head of the spectrometer.

Searching for resonances

Attempts were made to observe resonance signals of Fe^{57} and H^1 in several materials including synthetic and natural goethite, magnetite, hematite and metallic iron. In all of these materials the expected resonance frequencies were deduced from previously published work on resonance or Mössbauer effect, or, from work done previously on the compound by CW methods. Hence searching for the resonance signals was limited to small ranges about the expected resonance frequency with confidence of high sensitivity.

In order to establish the appropriate spectrometer conditions whilst searching for a resonance, the following method was used.

1) The resonance signal of an easily found isotope was first observed. Usually the electric quadrupolar resonance of Cl^{35} in the compound paradichlorobenzene (resonance frequency 34.27 MHz). Having found the resonance signal, the pulse duration was varied until the signal was maximised. This is then a 90 degree pulse so that, with the particular value of RF field intensity used, tp_{Cl} measured satisfies equation 3.10 with $\alpha = \pi/2$ i.e.

$$\pi/2 = \alpha = \gamma_{\text{Cl}} H_1 tp_{\text{Cl}} \quad 4.1$$

2) For another isotope a 90 degree pulse again satisfies equation 3.10 (assume Fe^{57})

$$\pi/2 = \alpha = \gamma_{\text{Fe}} H_1^1 tp_{\text{Fe}} \quad 4.2$$

The radio-frequency fields H_1 and H_1^1 are proportional to the peak-to-peak voltage of the RF pulse, so that keeping the RF voltage constant ensures that $H_1 = H_1^1$ then from 4.1 and 4.2 it follows that

$$tp_{\text{Fe}} = (\gamma_{\text{Cl}}/\gamma_{\text{Fe}}) tp_{\text{Cl}} \quad 4.3$$

3) the ratio $\gamma_{\text{Cl}}/\gamma_{\text{Fe}}$ was obtained from tabulated values of the nuclear magnetic moments (Brucker NMR-NQR Table of Isotopes) and relation 4.3 used to determine tp_{Fe} , the duration of the RF pulse to be used when searching for an unknown resonance, i.e. Fe^{57} .

In practice it was not possible to keep the RF voltage constant when changing the frequency in the spectrometer and the values obtained with equation 4.3 were used only as a rough guide in choosing the duration of the pulses. In the higher frequency ranges (60 - 75 MHz) faults were encountered in the operation of the instrument.

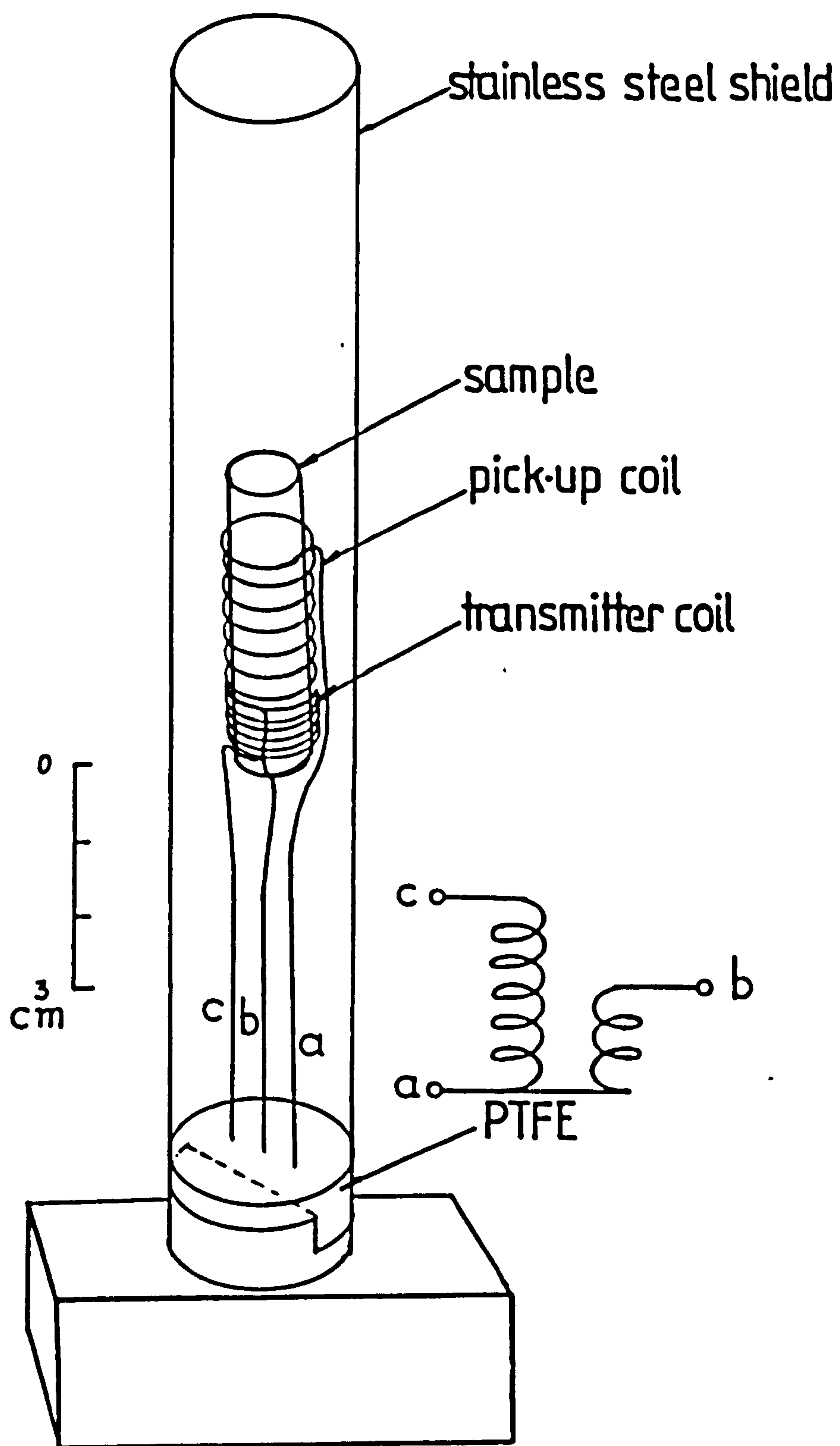


Figure 4.8 Pulse spectrometer probe head. Geometry of the transmitting and pick-up coils surrounding the specimen container.

The transmitter frequency response was such that only very low power pulses were obtainable. In these cases proportionately longer duration pulses were used although the requirement that the pulses be short compared to the linewidth was not being met.

Qualitative tests of the sensitivity of the spectrometer consisted in the detection of the proton NMR resonance in very small quantities of H-containing materials. An additional indication of the spectrometer sensitivity was the fact that a strong F^{19} (spurious) resonance signal was obtained from fluorine contained in the PTFE present in the base of the sample probe (Figure 4.8).

4.4 Mössbauer effect. Experimental

Spectrometer

Mössbauer effect experiments were carried out on spectrometers at three different laboratories: at the Chemistry Department, Birbeck College, University of London; at the Chemistry Department, Imperial College and at the Nuclear Engineering Department, Imperial College. All three spectrometers were basically similar in that the spectrum was run in a transmission geometry with a single line source driven by an electromechanical drive. A description is presented below of the spectrometer at Birbeck College where the majority of the spectra were obtained.

The spectrometer is of a conventional type based on an Elscint Ltd. "MEDA" Multichannel analyser connected to various purpose-built modules made by Elscint. A block diagram of the spectrometer is shown in figure 4.9.

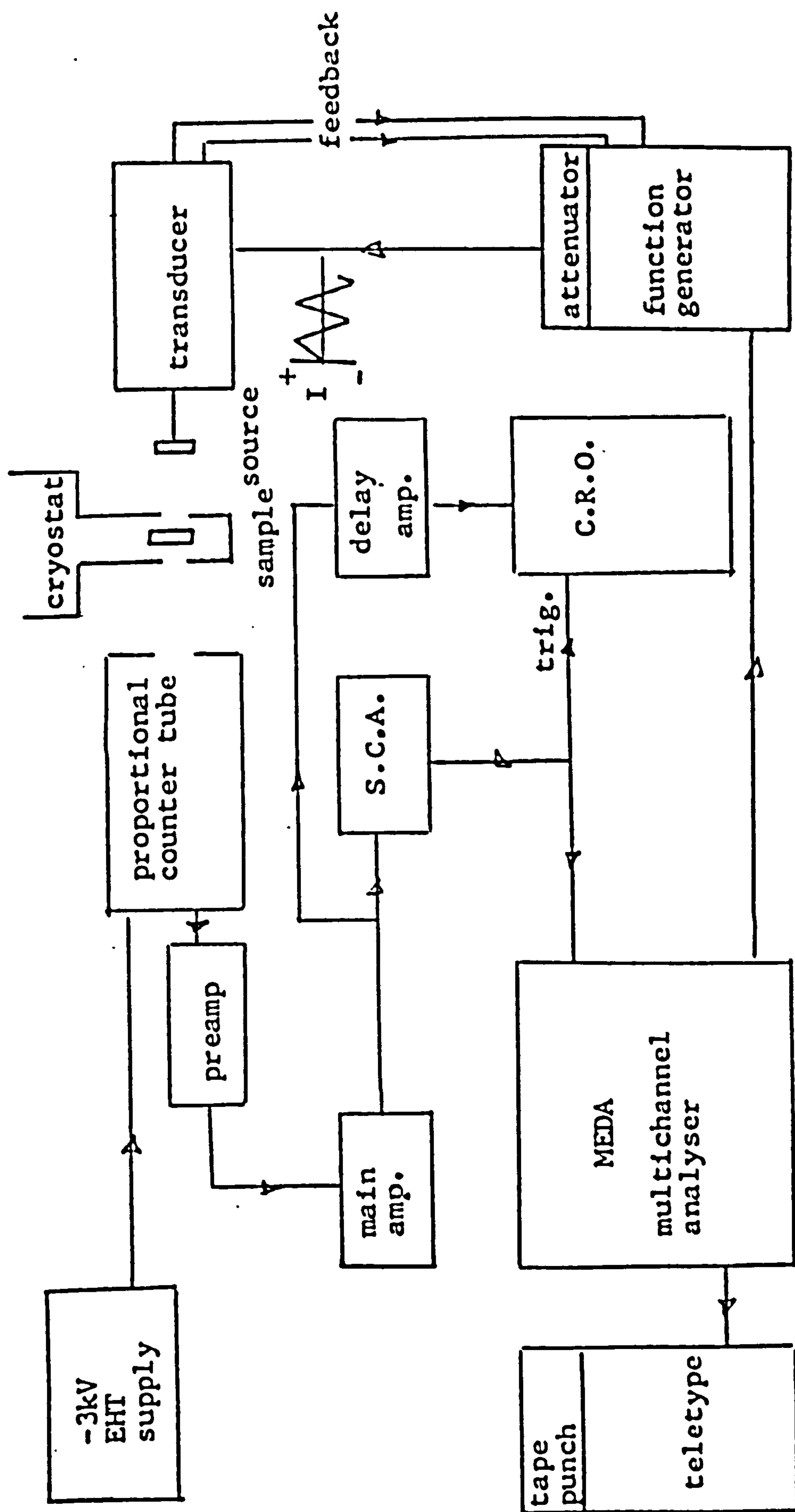


Figure 4.9 Block diagram of the Mossbauer spectrometer.

Source

The Co^{57} radioactive source for Fe^{57} gamma rays was a commercial one supplied by the Radiochemical Centre, Amersham. The source was nominally 25 mCi (at time of purchase) and consisted of Co^{57} diffused into a rhodium foil matrix 4 μm thick and 8 mm in diameter. This source was encapsulated in plastic and gave a linewidth of 0.107 mm/s when irradiating natural iron foil. The recoil-free fraction of the source was estimated at 75% at room temperature.

Source drive

The source drive consisted of an Elscint function generator and drive, model MFD-4, and transducer, Elscint type MVT-4, connected in a negative feedback loop. The transducer was capable of drive velocities of ± 300 mm/s. The function generator provided pulses to synchronise the source drive with the multichannel analyser address advance control. The drive waveform was a triangular type producing a linear variation of the source velocity with time.

Detector and counting system

Gamma rays from the source going through the absorber were detected with a methane-argon proportional counter made by the Mössbauer group, Harwell. This detector was specially designed to optimise the detection of 14.4 KeV gamma rays of Fe^{57} and to be relatively insensitive to higher energy radiation. This feature reduces the dead time of the system and results in shorter times required for production of spectra. The detector was supplied by a -3 kV high tension source and its output was connected to a pulse amplifier system. This consisted of a preamplifier, main amplifier and single channel analyser (SCA).

The preamplifier was a purpose-built unit based on a design by G. Auriemma, et al. (1973).

The main amplifier was an Elscint CAV-N-4 pulse amplifier which provided up to 52 dB (X400) of voltage gain.

The single channel analyser was an Elscint SCA-N-2A and was used to select the pulses corresponding to the 14.4 Kev radiation of Fe^{57} and to reject pulses produced by radiation of other energies.

The output of the SCA was stored in 512 channels of the MEDA multichannel analyser (MCA). Pulses were stored in the MCA in synchronism with the movement of the Co^{57} source so that the first cycle, from positive velocity to negative velocity, was stored in the first 256 channels and the second cycle, from negative velocity to positive velocity, was stored in the second 256 channels. The spectrum produced in this way consisted of a pair of mirror image spectra.

Data was retrieved from the MCA through a Westrex Teletype which produced a typed copy and an 8-hole ASCII-coded paper tape with the contents of the 512 channels of the MCA.

Cryostat

Spectra were obtained at room temperature and at the temperature of liquid nitrogen. The spectra at low temperature were obtained by cooling the absorber with a cryostat. The cryostat was an Oxford Instruments Mössbauer cryostat, Model MD 4.A controlled by a digital temperature controller of the same make, model DTC-2.

This cryostat controls the absorber temperature from approximately 80°K to room temperature with the use of liquid nitrogen. The temperature is measured with a cryogenic linear temperature sensor (CLTS) which is located in close thermal contact with the absorber. All low temperature spectra were obtained at the lowest attainable temperature (sometimes as high as 92°K).

Absorber preparation

Absorbers were prepared from the specimens to be studied by first crushing and grinding the material to a fine powder and then producing a disc with an approximate total iron content of 5 to 8 mg/cm².

These discs were produced either by mixing the weighed amount of material with an inert dispersant (high purity graphite) and enclosing the powder in purpose-made plastic absorber holder or by mixing the weighed amount of material with clear bakelite and hot pressing the mixture. Care was taken in the latter method not to exceed 85°C to avoid thermal decomposition of goethite. These different methods of absorber production were used to accommodate the different diameters required by the three spectrometers.

Data analysis

Analysis of the data was achieved with a Mössbauer computer fitting program. A copy of the program was made available by I. Morrison of the Chemistry Department, Imperial College. This program, MADGIC version G2, is a modification of the program MADG originated in the National Bureau of Standards, Washington, and described by Wilson, et al. (1974).

The fitting program was stored in permanent files in the computer centre at Imperial College and accessed through the Time Sharing terminal system. The data, in the form of 8-hole ASCII-coded paper tape, were read-in at the teletype terminal and permanent files were created with each spectrum. Short programs were developed

to edit the data of the different spectrometers, which were produced in different formats, into a unique format suitable to the fitting program.

The program produced a listing of the parameters fitted in each iteration in real time at the terminal and, when requested, produced a more detailed output on the line printer. This line printer output included a plot of the spectrum and of the fitted curve.

Line trace plots of the spectra were also produced with the Kingmatic plotting facility of the computer centre at Imperial College. These plots were produced with a FORTRAN program which was written for this purpose and with software contained in version G2 of the fitting program.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 Al²⁷ wide-line NMR

This section contains results of a very limited number of experiments performed in the wide-line NMR spectrometer described in Section 4.1.

Specimens studied

The Al-bearing mineral specimens studied in the wide-line NMR spectrometer were of two kinds: a) Pure or semipure synthetic minerals and b) natural minerals selected from the various fractions of the Al-laterite from Los Guaicas, Venezuela. In addition a sample of pure natural kaolinite was used. The natural mineral specimens were selected so that they would be representative of the range of materials likely to be encountered in the study of a laterite. Hence the specimens included a pure well crystalline mineral, a fine grained poorly crystalline mineral, a simple mixture of laterite minerals and a complex mixture of laterite minerals.

The specimens studied were:

- 1) Boehmite β -Al O OH (synthetic)
- 2) Bayerite β -Al (OH)₃ + gibbsite α -Al(OH)₃ traces (synthetic)
- 3) Iron stained gibbsite (lateritic, hand-picked grains)
- 4) Iron stained halloysite. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ (lateritic hand-picked grains).
- 5) Kaolinite. $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (light kaolin, supplied by BDH)
- 6) Mixed sample consisting of the -75- μm slimes of the Al-laterite from Venezuela containing gibbsite, kaolinite, goethite, hematite and quartz.

Results

The experiments were carried out to establish the feasibility of the technique and the possible usefulness of the observed spectra in the study of laterite minerals. Consequently, relatively fast sweep rates were used and no attempt was made to use time averaging techniques or any of the other finer adjustments to the apparatus which would have resulted in better quality spectra.

Resonance signals were detected in all the specimens studied. The spectra obtained are shown in Figures 5.1, 5.2 and 5.3. In Figure 5.1 the spectra of the six mineral specimens are shown under the same instrumental settings. Also shown in Figure 5.1 is a background spectrum which shows a signal produced by metallic aluminium present in the specimen probe. This background signal can be seen in all the other spectra.

Discussion

All the mineral samples show spectra that consist of a single absorption peak with approximately the same frequency and linewidth.

The resonance signals were found at the approximate value expected in the resonance of a "bare nucleus" of Al^{27} i.e. at 11.094 MHz in a 1 Tesla magnetic field. (Actual values were 22.180 MHz in a magnetic field of 2.00489 Tesla). The spectra of Figure 5.1 show small variations in position, intensity and linewidth that cannot be completely explained by the low signal to noise ratio. Unfortunately the spectra obtained are not of sufficient quality to quantify these differences and the results indicate that the technique, as carried out in these experiments, is of limited usefulness as a means of characterising these minerals.

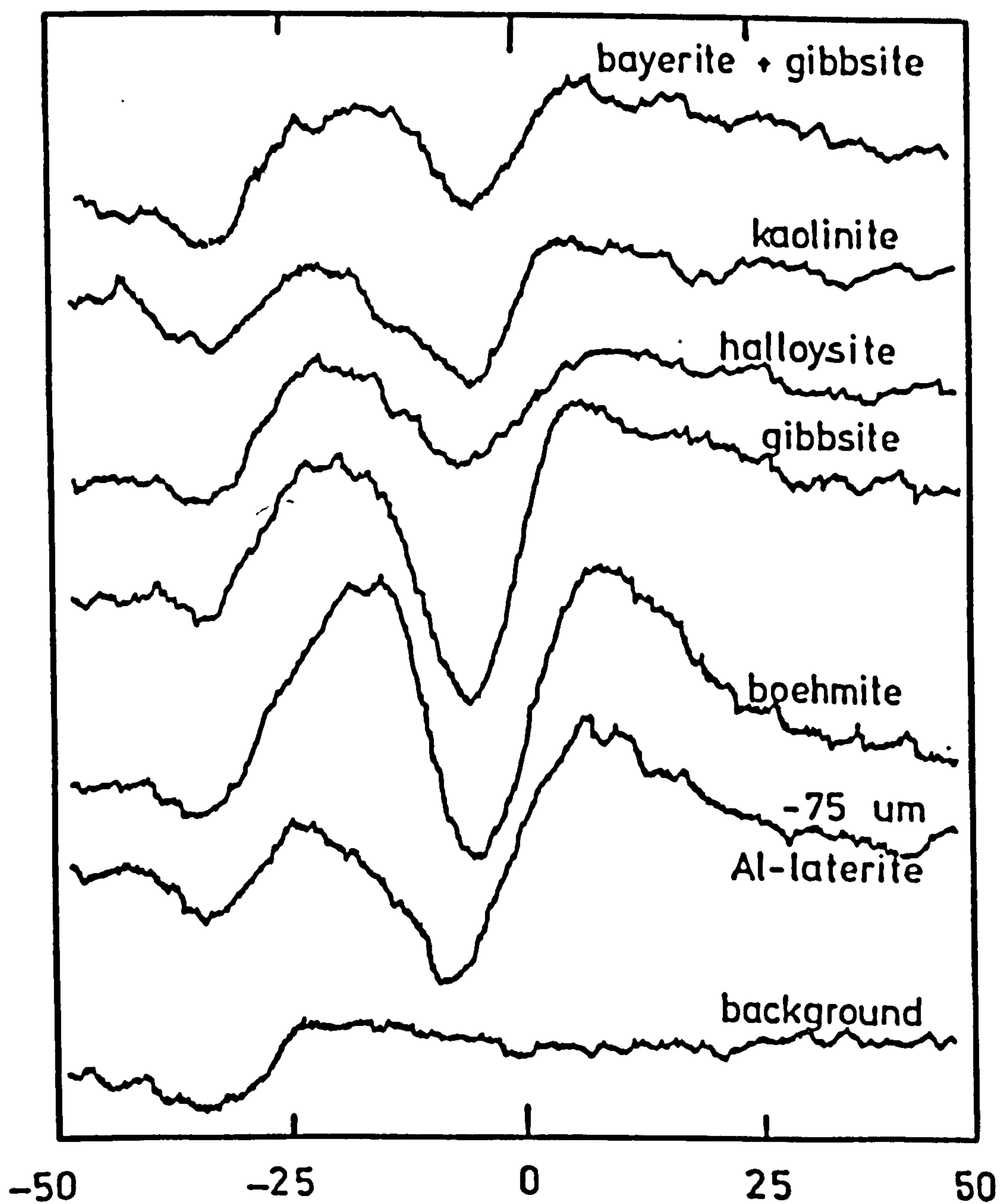


Figure 5.1 Wide-line NMR spectra of Al^{27} in aluminium bearing minerals. Scan range ± 50 Gauss, scan time approximately 15 minutes. Time constant 2 seconds.

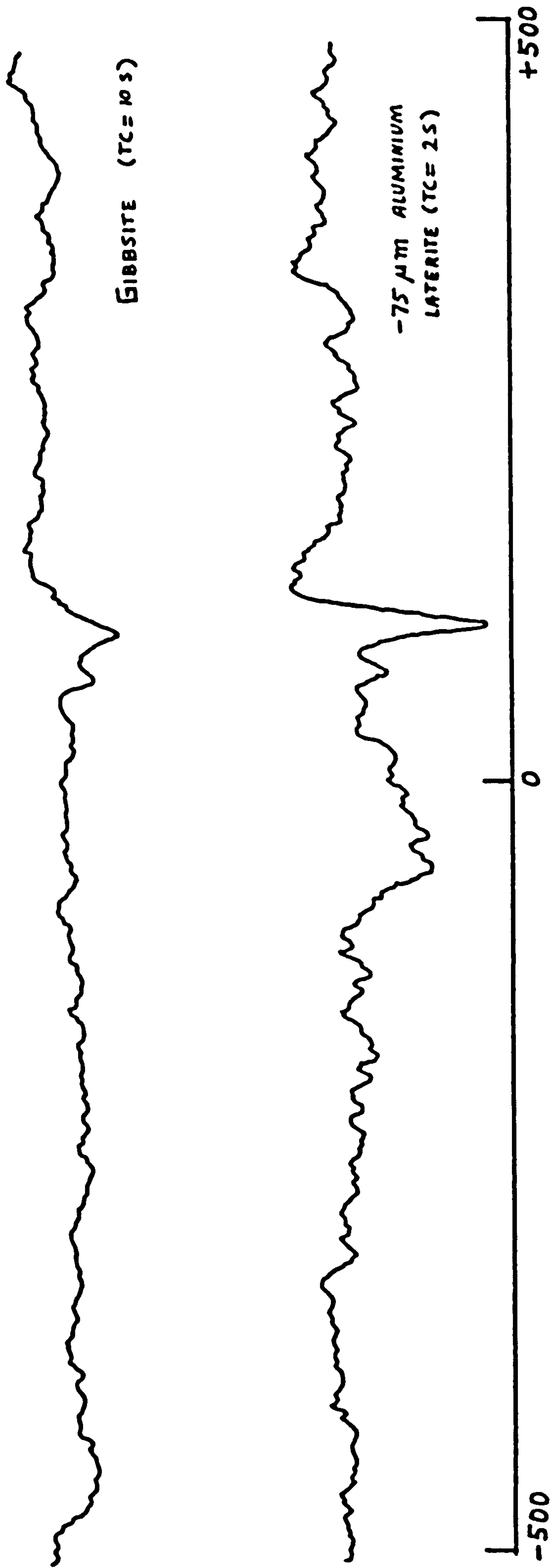


Figure 5.2 Wide-line NMR spectra of Al^{27} in aluminium bearing minerals. Scan done in the wider range of ± 500 Gauss. Scan time approximately 15 minutes.

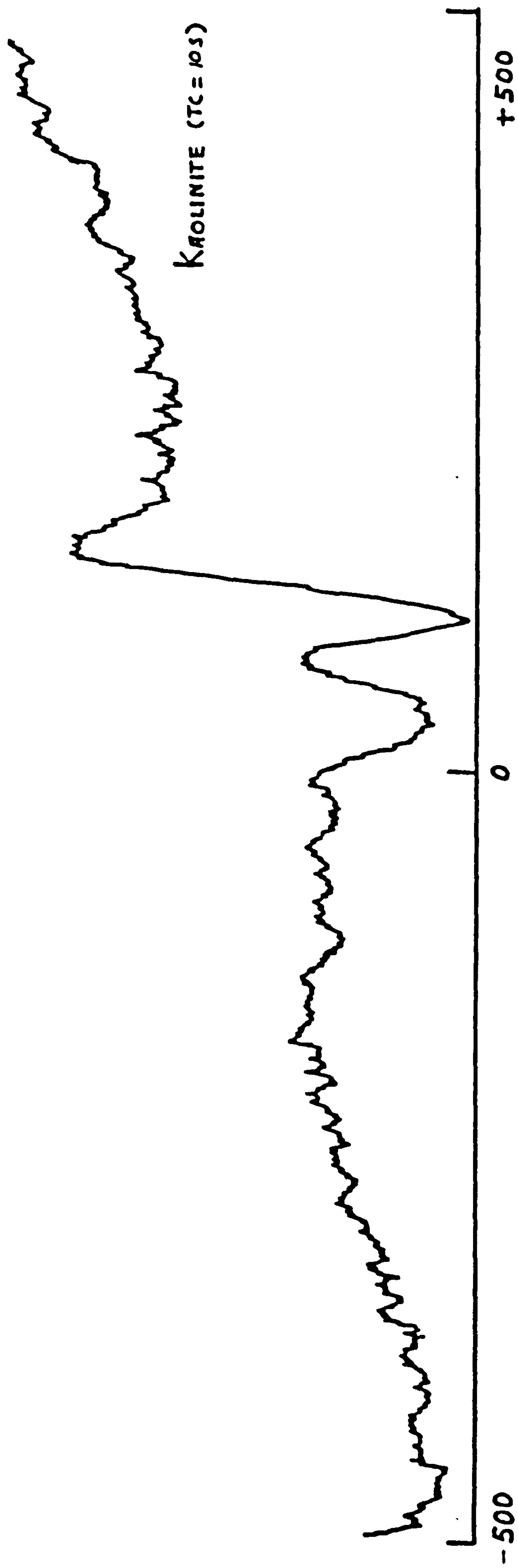


Figure 5.3 Wide-line NMR spectrum of Al^{27} in kaolinite sample done with a 30 minute sweep time showing enhanced S/N ratio.

In all the samples the observed signal intensity was weaker than expected for the amounts of aluminium present in the minerals (G.A. Styles, private communication). This result was not due to saturation of the transition by an excessively intense RF signal. This possibility was eliminated by reducing the RF level and observing that the signal intensity decreased proportionately.

In order to explain the results obtained it is necessary to consider the crystalline environment surrounding the aluminium atoms in the minerals studied, and to determine what are likely NMR spectra from such environments.

The crystal structures of all the Al-bearing minerals present in the specimens have been well described (Wyckoff, Vol. 2, P.80, 1964; Grim, P.52, 58 and 71, 1968; Vedrine, Imelik and Derouvane, 1974). In all cases the aluminium atoms are in octahedral symmetry. In the case of gibbsite and bayerite aluminium atoms are surrounded by six OH ions, in boehmite aluminium atoms are surrounded by four oxygens and two OH ions and in kaolinite and halloysite the octahedra are formed by two oxygens and four OH ions. (Appendix A shows further details of these structures).

From a consideration of the symmetry of the Al atoms in these minerals a non-zero electric field gradient (EFG) is expected at the aluminium nuclei. In addition in kaolinite, halloysite and boehmite the expected EFG is non-symmetric. Since the minerals are non-magnetic the expected hyperfine interactions are only the electric quadrupole interaction between the EFG at the aluminium nuclei and the Al^{27} electric quadrupole moment. In fact a quadrupole interaction has been detected in $\text{Al}(\text{OH})_3$ by Edmonds (1976) using the technique of nuclear quadrupole double

resonance. (See Table 5.1) Two Al sites are reported, each producing the three resonant lines of a pure electric quadrupole interaction. Unfortunately no indication is given whether the specimen was gibbsite α -Al(OH)₃ or bayerite β -Al(OH)₃ or perhaps a mixture of the two. If the sample was synthetic it is likely that it was composed of a mixture of bayerite and gibbsite and this would give a satisfactory account of the two Al sites found.

Table 5.1 Resonant frequency and derived quadrupole coupling constant e^2qQ/h and asymmetry parameter η in Al(OH)₃ reported by Edmonds (1976).

site	Resonant frequencies (kHz)	e^2qQ/h	η
1	2170(10); 1360(10); 810(10)	4670(20)	0.40(2)
2	990(15); 540(10); 450(10)	1970(20)	0.78(2)

In the wide-line NMR experiments carried out a strong external magnetic field was applied. In the absence of quadrupole interactions in the specimens, pure magnetic splitting of the $I = 5/2$ ground state of Al²⁷ would take place and the spectra would consist of single absorption lines. On the other hand, in the presence of quadrupole interaction in the specimens, and this is most likely the case in the Al minerals studied, the spectra depend on the relative magnitude of the electric quadrupole interaction and the magnetic dipole interaction.

Simultaneous electric and magnetic interactions have been discussed in Section 3.1. The broad single lines observed in Figure 5.1 have two likely explanations: a) If the quadrupolar interaction is very small compared to the magnetic interaction and to the absorption linewidth,

the splitting is unresolved and only a broadened absorption is observed. b) If the quadrupole interaction is larger, but still small compared to the magnetic interaction, the powder spectrum is a central absorption line with two broad satellite "peaks". (Cohen and Reif P.339, 1957). These satellite peaks could be present outside the range covered in the spectra of Figure 5.1 and they would account for the reduced absorption signal intensity observed. With the results reported by Edmonds (1976) for $\text{Al}(\text{OH})_3$, shown in Table 5.1 it is possible to make an estimate of the ratio of the magnitude of the electric quadrupole interaction and the magnitude of the magnetic interaction produced by the external magnetic field in our experiments. This ratio is 0.1 and lends support to the possibility of satellite peaks being present outside the range of Figure 5.1.

In order to check the possibility of the existence of satellite peaks scans were done with a 10 times wider range. The results are shown in Figure 5.2. These scans do not show the presence of satellite peaks, but in view of the low signal to noise ratio in these scans, the presence of satellite peaks cannot be ruled out.

Evaluation

In order to use this technique for the appraisal of aluminium-bearing minerals it is necessary to obtain spectra of very much higher quality. Better spectra can be achieved by much slower sweeps or by the use of a time-averaging computer. An indication of the improvement achievable may be gathered by Figure 5.3 in which a $\frac{1}{2}$ -hour sweep time spectrum is shown. The use of a time-averaging computer has been reported (Torgeson, 1979) in the study of powdered solid samples with NMR of a number of isotopes resulting in extremely

well resolved spectra which are amenable to curve fitting techniques. Hence the experiments that were carried out in this work, although not proving the usefulness of the technique, demonstrate the feasibility of obtaining wide-line NMR spectra of lateritic minerals and that further work with the use of time-averaging techniques is warranted to properly evaluate this resonance technique.

5.2 Measurements of particle size

In this section are presented the results of Mössbauer effect and nuclear resonance experiments which are related to particle size determinations. The results of Mössbauer effect experiments are discussed first and it is shown how this technique was used to detect superparamagnetic behaviour which in turn leads to measurements of particle size distribution in laterite samples. This is followed by a short discussion of the use of nuclear resonance instrumentation to excite piezoelectric and piezomagnetic oscillations in minerals and the possible use of this technique to determine particle size.

Mössbauer effect results

Mössbauer effect spectra were obtained from representative samples of each of the three laterites described in Chapter 2. The spectra were obtained at room temperature and at liquid nitrogen temperatures with the spectrometer described in Section 3.5. All the Mössbauer effect spectra at room temperature showed a strong doublet as the dominant feature. The room temperature spectrum of the sample of Al-laterite from Los Guaicas, Venezuela, showed only a partially resolved doublet, (Figure 5.4) while the room temperature spectra

of samples of the Ni-laterites from Guatemala and Venezuela showed the superposition of a doublet and a 6-line pattern. (Figures 5.5 and 5.6).

Interpretation

Goethite, hematite and magnetite all produce six-line patterns due to the magnetic hyperfine splitting in these minerals. Hence the Mössbauer spectra of the laterite specimens which contained these minerals were expected to consist of a superposition of 6-line patterns. The doublets that were found as the dominant feature in the room temperature spectra were interpreted as being produced by hematite and goethite which occur in the form of very small crystallites which behave as superparamagnetic (SPM) minerals. Such SPM behaviour of small particle iron-rich minerals has been reported previously in the literature and has been discussed above (Section 3.5).

In order to demonstrate whether or not the doublets were due to SPM behaviour, the same mineral specimens were cooled to liquid nitrogen temperatures and Mössbauer spectra obtained. Upon cooling, the thermal fluctuations producing the SPM behaviour are reduced allowing the magnetization of the crystallites to remain fixed for longer times. Under these conditions the Mössbauer spectrum of fine particles should show the six lines which are observed in coarse particles of these minerals.

The 77°K spectra shown in Figures 5.4, 5.5 and 5.6 show the expected six lines and demonstrate that the doublets were indeed produced by SPM behaviour.

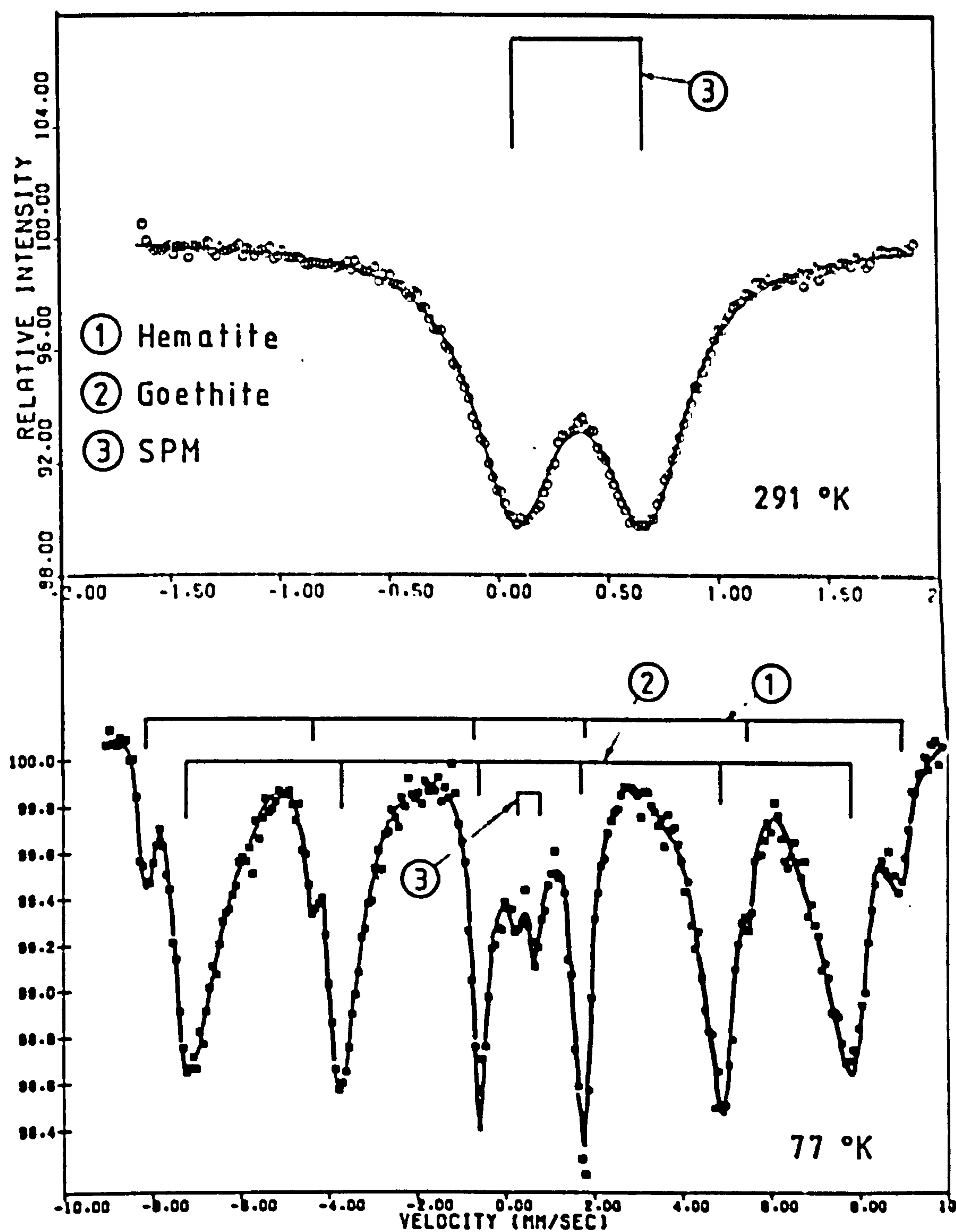


Figure 5.4 Mössbauer effect spectra of the aluminium laterite from Los Guaicas, Venezuela. S.P.M. = super-paramagnetic.

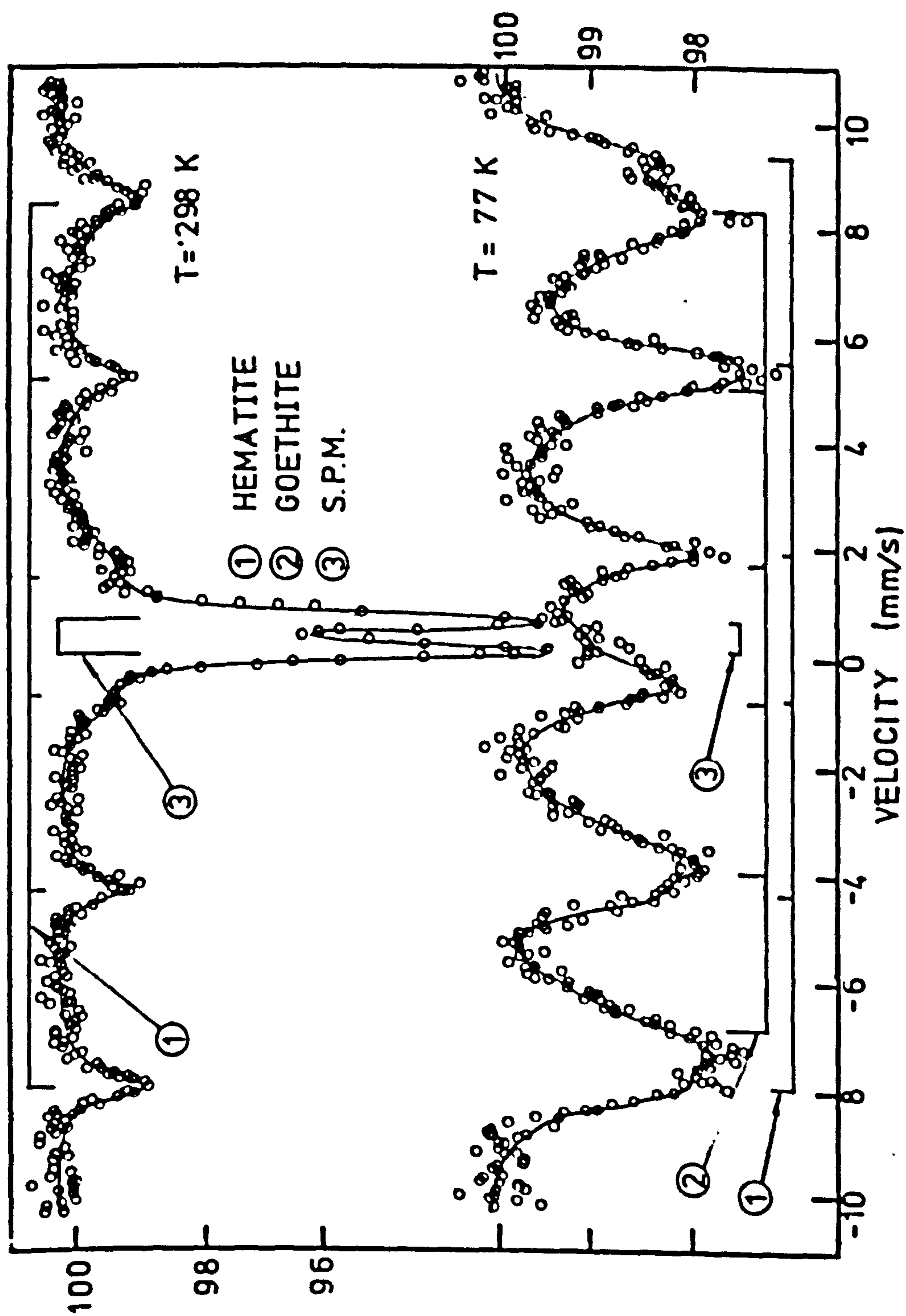


Figure 5.5 Mössbauer spectra of a representative sample of nickel laterite from Loma de Hierro, Venezuela. (Garnieritic laterite). Circled numbers indicate the positions and relative heights of the computer-fitted peak patterns. S.P.M. = superparamagnetic iron minerals.

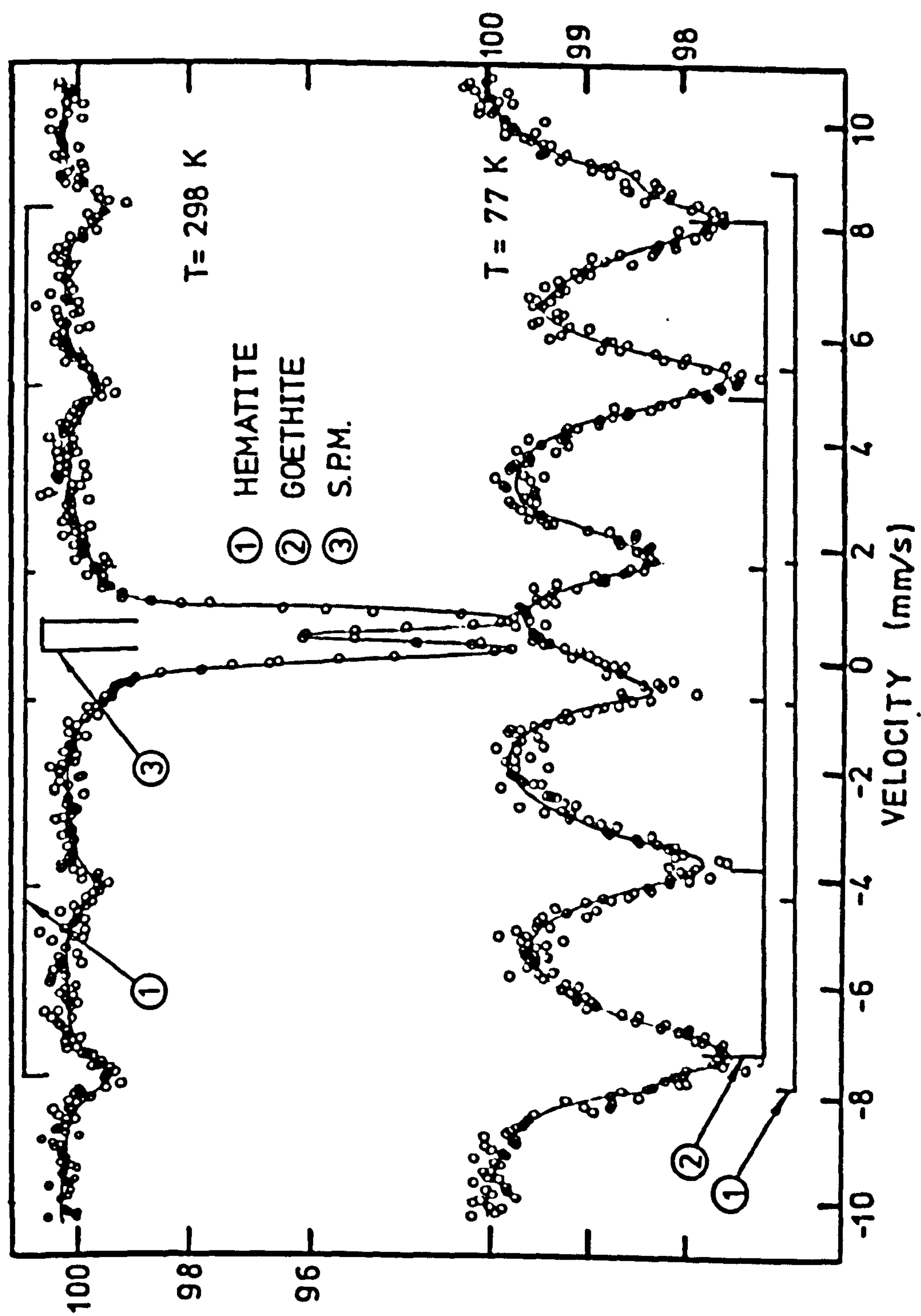


Figure 5.6 Mössbauer spectra of a representative sample of nickel laterite from Guatemala (Limonitic laterite) symbols defined in Fig. 5.5.

Once the doublets were recognized as having been produced by SPM behaviour of fine particles, the computer-fitted relative peak areas of the doublets were taken to be an indication of the proportion of fine particle material in the specimens. Thus, in the Al-laterite at room temperature (Figure 5.4) all the material behaves SPM and by calculating the critical particle diameter at room temperature for SPM behaviour it is possible to deduce that 100 percent of the material exists in crystallites below that critical diameter. With the relative peak areas of the doublets

Table 5.2 Particle size distribution of hematite and goethite in three laterites in the sizes below 18 nm derived from Mössbauer effect measurements.

Cumulative percent weight below stated size						
size (nm)	Al-laterite		Ni-Laterites			
	Los Guaicas Venezuela	Goethite	Loma de Hierro Venezuela	Goethite	Guatemala	Goethite
	Hematite		Hematite		Hematite	
18		100		100		100
15	100		73		84	
11		16		4		very small
9	16		4		very small	

obtained in the Mössbauer spectra at room temperature and at 77°K the particle size distribution of the laterite samples were deduced. These are shown in Table 5.2. The results show that significant proportions of the material in the samples exist as crystallites of very small size.

(The method used for the identification of the minerals shown in Table 5.2 are discussed in Section 5.3, and the parameters derived from computer fits to each of the spectra are shown in Table 5.6).

Discussion of the results.

The accuracy of the particle size determinations calculated on the basis of the critical particle diameter for SPM behaviour has already been commented upon in Section 3.2 . The accuracy of the proportions of material in any size fraction deduced from Mössbauer effect spectra depends on a number of factors: a) the experimental measurement of the relative areas of absorption peaks and on b) a theoretical relationship between the measured areas and the proportion of material. This last theoretical relationship is discussed in Section 3.5 above and in Appendix C. The first problem, which is concerned with the statistical limitation of Mössbauer computer fitting routines has been reviewed by Dollase (1975). The accuracy of the measured areas determined by the fitting routine depends on a number of factors which can be classified as a) errors due to counting statistics alone, and b) "instrumental" errors. Under instrumental errors are lumped a number of sources of error including systematic errors in the data such as spectrometer drift, absorber thickness broadening, errors in velocity calibration, temperature fluctuations during data collection, etc. The errors due to counting statistics alone are easier to quantify. Dollase (1975) establishes a "statistical quality" of the spectrum of an absorption peak by a quantity Z defined by

$$Z = (N_{\infty} - N_0) \sqrt{G/N}$$

where N_{∞} is the background count, N_0 is the count at the peak minimum

(absorption peaks are assumed) and G is the full width at half maximum (FWHM) of the peak (in channels). The statistical quality (Z) of peaks so defined should fall between 100 and 200. Peaks of $Z > 200$ are exceptionally well resolved while peaks with $Z < 100$ are only indistinctly resolved in a given spectrum. This treatment is applicable to isolated peaks. With non-isolated peaks, when it is possible to specify relationships between the parameters of the various peaks, the precision of the parameters which define a given peak are increased by the constraints between the different peaks. On the other hand the precision decreases as an inverse function of the separation between peaks which are only partially resolved. In particular, the precision of fitted parameters decreases dramatically for unconstrained and unresolved peaks when the separation falls below 0.6 times the peak width. At this value, or below, the eye no longer discerns separate maxima. Nevertheless if the peaks are not isolated and constraints between the parameters can be established by physical arguments, the uncertainties are markedly reduced and reasonable precision of the fitted parameters can be achieved even with visually unresolved peaks. Unfortunately it is not possible to establish universally applicable rules and therefore in this work the errors in the areas quoted are those calculated by the Mössbauer fitting program. (See Section 4.4). These errors are purely statistical and therefore are only lower limits of error.

Piezoelectric and piezomagnetic resonances

During the course of experiments with the Decca NQR spectrometer (described in Section 4.2) very strong resonance signals were detected with some mineral specimens. These signals had the peculiarity of extending over a very wide band of frequency, of the order of several Mc. The signals although resembling a very large noise background were found to be exactly repetitive with any given sample. See figure 5.7. These signals were found to be produced by the excitation of piezoelectric oscillations in the crystallites in the sample. The existence of such a phenomenon is well known in NMR experiments with solid powdered samples and for the NMR spectroscopist it is just a minor nuisance. The piezoelectric resonances will mask any nuclear resonance signals and they must, therefore, be avoided. This can be done by grinding the sample to decrease the crystallite size and so increase the piezoelectric resonance frequencies so that they are above the range of the nuclear resonance signals. In the experiments that were carried out some samples had to be ground in order to clear these resonance signals from the frequency band where nuclear resonance signals were being sought.

It was recognised that these strong resonance signals could conceivably be used to determine particle size in specimens of interest in mineral technology. No further experimentation was carried out to pursue this possibility because it was outside the main stream of interest of the work. Nevertheless it is considered interesting as a possible future avenue of research and hence a few

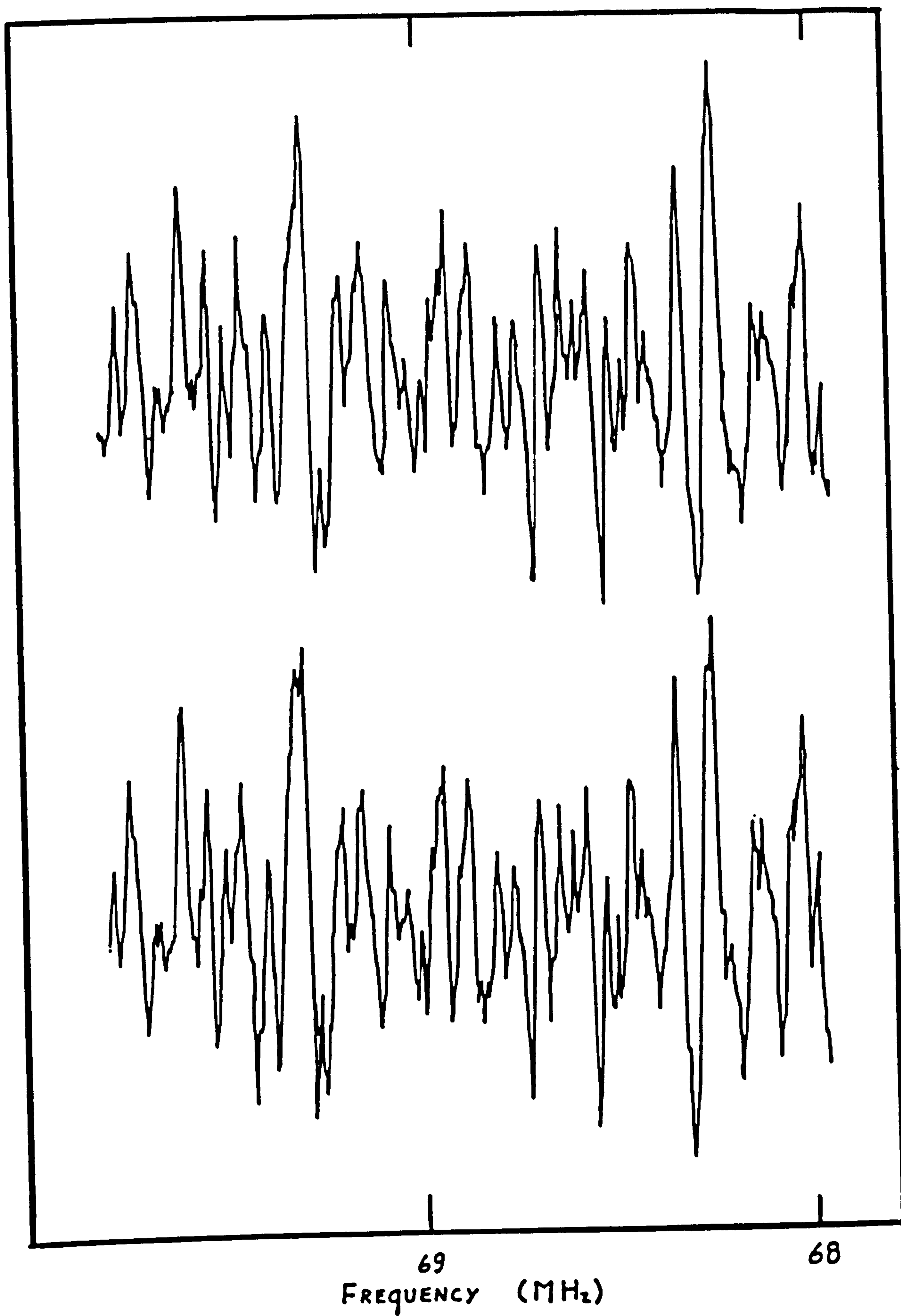


Figure 5.7 Piezoelectric resonance signals excited in hematite. The two patterns correspond to separate scans in the same frequency region.

comments on the phenomenon are presented.

The resonances were easily observed by placing the powder in a specimen tube and introducing the tube into the resonance coil of the Decca NQR spectrometer. The resonances were found to be so strong that only very moderate sensitivities of the spectrometers were needed to detect them.

Resonances were detected in hematite, magnetite, chromite and all samples that contained quartz.

Origin of the resonances

The application of a steady force to a piezomagnetic material results in a deformation of the material and a polarization of the ionic charges contained in the crystal. This polarization of charges produces a static electric field. Conversely the application of a static electric field results in a deformation of the piezoelectric material. Therefore if an oscillatory electric field is applied, the result is the production of elastic oscillations in the crystal. When the oscillatory electric field has the right frequency it will excite oscillations of the elastic resonance modes of the crystal. Such a phenomenon is commonly exploited in a variety of well known electroacoustic devices (Cady, 1946).

The fundamental resonance frequency of a single piezoelectric crystal is related to the crystal dimension(l) by (Joos, P.795, 1958)

$$f_0 = (\sqrt{E/\rho})/2l$$

where E is the elastic constant (Kg/m^2) and ρ is the density of the material (Kg/m^3).

Thus an ensemble of identical single crystals will resonate at the fundamental and all other higher harmonics. An ensemble of crystals with a distribution of sizes will have a corresponding distribution of resonant frequencies.

Whether a given material will exhibit the piezoelectric effect depends on its crystal symmetry. The appearance of piezoelectricity depends on the existence of a polar axis; an axis such that the plane normal to it is not a plane of symmetry of the crystal. This condition is only satisfied by a limited number of crystal symmetries. Hence, the crystal symmetry group to which a mineral belongs will indicate if a mineral is or is not piezoelectric. There are 21 classes which can show the piezoelectric effect and these classes are shown in Table 5.3.

Table 5.3 Classes of crystals which exhibit the piezoelectric effect (from Phillips, F.C., P.155, 1955).

Crystal system	Symmetry class
cubic	23, 43m, 432
hexagonal	6, $\bar{6}$, 6mm, 6m2, 62
tetragonal	4, $\bar{4}$, 4mm, $\bar{4}2m$, 422
trigonal	3, 3m, 32
orthorhombic	mm, 222
monoclinic	2, m
triclinic	1

The excitation of mechanical oscillations by an applied electromagnetic wave is not confined to piezoelectric materials. Piezomagnetic materials can also exhibit resonances. Piezomagnetism

is a phenomenon analogous to piezoelectricity. It occurs in antiferromagnetic materials which develop a small magnetic moment when mechanically strained. (Cullity P.281, 1972).

Piezomagnetism also depends on crystal symmetry and there are 66 classes of crystal symmetries that exhibit the phenomenon. R.R. Birss, P.137 (1964) lists these crystal classes.

There are a number of other magnetic and electric types of crystals such as ferroelectric, ferromagnetic, ferroelastic, ferrobielectric, etc. These classes of crystals have been reviewed by Newnham (1974) and undoubtedly a number of these classes, which couple mechanical with electromagnetic properties of the material, will lead to mechanical resonances when placed in oscillating electromagnetic fields.

The study of the relationship between the resonance frequency of these materials and the crystal dimension may lead to an alternative method of measuring particle size and particle size distributions in minerals.

5.3 Mineral identification and relative proportions

Hyperfine field measurements were made to evaluate the possibility of using the results to identify and quantify the various minerals in laterites. A significant amount of work in this field has been reported in the literature with pure mineral samples and with synthetic compounds of iron for the purpose of studying particular properties of these materials. Measurements of hyperfine field parameters have been made in some iron oxides with nuclear resonance techniques, but it is with Mössbauer effect spectroscopy that the most extensive and detailed studies have been reported. This technique has been used not only to

study pure compounds for their own sake, but also to provide information on problems of technological interest. The reason for this is the relative ease with which Fe^{57} Mössbauer effect spectra can be obtained. The hyperfine field parameters which are measured at the Fe^{57} nucleus are the isomer or chemical shift, the electric quadrupole splitting and the magnetic dipole splitting. The values of these parameters reported in the recent literature for the most common iron oxide minerals have been collected in Table 5.4. Examination of the values of the parameters in Table 5.4 show that there are significant differences between the parameters of the various minerals. These results suggest that the differences are sufficiently great for measurements of hyperfine fields to be used as a means of recognising the minerals even when present in mixtures. Additionally the results suggest that quantification or standardization of the signals used to derive the parameters could be used to determine the proportions of the minerals in mixtures.

In Mössbauer effect spectroscopy the Fe^{57} spectrum of a magnetically ordered mineral such as goethite and hematite consists of six absorption peaks (Section 3.5). Magnetite which contains iron atoms in two different sites produces a spectrum containing two groups of six absorption peaks. The linewidth of the absorption peaks (approximately 0.3 mm/s; equivalent to 0.9 Tesla) and the magnitudes of the splittings result in spectra of mixtures which contain partially resolved absorption peaks.

Table 5.4 Mössbauer effect parameters reported in the literature for some iron oxide minerals. Values at room temperature and at liquid nitrogen temperature. H - magnetic hyperfine field, I.S. - isomer shift (with respect to Fe metal) and Q.S. - quadrupole splitting, Th - tetrahedral sites, Oh - octahedral sites.

Mineral	H (Tesla) Room Temperature	I.S. mm/s Room Temperature	Q.S. mm/s	Reference
Hematite Fe_2O_3	51.8	.39	+0.43	1
Magnetite Fe_3O_4	49.1 Th 45.3 Oh	.36 .61	0 0	2
Goethite FeO OH	38.4	.35	-0.3	3
Akaganeite $\beta\text{-FeOOH}$	0	.79	.7	8
Lepidochrosite $\gamma\text{-FeOOH}$	0	.38	.54	7
Ilmenite FeTiO_3	0	1.2	0.3	5

Liquid Nitrogen temperature 77°K				
Hematite	54.2	0.48	-0.69	1,6
Magnetite	50.3 Th, Oh 48.0 Oh	.65 1.15	0 0	2,4
Goethite	50.4	.35	-0.3	3
Akaganeite	46.0	.99	-0.2	8
Lepidocrocite	0	.52	0.62	7
Ilmenite	0	1.25	0.65	5

1 Kundig, et al. (1966)

2 Greenwood & Gibb P.241, (1970)

3 Forsyth, et al. (1968)

4 Danon P.215 (1968)

5 Ruby and Shirane, (1961)

6 F van der Woude, (1966)

7 Rossiter and Hodgson (1965)

8 Dezsi, et al. (1967)

Nuclear resonance experiments of Fe^{57} in the iron oxides yield only the resonance frequency from which the magnetic hyperfine field is deduced. If the experiment is done with pulse resonance techniques the spin-lattice and spin-spin relaxation times can in principle be obtained. From the fields measured with the Mössbauer effect quoted in Table 5.4 and the known magnetic dipole moment of the Fe^{57} ground state: $\mu = 0.0903(7) \text{ n.m.}^*$ (Greenwood and Gibb, P.102, 1971) it is possible to calculate the resonance frequencies expected in goethite, hematite and magnetite. The results of this calculation are shown in Table 5.5. (The electric field gradient which leads to the electric quadrupole splittings shown in Table 5.4 cannot be detected with nuclear resonance of the ground state of Fe^{57} as this state has spin $\frac{1}{2}$ and hence no quadrupole moment).

Table 5.5 Fe^{57} resonant frequencies in iron oxide minerals calculated on the basis of the measured magnetic fields of Table 5.4 (Calculated with $f(\text{MHz}) = 1.365 \times B(\text{Tesla})$)

Mineral	f (At room temp.) (MHz)	f (At liquid N_2 temp.) (MHz)
Hematite	70.7	74.0
Magnetite	67.0 Th	68.6
	61.8 Oh	65.5
Goethite	52.4	68.8

The resonant frequencies, at room temperature, are very different and since resolution in NMR is very much higher than in Mössbauer spectroscopy the resonance signals of a hypothetical mixture

*n.m. = nuclear magneton

of these minerals should be completely resolved. Therefore, in principle, the measurement of the magnetic hyperfine fields with NMR should allow recognition and possible quantification of components in natural mixtures of iron minerals. On this basis NMR appears much more favourable than Mössbauer spectroscopy.

Results of Mössbauer experiments

The Mössbauer effect spectra of representative samples of the laterites are shown in Figures 5.4, 5.5 and 5.6 above. The spectra were computer fitted and Table 5.6 shows the parameters measured. Also shown in this table is the interpretation that was given to each of the six-line patterns that produces the best fit.

The minerals hematite and goethite were clearly identified by comparing the fitted parameters with those published in the literature and collected in Table 5.4. As discussed in Section 3.5 the proportions of each mineral can be derived from the relative absorption areas. The measured areas in Table 5.6 can be taken directly as a measure of the proportion of each mineral with the usual assumption that the recoil-free fractions of all the minerals concerned are the same. (Bancroft, P.233, 1973). If, on the other hand, the recoil-free fractions are different, then the relative proportions of the various minerals can be corrected using relation C.4 (Appendix C). The values of the recoil-free fractions can either be calculated from the Debye temperatures or an experiment performed to determine their relative values.

Since recoil-free fractions calculated from the Debye temperatures are not very reliable, spectra were obtained of a synthetic mixture with equal quantities of each of the minerals goethite and

Table 5.6 Parameters measured in the Fe⁵⁷ Mössbauer effect spectra of the laterites. (I.S. = isomer shift, Q.S. = quadrupole splitting (2), H = magnetic field, AREA = percent of the total area under the absorption curve. This is proportional to the relative amount of the mineral). Bracketed numbers show the uncertainty in the last figure(s) of the preceding number.

TEMPERATURE (K)	GARNIERITIC LATERITE (Loma de Hierro, Venezuela)				LIMONITIC LATERITE (Guatemala)				Interpretation
	I.S. (mm/s)	Q.S. (mm/s)	H (tesla)	AREA (%)	I.S. (mm/s)	Q.S. (mm/s)	H (tesla)	AREA (%)	
298	.37(1)	-.18(2)	50.9(1)	23(4)	.36(2)	-.09(3)	49.8(1)	16(4)	Hematite
	.431(2)	.577(4)	-	76(4)	.427(2)	.562(4)	-	83(4)	Superparamagnetic Fe minerals
77	.51(2)	.01(3)	53.3(2)	15(6)	.51(4)	-.05(8)	52.1(4)	7(6)	Hematite
	.50(1)	-.28(2)	47.9(1)	80(10)	.49(1)	-.29(2)	47.4(2)	93(10)	Goethite
	.29(9)	.3(4.5)	-	4(4)				Very Small	Superparamagnetic Fe minerals

ALUMINIUM LATERITE (Los Gualcas, Venezuela)				
Temp. K	I.S. mm/s	Q.S. mm/s	H (Tesla)	Area (%)
298	.375	.5888(1)	-	100
77	.49(2)	.51(3)	-	16(2)
77	.48(1)	-.51(3)	46.7(1)	70(6)
77	.48(2)	-.18(3)	52.6(2)	14(4)

		Interpretation
		superparamagnetic
		superparamagnetic
		goethite
		hematite

hematite. The spectra are shown in Figure 5.8. These spectra were computer fitted and the ratio of the absorption areas corresponding to each mineral derived.

The results are:

Room temperature	hematite area = $76 \pm 5\%$
	goethite area = $24 \pm 5\%$
85° K	hematite area = $49.9 \pm 2\%$
	goethite area = $50.1 \pm 2\%$

The results show that the recoil-free fractions of the minerals are quite different at room temperature and that very significant errors would be derived for the mineral proportions if no corrections were applied to values deduced from Mössbauer effect at room temperature. Hence these results were used to establish correction factors so that the measured absorption areas could be converted to mineral proportions. The mathematical method used to derive the correction factor is described in Appendix C.

It is not easy to derive a correction factor for the fraction of material that behaves superparamagnetically. It has been suggested by J.S. van Wieringen (Greenwood and Gibb, P.246, 1971) that the recoil-free fraction of small particles differs from that of bulk material. The theoretical argument rests on the prediction that the phonon spectrum in small particles is different from that of coarse particles and also on calculations of the limiting size of particle such that the whole-particle recoil energy is of the same magnitude as the linewidth. Consequently one might expect that the recoil-free fraction of particles small enough to show SPM behaviour should be

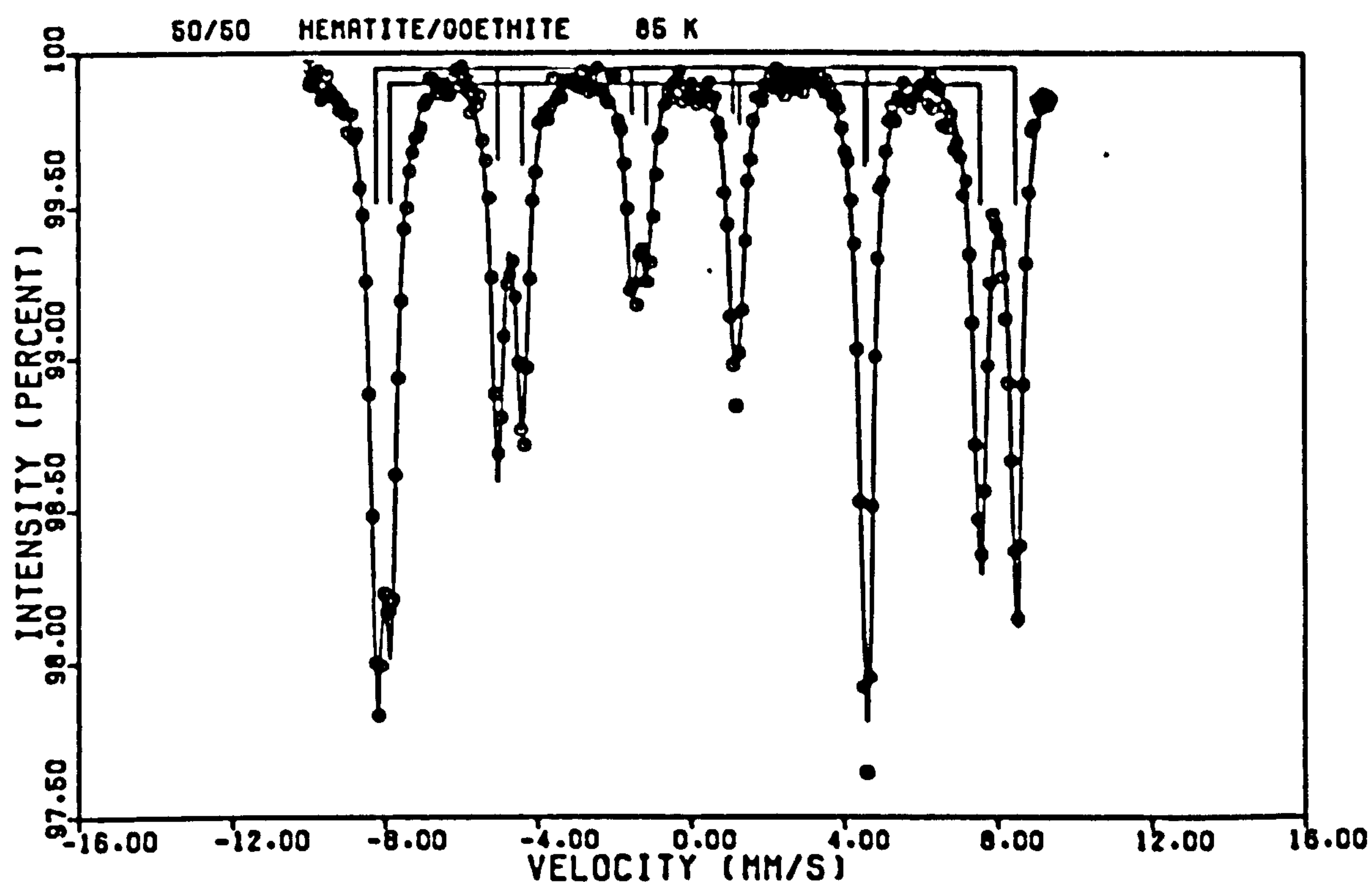
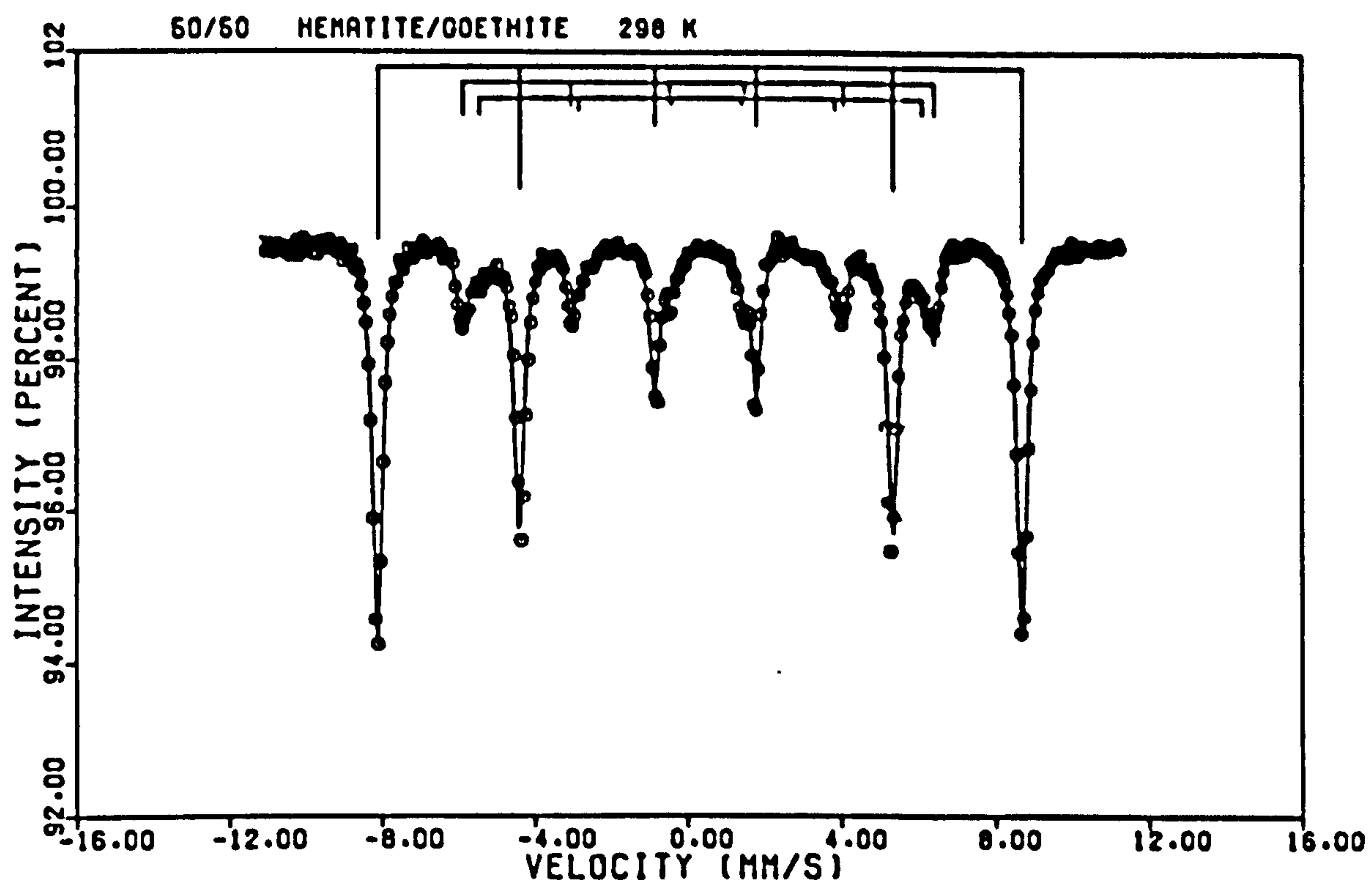


Figure 5.8 Mössbauer effect spectra of 50/50 mixtures of pure hematite and goethite. Computer fits resulted in the following relative areas: At 295 K. Hematite $76 \pm 5\%$, goethite $24 \pm 5\%$; At 80 K Hematite $49.9 \pm 2\%$, goethite $50.1 \pm 2\%$.

different from that of bulk material. Nevertheless the proportion of SPM material was taken to be directly proportional to the absorption area and no correction for a possible difference in the recoil-free fraction was applied. The reason for this is that pure samples of the minerals showing SPM behaviour were not available to derive the necessary correction factors.

The results of the mineral proportions, corrected for differences in recoil-free fractions for a representative sample of the three laterites are shown in Table 5.2 above.

Limitations of the method

The method has some limitations derived from instrumental and theoretical difficulties. The specimen of a mixture of minerals is only sensitive to the iron bearing minerals, the proportion of other non-iron bearing minerals has a relatively minor importance. Nevertheless the presence of non-iron minerals does influence the time it takes to obtain a spectrum because the mass absorption coefficient of these minerals reduces the overall counting rate.

Very good quality spectra are required to detect and quantify an iron mineral which exists in small proportion in relation to the other iron minerals. The lower limit of detection is determined by the counting statistics of the spectrum. An estimate of the total count required can be derived from the spectrum signal to noise ratio which depends on the percentage absorption of the iron minerals (P) and the total number of counts in the baseline (N):

$$\text{Signal to noise} = \frac{P N}{\sqrt{N}} = P \sqrt{N}$$

For example: to detect 5% hematite (with a S/N ratio of 10) in a specimen of goethite that produces 10% absorption it is necessary to have a baseline with about 4×10^6 counts in each channel*. To detect 1% of hematite under the same conditions requires to have about 100×10^6 counts in each channel; while the first spectrum could be obtained in about 12 hours, at the same counting rate the second spectrum would require a counting time in excess of a week. (These estimates assume identical recoil-free fractions).

For analysis of the spectrum data it is necessary to use a curve fitting computer program and the large data storage requirement of these programs require the use of a large computer.

The method assumes tacitly that the Mössbauer spectrum of a mineral is invariable. If this proved not to be the case, the method would require the use of standards identical to the unknown minerals. With some materials, such as laterites, the isolation of pure minerals with the same characteristics as in the unknown mixtures is quite difficult and this would limit the applicability of the method.

Results of nuclear resonance

Pure specimens of hematite, magnetite, goethite, metallic iron and metallic nickel were used in order to establish the operating conditions of the spectrometer and to determine the exact resonance frequencies.

The purity of the specimens was checked by optical examination and by XRD. Figure 5.9 and 5.10 shows the XRD patterns of these three minerals. The hematite sample consisted of coarse (1 mm) grains

*Goethite signal = $0.1 \times N$, hematite signal = $0.05 \times$ goethite signal, noise = $\sqrt{N}$. Hence hematite S/N = $10 = 0.005 N / \sqrt{N} = 0.005 \sqrt{N}$, from where $N = 4 \times 10^6$ counts.

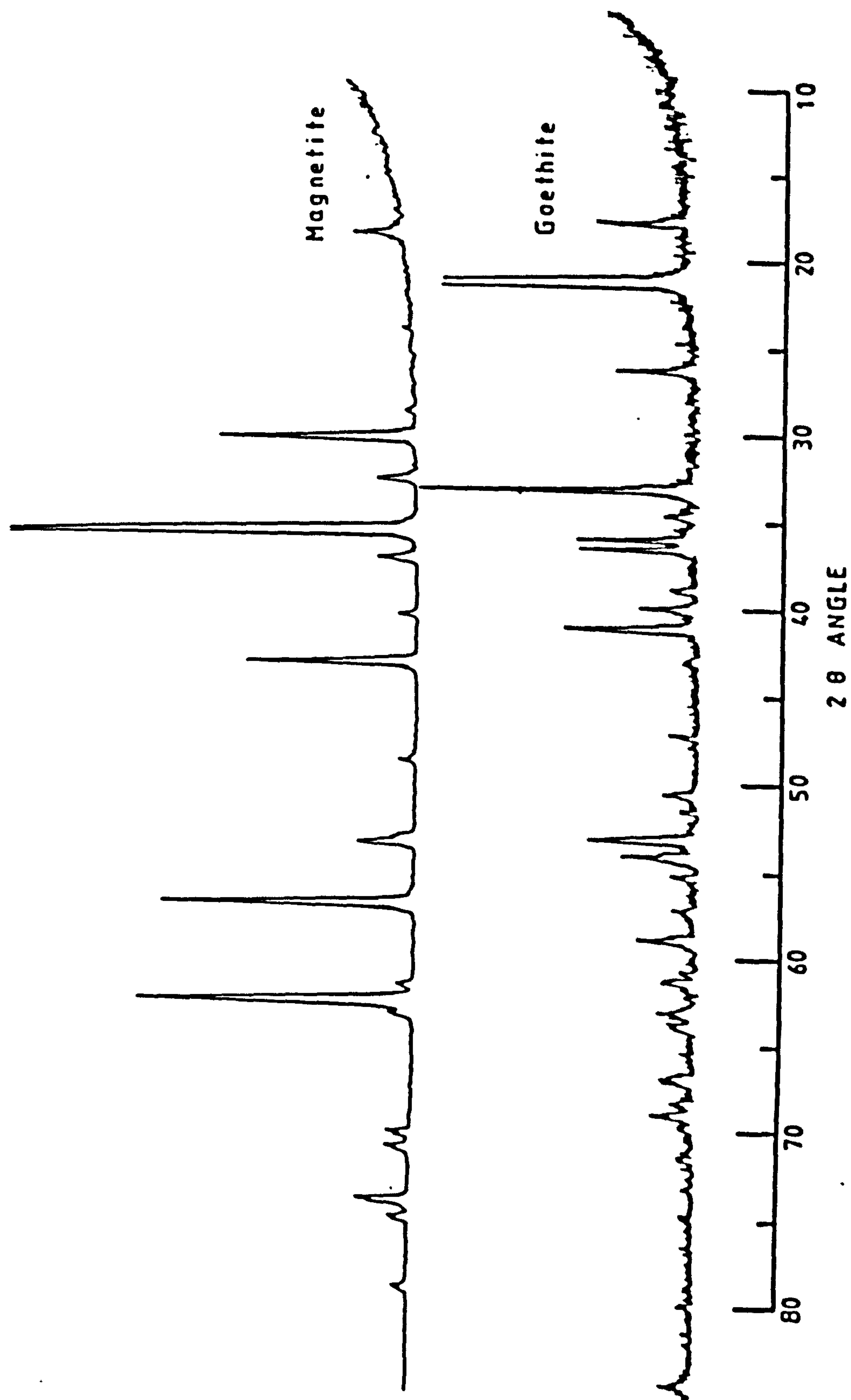


Figure 5.9 XRD pattern of pure magnetite and goethite samples used in the zero field NMR experiments.

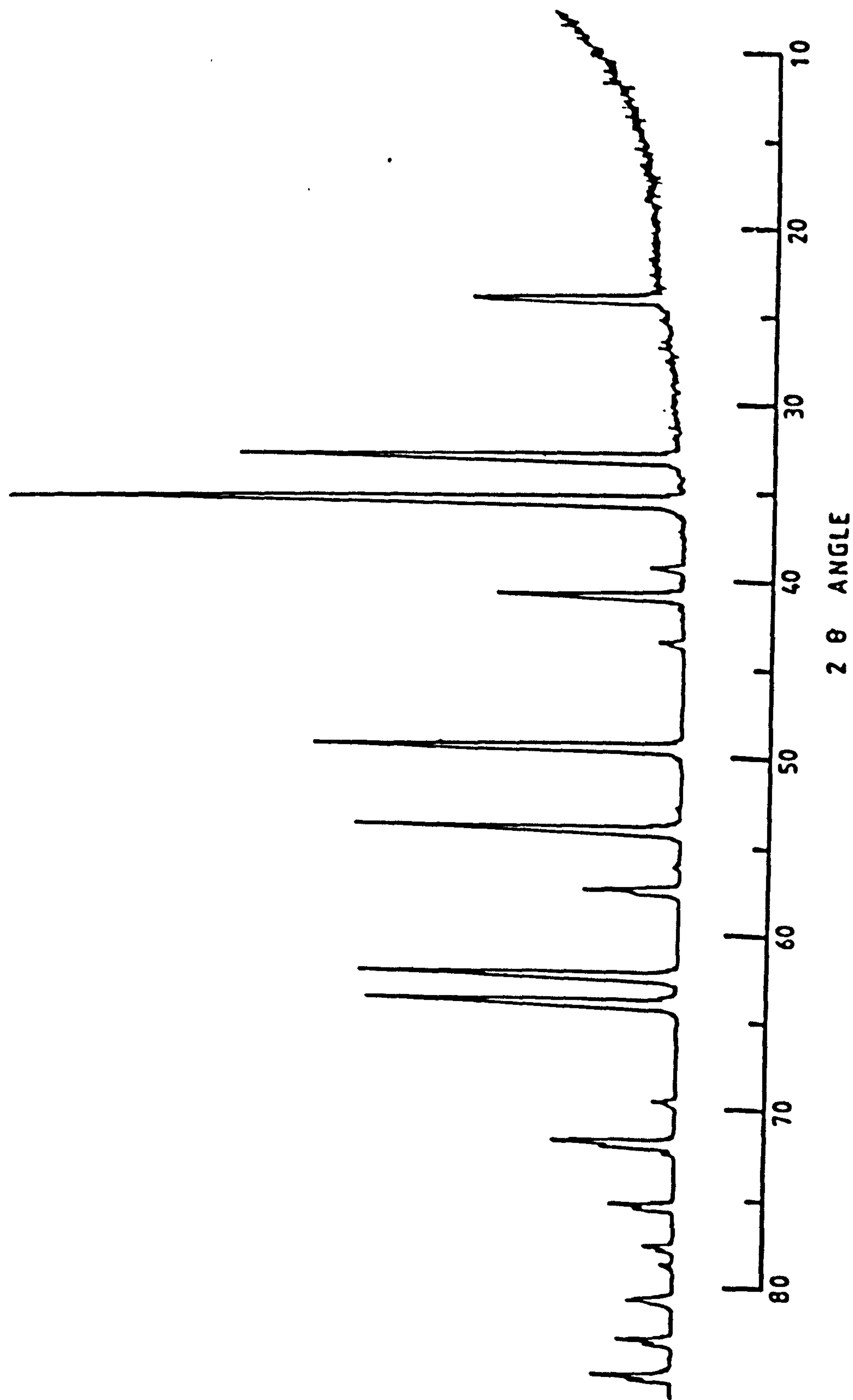


Figure 5.10 XRD pattern of pure hematite sample used in the zero field NMR experiments.

of specular hematite, the goethite sample consisted of a rock specimen of pure fibrous goethite from which crystals were selected. The magnetite specimen was selected from among a number of "pure" magnetites. The XRD of hematite and goethite showed pure phases, while the XRD of the best magnetite specimen showed traces of ilmenite. The metallic iron and nickel were commercially pure metal powders (Hopkins and Williams).

Fe^{57} resonance signals were searched for in the mineral specimens using the Decca NQR spectrometer in zero applied field around the frequencies shown in Table 5.5. The experiments were carried out at room temperature and at liquid nitrogen temperatures and under a variety of spectrometer conditions. In both hematite and magnetite piezoelectric resonances were initially found as described in Section 5.2 but were removed by grinding the samples to pass through B.S. 240 mesh sieve ($63\ \mu\text{m}$). With the ground specimens, strong resonance signals were found at room temperature at 71.43 MHz in hematite and at 67.84 MHz in magnetite. (See Figures 5.11 and 5.12). A second weak and broad (2.5 MHz wide) resonance signal centred at 63.5 MHz was found in magnetite at room temperature after very careful optimization of spectrometer settings. (See Figure 5.13). Very strong resonance signals of Fe^{57} and Ni^{61} were detected at 45.53 MHz and 26.21 MHz in iron and nickel metals respectively in agreement with previously published work (Dudnick, et al, 1961; Streever and Bennett, 1963); Appendix D. No resonance signals were obtained of goethite or in the three mineral specimens at liquid nitrogen temperatures. The results at room temperature and at 0°C are shown in Table 5.7.

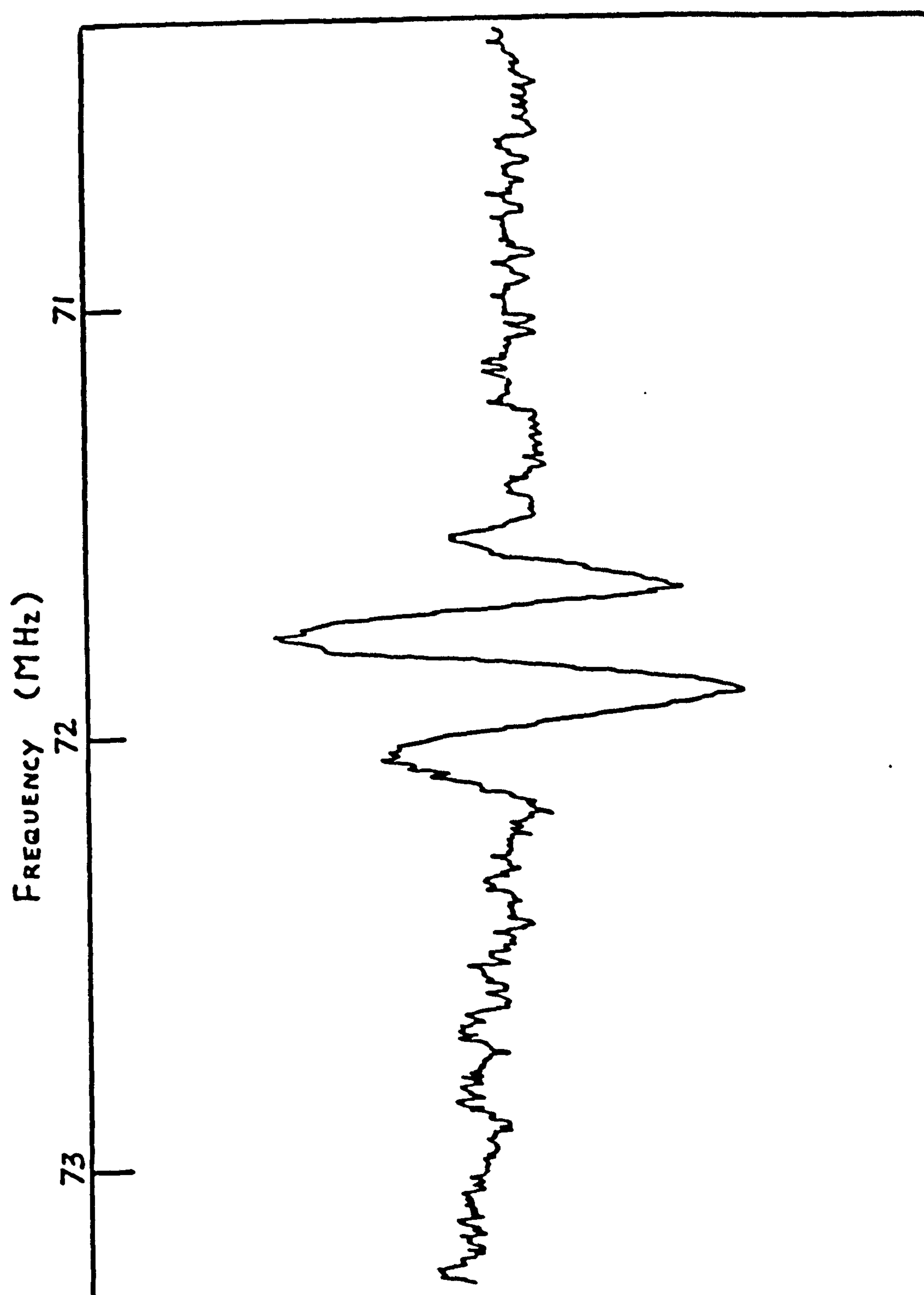


Figure 5.11 Fe^{57} resonance signal in hematite at 273°K

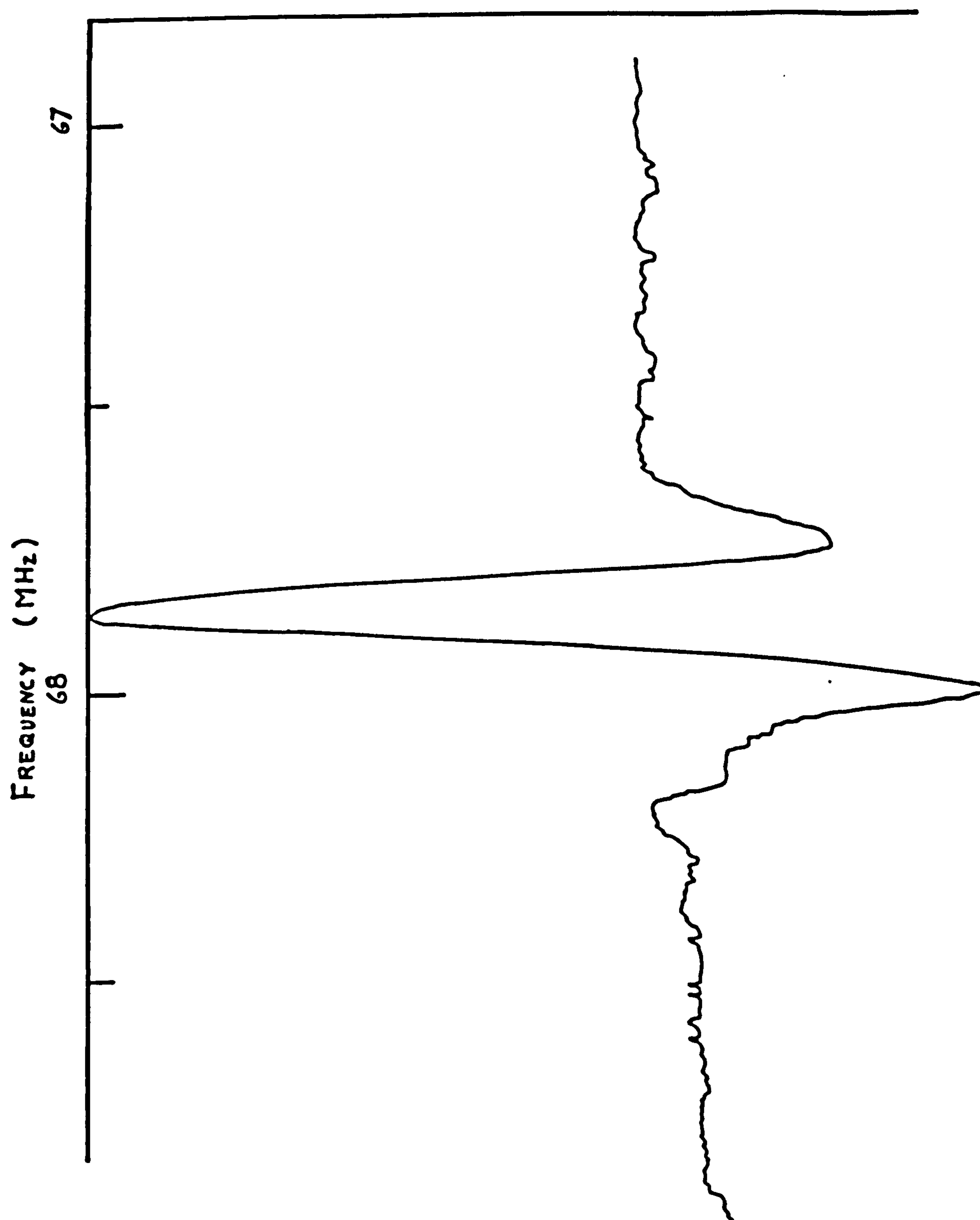


Figure 5.12 Fe^{57} resonance signal in magnetite at 273°K corresponding to the tetrahedral Fe site.

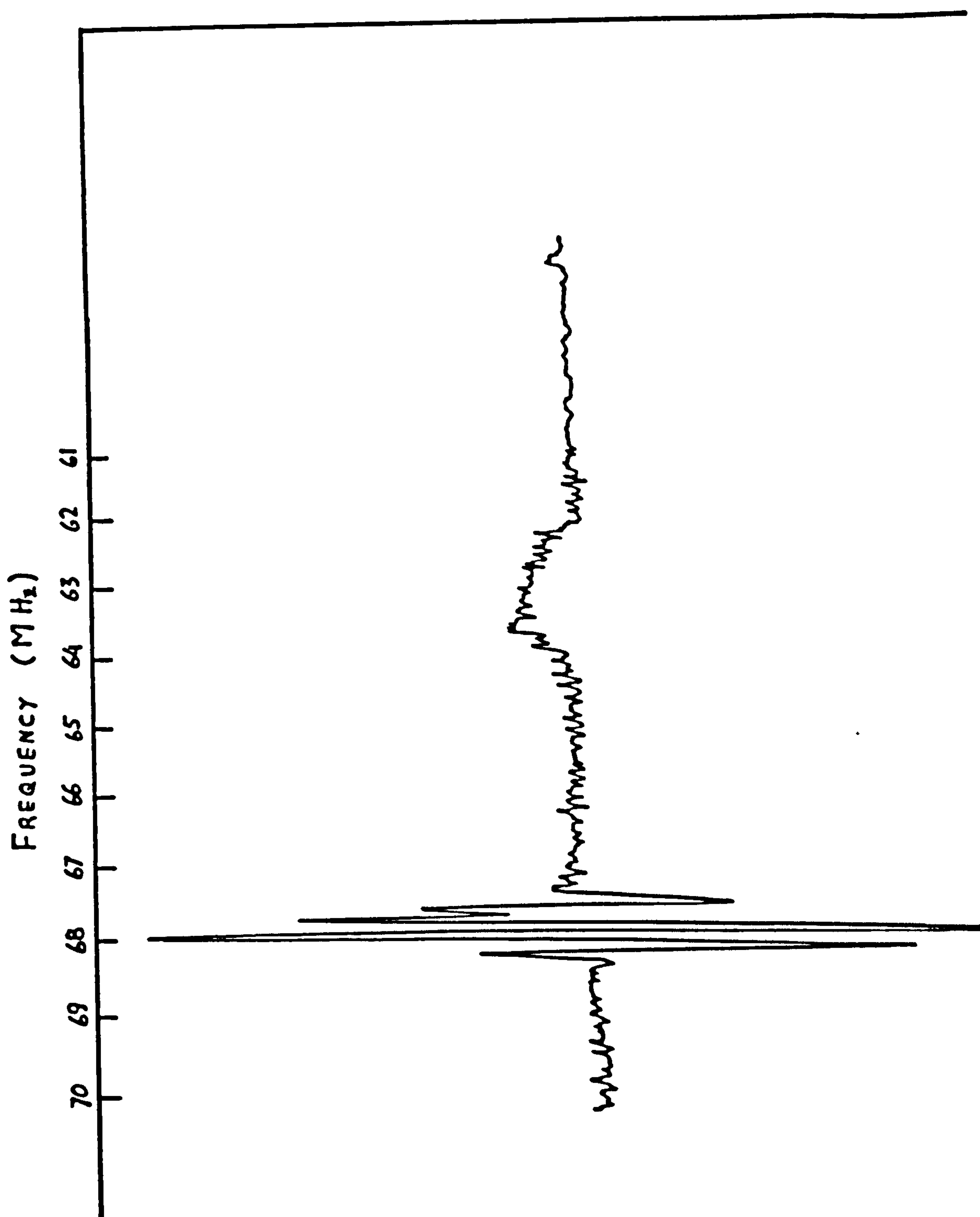


Figure 5.13 Fe^{57} resonance in magnetite at 298°K showing the 63.5 MHz weak signal corresponding to the octahedral Fe site. Spectrometer conditions: RF level maximum, CSC = 999, amplifier level 9, FM modulation X1, 4 (60 KHz modulation depth), quench PRF 50 KHz lock, AGC auto, coherence 6, sweep 256, chart 600/h, 0.5V, time constant 10s.

Table 5.7 Measured Fe^{57} resonance frequencies at room temperature and at 0°C in hematite and magnetite.

Mineral	Temp. $^\circ\text{K}$	frequency MHz	Linewidth (full signal width) MHz	Derived Magnetic field Tesla
Hematite	298	71.0	0.6	52.01
	273	71.833(1)	0.55	52.625(1)
Magnetite	298	67.84	0.5	49.70
		63.5	2.5	46.5
	273	67.866(3)	0.5	49.719(2)
		-	-	-

In order to test the limits of hematite detectability by this method a set of synthetic mixtures were prepared with decreasing amounts of hematite in an inert medium (sugar). The signal to noise ratios of spectra of the diluted samples were used as quantitative indication to establish the limit of detectability. Spectrometer settings optimised for the best signal to noise ratio were used during these tests (Appendix D). A plot of signal to noise as a function of hematite content in the specimen tube (Figure 5.14) shows that the minimum detectable amount of hematite is of the order of 0.5 gr. An increased sensitivity could probably be achieved with some refinements of the technique, but such effort is not really justified because it was found that the characteristics of the particular hematite sample have a decisive influence on whether a signal is detected or not. This point is illustrated by the fact that it was impossible to obtain resonance signals from a specimen of pure chemical grade hematite (Hopkin & Williams, Fe_2O_3 calcined) which according to the XRD pattern, had very good crystallinity. Neither was it possible to

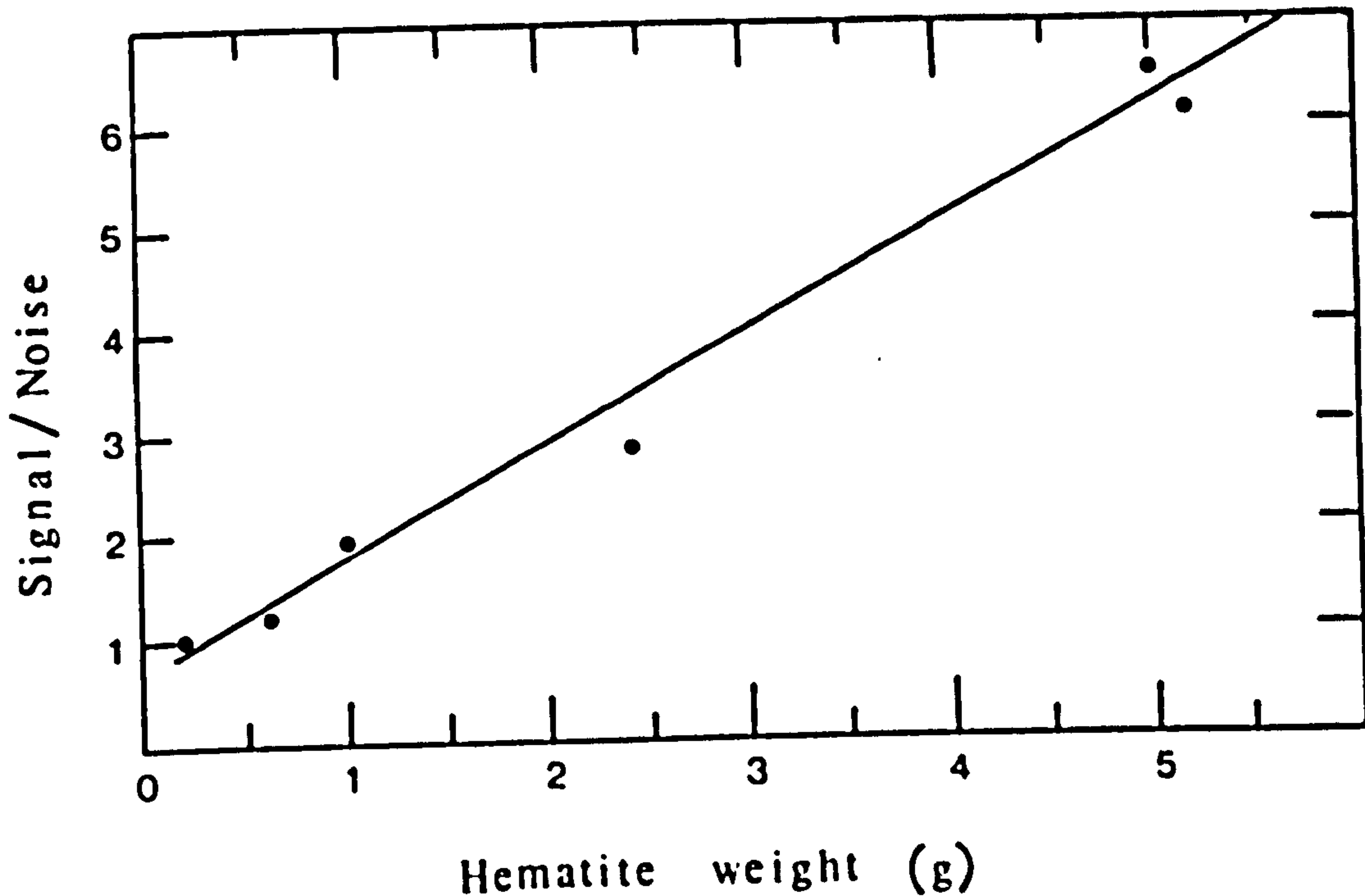


Figure 5.14 Signal to noise ratio of the Fe^{57} nuclear magnetic resonance in hematite as a function of total weight in the specimen coil.

obtain resonance signals from a number of lateritic specimens which the XRD analysis and previous Mössbauer spectra had shown to contain hematite. The average particle size of the hematite in the lateritic samples was known to be very small (Section 5.2) and the particle size of the chemical grade hematite was also small. ($<0.5 \mu\text{m}$). Similar difficulties in detecting resonance signals from small particle hematite samples have been reported by Matsuura, et al. (1962). All of these results support the contention, discussed in Section 3.4, that if the mechanism through which nuclear resonance detection takes place is domain wall displacement, then resonance detection becomes impossible as the particle size decreases and approaches single domain size.

A test of detectability of magnetite with increasingly diluted specimens showed results very similar to those in hematite. The minimum detectable amount of magnetite being about 0.3 g. Several laterite samples containing mixtures of minerals which included magnetite were studied in order to test the possibility of detecting the Fe^{57} resonance in magnetite from a mixed sample. A very weak resonance signal was detected in specimens of the Guatemala laterite which had a highly magnetic behaviour and contained magnetite, hematite and goethite. The resonance signal at 67.56 MHz coincides to within the experimental uncertainty (the linewidth $\simeq 0.5$ MHz) with the frequency of the pure magnetite specimen demonstrating that this resonance was indeed due to magnetite.

A resonance signal is expected at 52.4 MHz in goethite but a large number of attempts with the Decca NQR spectrometer to detect this signal were unsuccessful. The searches were conducted from well above to well below the expected frequency with a variety of spectrometer conditions known to give strong signals with hematite and magnetite. The possible reasons for these results are discussed below (Section 5.4).

Evaluation

The results of the zero-field nuclear resonance of Fe^{57} in the three most common iron oxide minerals: hematite, magnetite and goethite show that the technique is not a good method of mineral identification and quantification. Although resolved resonance signals were obtained from the first two of these minerals and from selected samples of laterite minerals, the difficulties in detecting minerals which occur

in small sizes, with a low degree of crystallinity, or in small proportions, indicate that the technique as carried out in those experiments has very limited usefulness in the appraisal of laterites.

5.4 Mineral Structure

In this section are discussed the results related to the internal structure of the minerals studied. Topics covered are:

1. The influence of the magnetic structure on the detectability of nuclear resonance signals.
2. The atomic distribution and internal structure of pure chromite minerals.
3. The problem of the presence of nickel in goethite.

5.4.1. Nuclear resonance and magnetic structure

The facts that no resonance signals were detected in goethite nor in hematite and magnetite at 77°K are difficult to explain. The magnetic hyperfine fields at the iron nuclei in these three minerals have been studied with Mössbauer spectroscopy as a function of temperature. They are found to increase in a slow and systematic way from the values at room temperature to asymptotic values near 0°K. (Goethite: Forsyth, et al, 1968; Hematite: F. van der Woude, 1966, Ono and Ito, 1962; Magnetite: Ito, et al, 1963). Furthermore, Fe⁵⁷ resonance has been reported in a synthetic magnetite sample enriched in Fe⁵⁷ down to 100 K (Boyd and Slonczewski, 1962) and in natural magnetite at 77°K. (Ogawa and Morimoto, 1962).

In order to study the effect of temperature on the resonance signal, the samples were cooled in a cryostat (Section 4.2) and the resonances were followed as a function of temperature. The measured Fe^{57} resonance frequencies and derived magnetic hyperfine fields for hematite are shown in Table 5.8 and Figure 5.15. It was found that the resonant signal intensity increases slightly with a decrease in temperature, reaches a maximum at about 0°C and then decreases until it disappears in the noise at about 215°K . These results are in general agreement with those of Matsuura, et al. (1962). The calculated magnetic hyperfine fields coincide with less precise values deduced from Mössbauer effect measurements (F. van der Woude, 1966).

In magnetite it was possible to follow the sharp resonance signal at 67.8 MHz from room temperature to about 140°K . The second resonance signal in this mineral was very difficult to detect and no attempt was made to follow it as a function of temperature. Table 5.9 and Figure 5.16 show the results. The sharp resonance signal in magnetite has a maximum intensity at about 210°K and then decreases gradually until it disappears at about 140°K . Near the minimum temperature at which resonance was observable changes in the magnetite sample radically affected the operating conditions of the spectrometer either by stopping the spectrometer R.F. oscillation or by suddenly shifting the oscillator frequency by up to several MHz. (It should be noted that the introduction of the magnetite and hematite specimens

Table 5.8 Hematite resonant frequencies and calculated effective magnetic fields at Fe⁵⁷ as a function of temperature

Temperature (°K)	Frequency (MHz)	Field* (Tesla)	S/N ratio
296.9	71.437	52.33	10.4
293.1	71.38	52.29	7
273.16	71.8339(5)	52.6255(4)	11
261.8	72.044	52.750	7.5
257.8	72.094	52.82	9.5
255.9	72.133	52.844	7
251.1	72.206	52.898	6
243.6	72.344	52.999	6.5
242.7	72.344	52.999	5
232.7	72.464	53.087	4.
232.4	72.534	53.138	3.5
224.7	72.582	53.173	2
220.0	72.698	53.258	2.5
216.3	72.700	53.260	3
211.9	72.836	53.359	2

*Calculated assuming the ground state magnetic moment of Fe⁵⁷ $\mu = 0.0903$ n.m. (numerical $H(\text{Tesla}) = 0.7326 \times f$ (MHz) applicable only for Fe⁵⁷).

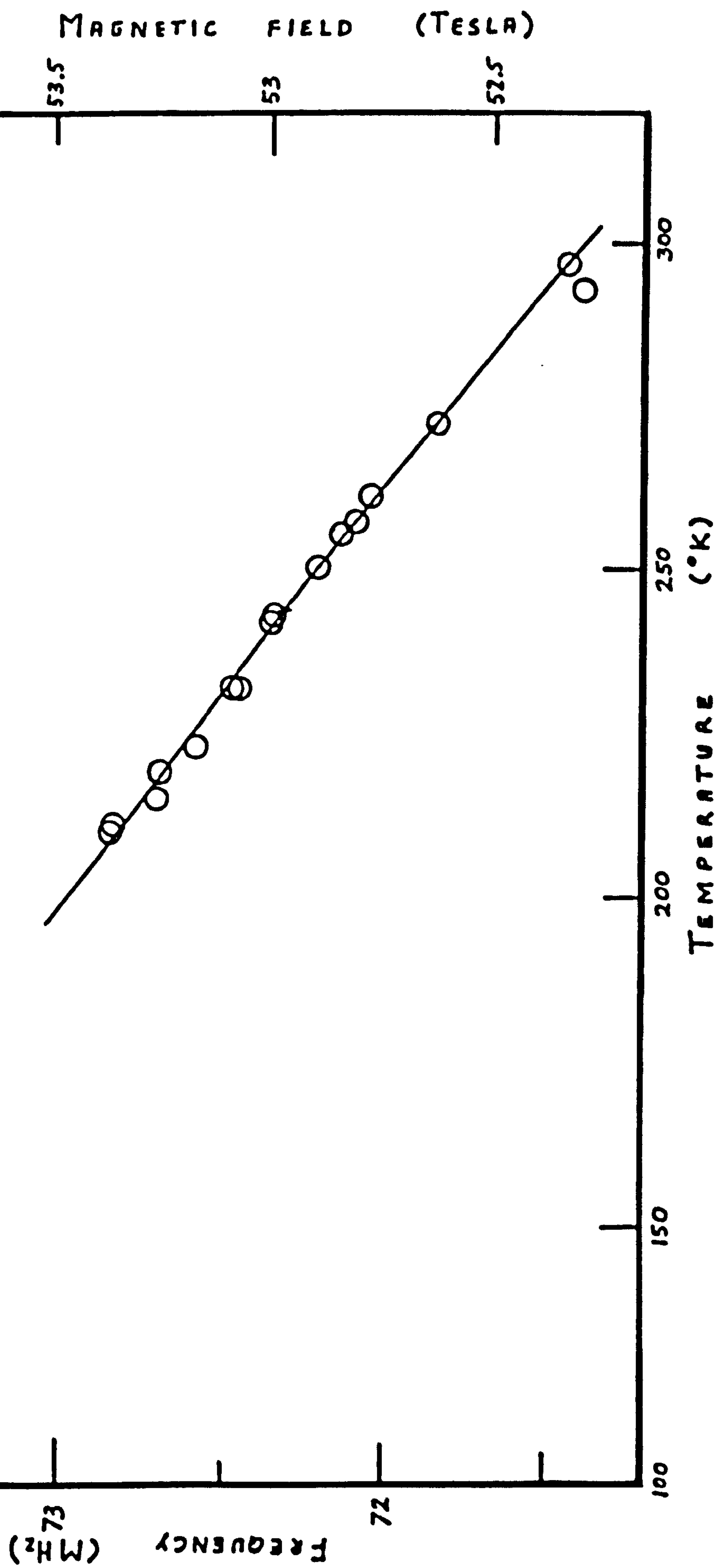


Figure 5.15 ^{57}Fe resonance frequency in hematite as a function of temperature.

Table 5.9 Measured resonant frequencies and calculated effective magnetic field at Fe^{57} in magnetite (Fe_3O_4) as a function of temperature (strong resonance).

Temperature (oK)	Resonance Frequency (MHz)	H Field* (Tesla)	S/N
295.9	67.66	49.56	12
282.6	67.90	49.74	14
273.1	68.08	49.87	14
262.6	68.26	50.01	17
252.7	68.41	50.12	18
243.3	68.56	50.23	18
233.2	68.71	50.34	22
221.8	68.84	50.43	35
212.6	68.97	50.53	45
201.4	69.10	50.62	30
191.7	69.20	50.69	27
180.9	69.30	50.77	17
171.1	69.41	50.85	13
160.7	69.53	50.94	11
151.5	69.61	50.99	9
148.8	69.68	51.05	6.3
146.9	69.68	51.05	6
144.9	69.66	51.03	3
142.7	69.71	51.06	1.8
140.7	69.69	51.05	3.7
138.9	69.73	51.08	3

*See footnote to Table 5.8

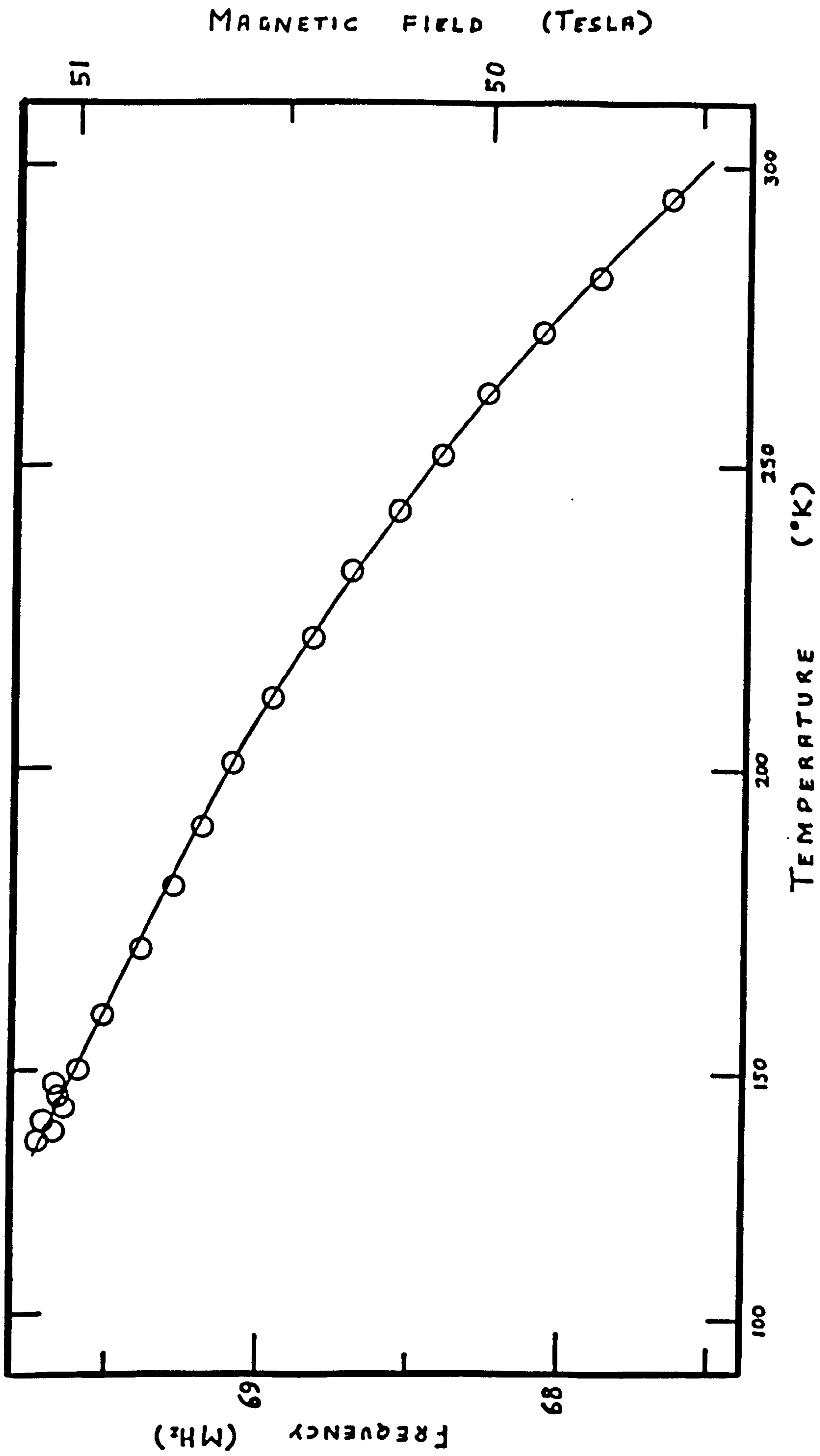
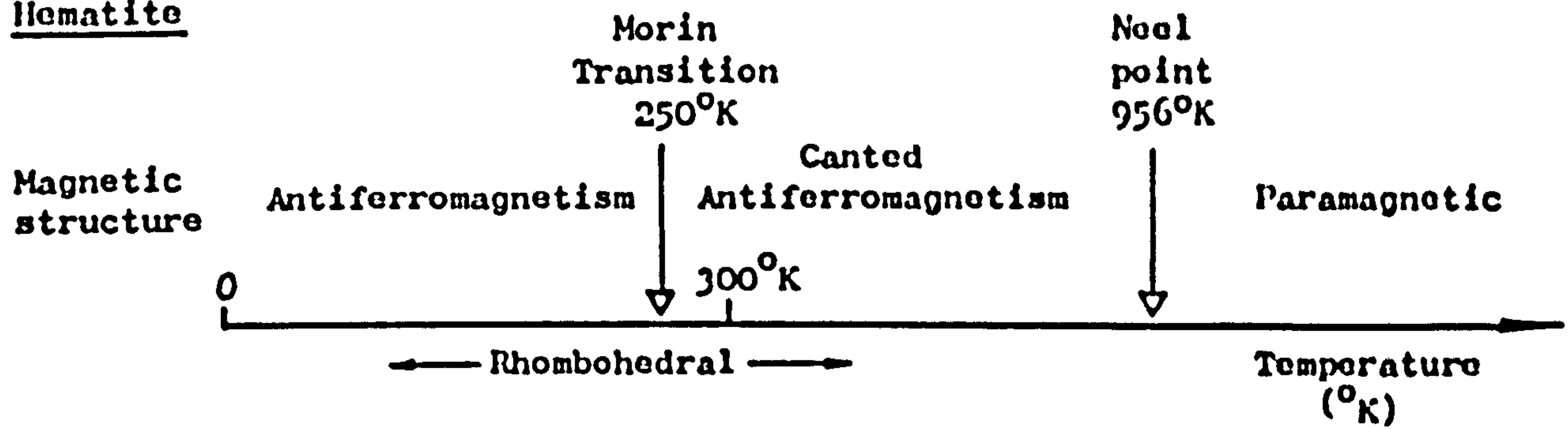


Figure 5.16 ^{57}Fe resonance frequency in magnetite as a function of temperature.

into the spectrometer coil, at room temperature, increased the effective inductance of the coil and shifted the spectrometer operating frequency down by about 5 MHz with magnetite and by about 40 KHz with hematite).

Resonance signals were searched for, without success, in both magnetite and hematite from the temperatures at which signals first disappeared down to the minimum temperature of 100°K attainable with the cryostat and also at 77°K , by immersion of the sample and coil in liquid nitrogen.

In hematite and magnetite there is a net magnetic field at the Fe site which is present above and below the temperature at which the resonance signal disappears. Consequently, one is forced to conclude that the failure to observe resonance signals at some temperatures indicates that the mechanisms through which the resonance signals are detected ceases to function. The evidence indicates that this mechanism is intimately related to the magnetic structure of the minerals: Figure 5.17 summarises some magnetic and crystallographic properties of hematite and magnetite. With hematite the disappearance of the signal takes place at about 215°K which is just below the Morin temperature. This is a point where hematite undergoes a magnetic transition. Macroscopically, at this temperature, the magnetic susceptibility and the magnetization suffer a sharp reduction in value, from weak ferromagnetism to antiferromagnetic behaviour. Microscopically the change has been explained as a switch from canted antiferromagnetism to perfect antiferromagnetism. (Birss P.132, 1964;

Hematite

Crystallographic
structure

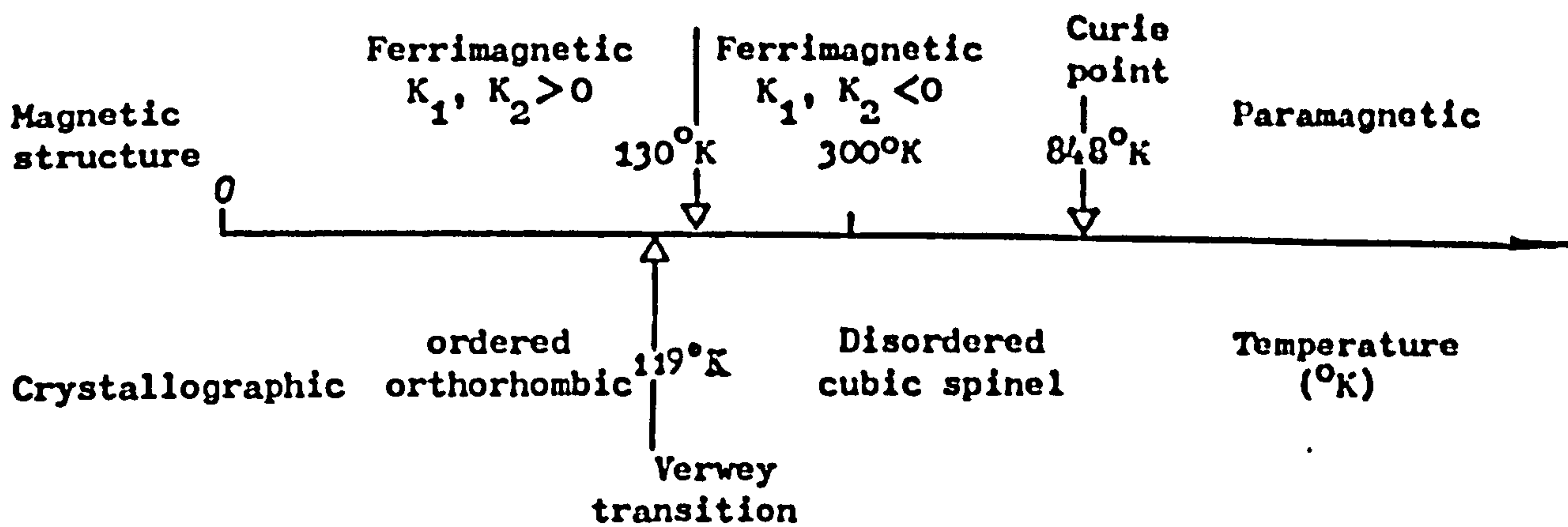
Magnetite

Figure 5.17 Diagram summarising some of the magnetic and crystallographic properties of hematite and magnetite as a function of temperature.

Scheiber P.168, 1967). With magnetite the temperature at which the resonance signals disappear is about 140°K which is higher than the Verwey transition temperature of 119°K . At about 119°K magnetite suffers a crystallographic order-disorder transition: from a disordered cubic structure above, to an ordered orthorhombic structure below. This transition is accompanied by a sharp decrease in the electrical resistivity which could account for the strong changes observed in the operation of the Decca spectrometer in this temperature range. The fact that the resonance signals disappears at a temperature above the Verwey transition temperature seems to be related to a magnetic transition which occurs in magnetite just above the Verwey transition temperature: In a study of the magneto-crystalline anisotropy constants of magnetite, Bickford, et al. found (see: Scheiber P.162, 1967) that the anisotropy constants K_1 and K_2 are both positive below and negative above about 130°K . This anisotropy crossover temperature was found to be higher than the Verwey transition temperature of the specimens. At the crossover point the magnetic anisotropy disappears, the material becomes magnetically isotropic and the magnetization direction has no preferred orientation. Under these conditions an applied field will orient all domains into a single direction without much difficulty with the consequence that domain walls are all pushed out of the material*. If the mechanism of nuclear resonance

*It is likely that these magnetic changes contributed to the observed changes in the spectrometer operation.

enhancement in magnetite is domain wall motion, the disappearance of the domain walls at the magnetic isotropy point would explain the absence of resonance signals in this temperature range.

No Fe^{57} resonance signals were detected in zero field with the Decca spectrometer in a variety of synthetic and natural goethite specimens. For this reason an attempt was made to obtain proton magnetic resonances in the α - FeO OH samples in an externally applied field. These experiments were carried out with the Decca NMR spectrometer and with the Bruker Pulse NMR spectrometer at the expected resonance frequency of 40.27 MHz in an applied field of 0.9458 T). Neither of these methods yielded resonance signals. The high sensitivity of the spectrometers which were proved by detecting proton resonances in extremely minute quantities of H containing specimens, rules out the possibility of insufficient sensitivity. Additionally, very strong proton signals were found in crystallographically similar synthetic boehmite, Al O OH , and in bayerite Al(OH)_3 (Appendix D). One is forced to look for a more fundamental cause for the lack of resonance signals.

The difficulty in detecting proton resonance in goethite could be attributed to the presence of a net local field at the hydrogen sites. This net local field could be produced by the sum of the fields of the neighbouring magnetic Fe atoms. The net local field (also sometimes called the dipolar field) at the site of a non-magnetic atom when inside a magnetic compound has been discussed by Jaccarino, (P.313, 1965). Its magnitude can range from 0.7 to 0.05 Tesla. Some examples of the local field in antiferromagnetic

compounds are $H = 0.076$ T at H nuclei in $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Ibulla, et al, 1958) and $H = 0.34$ T at I^{127} nuclei in $\text{Ni}(\text{IO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Burgiel, et al, 1961). The presence of a local field at the H atoms in goethite could, in an NMR experiment of a powder, broaden the resonance signal beyond detectability. If such a local field is indeed present, a better proposition might be to try to detect H^1 resonance signals in zero field. Unfortunately without prior knowledge of the magnitude of the field at the H atoms it becomes very difficult to find the resonance frequency due to the large frequency range to be searched.

An alternative explanation of the failure to detect the Fe^{57} and the proton resonance in goethite is that goethite has a magnetic structure such that the mechanism of signal enhancement does not take place. The published experimental evidence, reviewed in Appendix B, indicates that goethite is a perfect antiferromagnet and in this respect its behaviour in an exciting RF field would be similar to that of hematite below 250°K : the region in which no resonance signals were detected. In spite of the antiferromagnetic internal structure, weak ferromagnetism has been reported in goethite (Appendix B) and, in particular, it has been reported that stable thermoremanent magnetization can be induced in goethite by cooling the material through its Neel point at 130°C in an applied field. It was felt that such treatment might improve the chances of detecting nuclear resonance signals in goethite by promoting the formation of a domain structure and the presence of well defined domain walls.

Consequently, samples of goethite were subjected to the magnetic and heat treatment described by Banerjee, (1970) and the magnetic susceptibility and magnetization of the samples were measured before and after the treatment.

The treatment consisted of simply heating the specimens to 130°C and then allowing them to cool in the field of a strong permanent magnet. The magnetic susceptibility were measured by the Faraday method (Cullity P.76, 1972).

Figures 5.18 and 5.19 show the magnetic susceptibility of three goethite samples as a function of magnetic field before and after the heat treatment and Table 5.10 shows the magnetic susceptibilities extrapolated to infinite field. The results indicate that, within the measurement uncertainties, the specific magnetization and magnetic susceptibility of the specimens tested is unaffected by the magnetic-heat treatment. These results disagree with the results of Banerjee (1970) quoted above.

The magnetic susceptibilities measured in pure specimens of hematite and goethite closely agree with the accepted values for these minerals (Pastrana and Hopstock, 1977), demonstrating the reliability of the measuring instrument.

Table 5.10 Specific magnetic susceptibilities extrapolated to infinite magnetic field of some untreated and heat treated specimens. (SI units $\text{J}/(\text{T}^2 \times \text{Kg})$)

Specimen	Untreated $\times 10^{-10}$	Heat treated $\times 10^{-10}$
Natural goethite	28	27
Synthetic goethite (1.52%Ni)	25	33
Synthetic goethite*(1.74%Ni)	56	68
Specular hematite	25.5	-

*specimen supplied by W. Schellmann, Nickel as weight percent of iron.

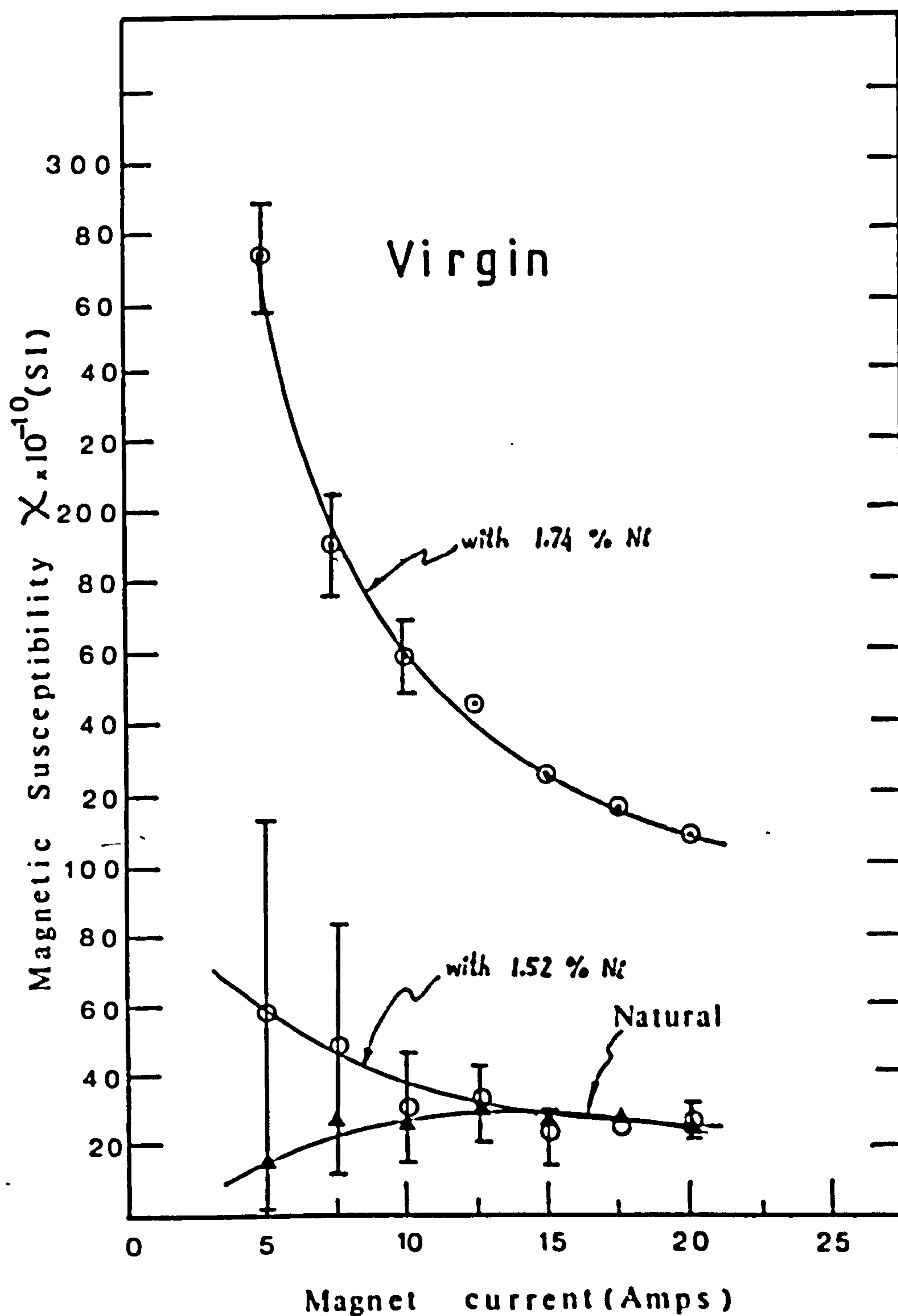


Figure 5.18 Specific magnetic susceptibility of virgin goethite specimens as a function of magnetic field.

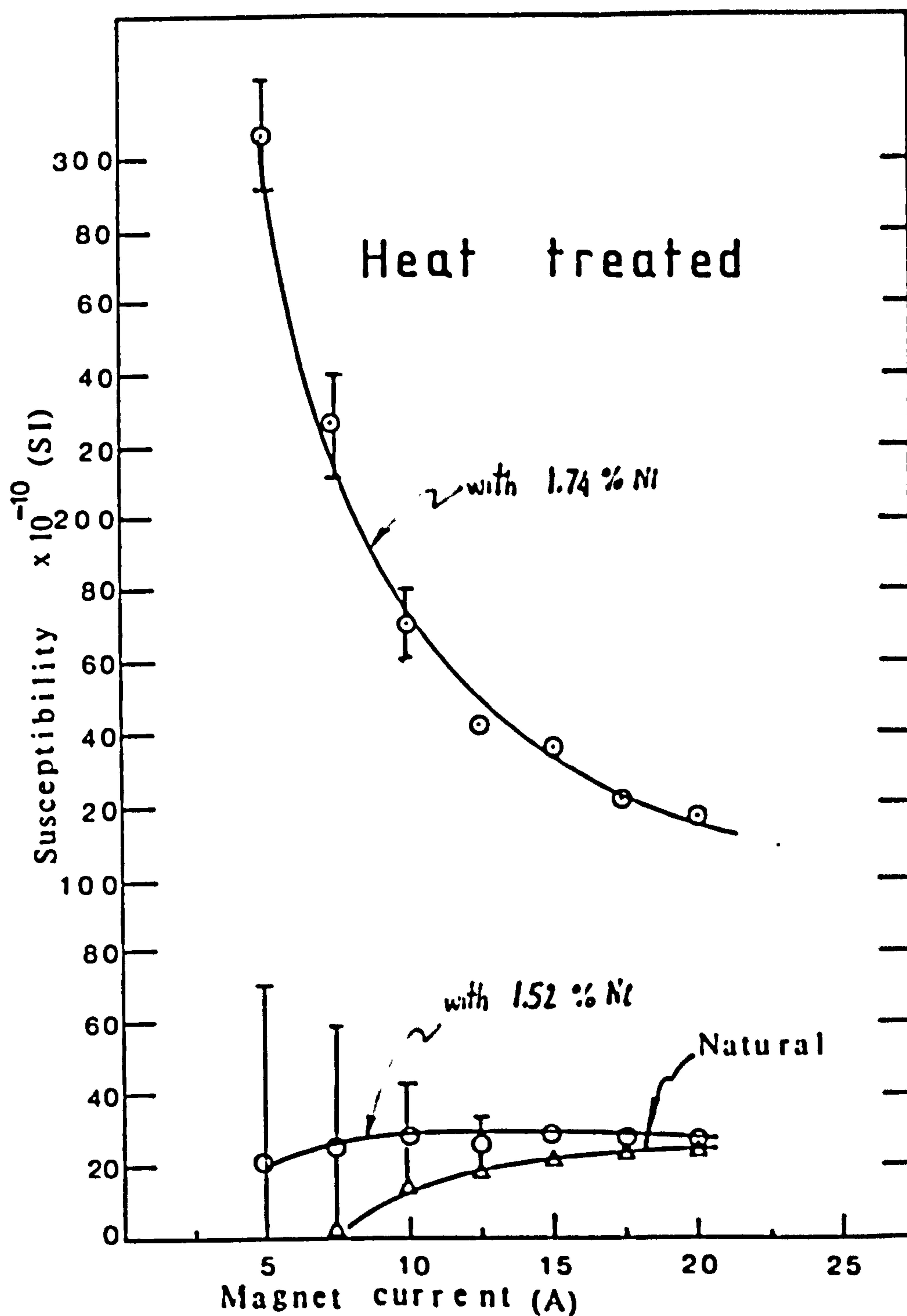


Figure 5.19 Specific magnetic susceptibility of heat treated goethite specimens as a function of magnetic field. (Measurement uncertainties similar to Fig. 5.18).

A search for Fe^{57} resonances in the Decca spectrometer in the heat treated specimens did not produce resonance signals or reveal a different behaviour from the untreated specimens.

Conclusion

Although the nuclear resonance experiments do not supply conclusive evidence, the results are consistent with the following conclusions:

- 1) The possibility of observing nuclear resonance signals from magnetically ordered minerals is strongly dependent on the detailed sub-microscopic magnetic structure of each mineral.
- 2) Factors such as crystallinity, particle size and particle shape which influence the magnetic behaviour of a particular mineral specimen have a determining influence on the mechanism of nuclear resonance detection.
- 3) The mechanism of enhancement through which nuclear resonance signals are detected in hematite and magnetite is domain wall displacement.
- 4) The mechanism of domain wall displacement is not present in goethite due to the particular antiferromagnetic ordering of this mineral.

5.4.2 Chromites internal structure

As indicated in Section 2.2 and 2.3 the presence of spinel-type mineral phases was detected in the two nickel laterites. These minerals were eventually classified as chromites and as such are identified here. Purified specimens of these chromites were produced by attacking with hot 40% HF acid for 15 minutes the residues of HCl treatment of samples of the nickel laterites.

The optical characteristics of the chromites from the two laterites were found to be very similar. In grain fractions they are black or very dark brown in colour with a shiny surface, angular faces and occasionally conchoidal fractures. Very fine grains, thin sections or the borders of grains are seen to be transparent with a dull amber colour. The grains are very brittle and may be crushed with a needle with relative ease. In comparison with magnetite they look less brown and have more shiny less iridescent surfaces. In polished sections they show a grey-bluish colour and are optically isotropic.

The XRD pattern of these minerals showed a single phase with sharp lines indicative of a very well crystalline mineral. Careful measurement of the XRD patterns produced the d-spacings and intensities shown in Table 5.11 and 5.12. It was found possible to index all the lines found as belonging to cubic spinel-type structures.

It is worth noting that comparison with published d-spacings in the ASTM data file indicates that a very close agreement is attained with the d-spacings of the compounds NiCo_2O_4 and FeAl_2O_4 (Hercynite). This close agreement extended to the reflection intensities. Chemical analyses of these minerals however are incompatible with either NiCo_2O_4 or FeAl_2O_4 .

The chemical analyses carried out by electron probe micro-analysis, showed that the composition was analogous to natural chromites. (See Table 5.13). These results highlight the known limitations of the XRD method in identifying members of the spinel-type family of minerals and compounds (Zussman, P.461, 1977).

Table 5.11 Results of the XRD of the chromite found in the Ni-laterite from Venezuela

$d\text{\AA}$	I/I_0	hkl
4.75	24	111
2.91	30	220
2.48	<u>100</u>	311
2.38	4	222
2.058	<u>41</u>	400
1.679	8	422
1.583	26	511,333
1.455	29	440
1.39	2	531
1.30	2	620
1.254	5	542,533
1.24	3	622
1.19	3	444
1.15	1	711,551
1.10	2	642
1.071	5	553,731

Radiation Cu $k\alpha_1$ $\lambda = 1.5405$ Filter: none

Monochromator I/I_0 : Diffractometer

System: Cubic (spinel type) $a_0 = 8.2346 \pm 0.004$

Table 5.12 Results of the XRD of the chromite found in the Ni-laterite from Guatemala.

$d\text{\AA}$	I/I_0	hkl
4.68	30	111
2.974	24	220
2.455	100	311
2.368	4	222
2.038	47	400
1.664	8	422
1.570	35	511,333
1.443	54	440
1.380	3	531
1.290	2	620
1.245	6	542,533
1.230	2	622
1.178	4	444
1.142	1	711,551
1.090	2	642
1.062	8	553,731

Radiation: Cu $k\alpha_1$ $\lambda = 1.5405$ Filter: none

Monochromator I/I_1 : Diffractometer

System: Cubic (spinel type) $a_0 = 8.1575 \pm 0.0028 \text{ \AA}$

Table 5.13 Results of electron probe microanalysis of chromite minerals isolated from the Venezuelan and Guatemalan nickel laterites (O by difference).

Element	Venezuela		Guatemala	
	% weight	Formula (O=4)	% weight	Formula (O=4)
Mg	7.40	0.57	8.16	.57
Al	12.38	0.86	21.12	1.31
Cr	31.79	1.14	21.33	.73
Mn	0.31	0.011	-	
Fe	12.75	0.43	11.96	.39
O	35.37	4.00	37.43	4.00
	100.0		100.0	

Mössbauer effect measurements were carried out on these minerals at room temperature and at 77°K. Figure 5.20 shows the spectra obtained. These spectra show that the minerals are not magnetically ordered even at liquid nitrogen temperature. Iron was found to be present in three different and non-equivalent sites which show non-zero EFG. The parameters derived from the computer fits are shown in Table 5.14, as well as the interpretations given to each doublet line. In these interpretations the following criteria were used: Peak doublets with splitting due to lower EFG (0.7 - 0.9 mm/s) were attributed to iron atoms in the tetrahedral sites; doublets with higher EFG (1.1 to 3.0 mm/s) were attributed to iron atoms in octahedral sites; the ferric/ferrous ratio was derived from the measured isomer shift. (high: ferrous, low: ferric). These criteria were derived from a more detailed discussion on the interpretation of Mössbauer spectra of spinel-type minerals reported by Greenwood and Gibb, P.258 (1971).

The results of the Mössbauer spectra in conjunction with the electron microprobe analysis provided a unique assignment of the constituent ions to crystallographic sites. The assignment was derived by requiring it to be consistent with the number of atoms and the charge balance expected in either a normal or an inverse spinel structure. The ideal arrangement of the number of atoms and charges in normal and inverse spinels are shown in Table 5.15.

NATURAL SPINEL TYPE MINERALS

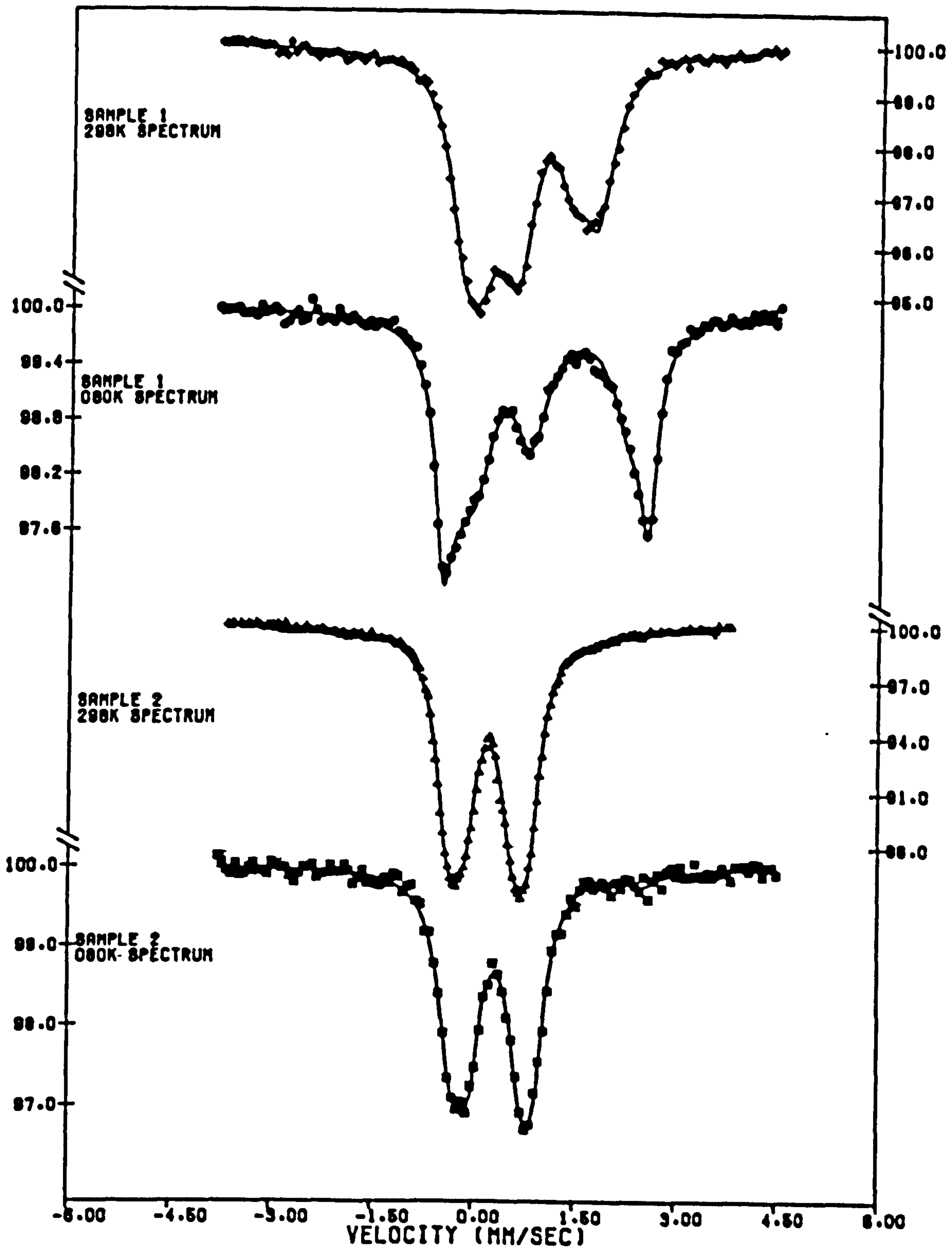


Figure 5.20 Mössbauer effect spectra of the chromites isolated from the Venezuela (sample 1) and Guatemalan (sample 2) laterites.

Table 5.14 Parameters derived from the Mössbauer effect spectra of the chromites isolated from the Venezuelan and Guatemalan laterites. I.S. = Isomer shift; HWHM = half-width at half maximum; Q.S. = quadrupole splitting; H = magnetic field (in Tesla = weber/m² = 10 K O_e = 10 kG); Oh = Octahedral hole; Th = tetrahedral hole, Area = area under the absorption curve

Chromites from Venezuela						
Temp. °K	I.S. mm/s	HWHM mm/s	Q.S. mm/s	AREA %	oxida- tion	Probable site
298	.245(7)	.253(10)	.860(12)	34.9(1.7)	3+	Th
298	.933(9)	.258(30)	.970(40)	23.1(3.5)	2+	Oh
298	.935(5)	.285(19)	1.720(29)	42.0(3.7)	2+	Oh
77	.430(9)	.300(13)	.791(15)	38.0(1.9)	3+	Th
77	1.056(4)	.151(14)	3.039(12)	29.4(3.8)	2+	Oh
77	1.019(9)	.289(30)	2.534(7)	32.6(5.4)	2+	Oh
Chromites from Guatemala						
Temp. °K	I.S. mm/s	HWHM mm/s	Q.S. mm/s	AREA %	oxida- tion	Probable site
298	.247(3)	.214(8)	.710(15)	47.7(3.0)	3+	Th
298	.237(2)	.203(7)	1.192(12)	49.0(3.0)	3+	Oh
298	1.169(91)	.340(129)	1.395(17)	3.3(1.4)	2+	Oh
77	.315(23)	.215(29)	1.133(30)	46.5(12.0)	3+	Oh
77	.350(7)	.217(17)	.759(43)	48.0(12.0)	3+	Th
77	1.174(388)	.273(154)	2.679(751)	5.5(3.4)	2+	Oh

Table 5.15 Ideal arrangement of atoms and charges in normal and inverse spinels* (Cullity, P.184, 1972)

Type	Tetrahedral (A) site	Octahedral (B) site	Oxygen
<u>Normal</u>	M^{2+}	M^{3+}, M^{3+}	
No. of atoms	1	2	4
No. of charges	2+	6+	8-
<u>Inverse</u>	M^{3+}	M^{2+}, M^{3+}	
No. of atoms	1	2	4
No. of charges	3+	5+	8-

*2,3 spinels shown; 4,2 spinels are also possible in which case M^{4+} takes the place of M^{2+} and M^{2+} takes the place of M^{3+}

The assignments derived for the chromites from the nickel laterites are shown in Table 5.16. With the chromites from Venezuela a good agreement with the expected number of atoms and charges was obtained if an inverse spinel structure was assumed. On the other hand with the chromites from Guatemala the results are not so clear: a normal spinel structure can definitely be ruled out because of the approximately equal quantities of ferric iron in tetrahedral and octahedral sites found with the Mössbauer spectra; but a satisfactory inverse spinel structure can only be achieved with the further assumption that Al^{3+} is distributed in both tetrahedral and octahedral sites. The partition of Al between the two sites shown in Table 5.16 was arbitrarily assumed such that the number of atoms in each site had the correct value for an inverse spinel. The resultant assignment has a slight defect in the number

Table 5.16 Scheme showing the internal atomic structure of the chromites isolated from the nickel laterites from Venezuela and Guatemala

Specimen	Tetrahedral (A) site			Octahedral (B) site			
<u>CHROMITE FROM VENEZUELA</u>							
Formula	Al ³⁺	Fe ³⁺	(Fe ²⁺	Fe ²⁺	Mg ²⁺	Cr ³⁺)	O ²⁻
Number of	.86	.15	.10	.18	.57	1.14	
Atoms	1.01		1.99			4.0	
Number of	3.03		5.12				
charges	8.15			8.00			
Spinel type: Inverse							
<u>CHROMITE FROM GUATEMALA</u>							
Formula	Al ³⁺	Fe ³⁺	(Al ³⁺	Fe ³⁺	Cr ³⁺	Mg ²⁺	Fe ²⁺
Number of	.81	.18	.50	.19	.72	.56	.01
Atoms	.99		1.98				
Number of	2.97		4.37				
charges	7.34						
Spinel type: Inverse							

of charges in the octahedral site. This discrepancy is possibly due to errors in the electron microanalysis of the sample which was not as repeatable in different grains as the microanalysis of the chromite from Venezuela.

The assignment of lattice sites shown in Table 5.16 for the chromite from Venezuela gives a satisfactory account of the number of charges and the number of atoms in each site of the crystal lattice. Nevertheless, it raises the question of why should Fe²⁺

atoms in the octahedral sites exhibit two different values of the electric field gradient in this mineral. A possible explanation is that the mineral is ordered; and that the EFG of the Fe atoms in the octahedral sites is influenced by the presence of magnesium or chromium atoms in adjacent octahedral sites. This hypothesis is supported by the fact that, within experimental uncertainty, the measured ratio of Mg/Cr (1:2) is the same as the measured ratio of Fe atoms showing the two different values of EFG (1:1.8).

5.4.3 Presence of nickel in goethite

It has been repeatedly suggested in the literature that a large proportion of the nickel contained in nickel-bearing limonitic laterites is intimately associated with goethite. The suggestions are derived from circumstantial evidence as well as from a number of careful laboratory tests. Some of the evidence put forward by the various authors in support of this suggestion are as follows:

- a) The inability to find nickel minerals in limonitic samples whose chemical assay shows the presence of nickel (A typical example is the limonitic laterite from Guatemala described in Section 2.3).
- b) Observations of the rate of chemical extraction of Fe and Ni in leaching tests (Carlson and Simons, 1961; Rice and Strong, 1974; Canteford, 1978a).
- c) Linear laboratory correlations between the release of nickel and iron during progressive dissolution of nickel limonite as well as from the same material after transformation of goethite into hematite by heating (Schellmann, 1978).

d) The high temperature reduction, under identical conditions, of natural nickel limonite and synthetic mixtures of nickel and iron oxides produces, in the first case, ferronickel alloy and in the second, separate phases of metallic nickel and iron. (Canteford, 1978b).

e) Correlations between Fe and Ni established with the electron probe microanalyser either by comparison of the Fe and Ni X-ray images, (Roorda and Quenau, 1973; Kühnel, et al. 1974; Kühnel, et al, 1978) by simultaneous counting of the Fe and Ni X-rays while performing linear transverses of goethite grains (Canteford, 1975) or by microprobe correlation analysis of Fe and Ni in goethite grains (Schellmann, 1978).

These studies have indicated without doubt that there is a very intimate relationship between Ni and goethite, but the nature of the association of Ni with goethite has not been established. Hence the evidence presented above can be explained by more than one of the following association possibilities (diagrammatically shown in Figure 5.21)

- 1) The presence of submicrometer particles of a distinct nickel mineral dispersed among the iron oxide grains
- 2) The presence of nickel atoms adsorbed on the surface of the iron minerals either loosely bound or chemically bound to the surface (the term chemisorbed has been used to describe this last case: Kühnel, et al. (1978).
- 3) The solid solution of a nickel mineral phase in the iron minerals, or
- 4) Nickel incorporation into the structure of the iron minerals either substitutionally in the site of Fe atoms, in an ordered or disordered way, or interstitially trapped in the goethite lattice.

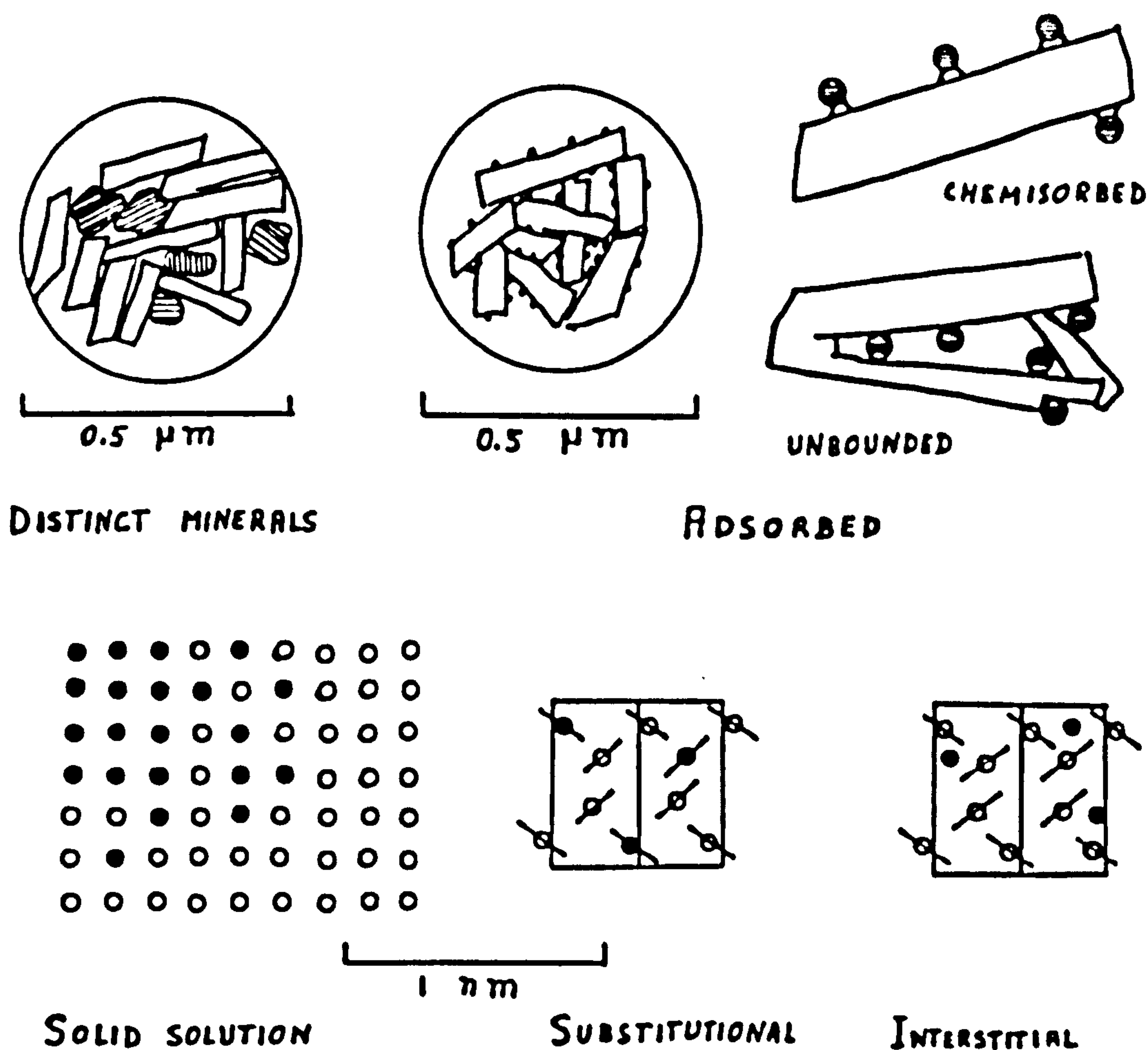


Figure 5.21 Schematic diagram showing the different possible nickel-iron mineral association.

The nature of the Ni-goethite association is of great importance in deciding processing routes for Ni-bearing limonitic laterites, and it was hoped that the Mössbauer effect spectra could help in deciding between the various association possibilities.

As seen above (Section 5.3) the 6-line patterns in the Mössbauer effect spectra of the Ni-laterites were attributed to goethite and hematite. The measured magnetic hyperfine fields in the samples (Table 5.6) were found to be lower than the values reported for pure goethite and hematite, both at room temperature and at liquid nitrogen temperatures.

The lowering of the magnetic hyperfine field can be attributed to the presence of solid solutions of certain elements in goethite and hematite. Such lowering of the magnetic hyperfine field has been observed in synthetic specimens of hematite in which a proportion of the Fe has been substituted by Al, Cr or V. (Shirane, et al. 1962), in natural Al-bearing goethite, (Janot, et al. 1968) and in natural Al-bearing hematite (Janot and Gibert, 1970).

As discussed in Section 3.1 it is very difficult to calculate from first principles the magnitude of the magnetic hyperfine field and it is likewise difficult to explain the detailed reasons for the observed lowering of the field as a function of atomic substitution, but the empirical results can be used to obtain an estimate of the amount of foreign atoms which may be present as substitutions in the minerals.

By interpolating between the data of Shirane, et al. (1962) the total amount of atomic substitution in hematite in the two nickel laterites is estimated to be in the range of 13-20% in the limonitic laterite from Guatemala and 6-10% in the garnieritic laterite from Loma de Hierro, Venezuela. Essentially the same results of atomic substitution are obtained if the measured hyperfine fields are interpolated between the data of Janot and Gibert (1970). These results agree with a prior semiquantitative estimation that a larger proportion of the Al, Ni and Cr is associated with the Fe minerals in the limonitic laterite than is the case of the garnieritic laterite. (Chapter 2).

Synthetic Ni-bearing goethites

In order to study the nature of the presence of nickel in goethite, a series of goethites were synthesised with various amounts of nickel. Mössbauer effect spectra were obtained of these samples and an attempt was made to correlate the measured parameters with the amount of nickel present in the goethite.

Goethite can be synthesised in various ways. (Appendix B). Although details differ, the processes are either by ageing of trivalent iron hydroxide or by oxidation of divalent iron hydroxide. The first method is not suitable for the incorporation of divalent nickel into goethite.

The method actually used was developed by Schellmann (1978) and consists of the simultaneous precipitation of divalent nickel and iron hydroxide. Then the precipitate is oxidised with air by stirring the alkaline suspension. If the oxidation is too quick or too slow δ -Fe OOH or γ -Fe₂O₃, maghemite, is produced in addition to goethite. (Schellmann. Private communication).

Details of the method of synthesis used for the nickel-bearing goethites are as follows:

A solution of divalent iron and nickel chloride was made by dissolving 5 g of FeCl₂·4H₂O with amounts varying from 0.05 to 0.4 g of NiCl₂·6H₂O into 30 ml H₂O in a plastic beaker 19.5 mm in diameter and 80 mm high. Into this solution was poured 50 ml of 2 N KOH and the mixture allowed to rest for 10 minutes. Then the mixture was stirred gently with a magnetic stirrer for 2 days during which the oxidation takes place. The end of the oxidation was determined by the raising of the redox potential to a steady

value. This was monitored by intermittently introducing into the stirred mixture a Pt electrode and a standard calomel electrode and measuring the potential with a pH meter in the mV range. The potential was found to reduce to about -700 mV during the first minute and then to increase exponentially to about -50 mV with a time constant depending on the stirring rate. The whole process was carried out at room temperature. After oxidation the precipitate was washed and then boiled for 5 hours in 0.1 N H_2SO_4 . This was performed in order to remove the nickel which was not lattice-bound. The samples were then washed in H_2O several times and then allowed to dry in air at 98°C .

The proportions of Ni and Fe obtained were determined by chemical assay. These were performed by dissolving the goethites in concentrated HCl and assaying the solution by atomic absorption.

The crystallinity and purity of phase was checked by X-ray diffraction. Figure 5.22 shows the XRD pattern of one of the synthetic goethites.

Increasing the amount of initial nickel did not necessarily produce a higher Ni/Fe ratio in the goethite. The highest percentage produced was 1.36% of nickel, as weight percent of iron.

Nevertheless refinement of the technique might result in slightly higher values of Ni, as an acceptable specimen made and supplied by W. Schellmann assayed 1.74% Ni.

All the specimens made by the method described above contained a total weight percent of Fe + Ni of 54%, (which is short of 62% for stoichiometric goethite). The particle sizes of the specimens were

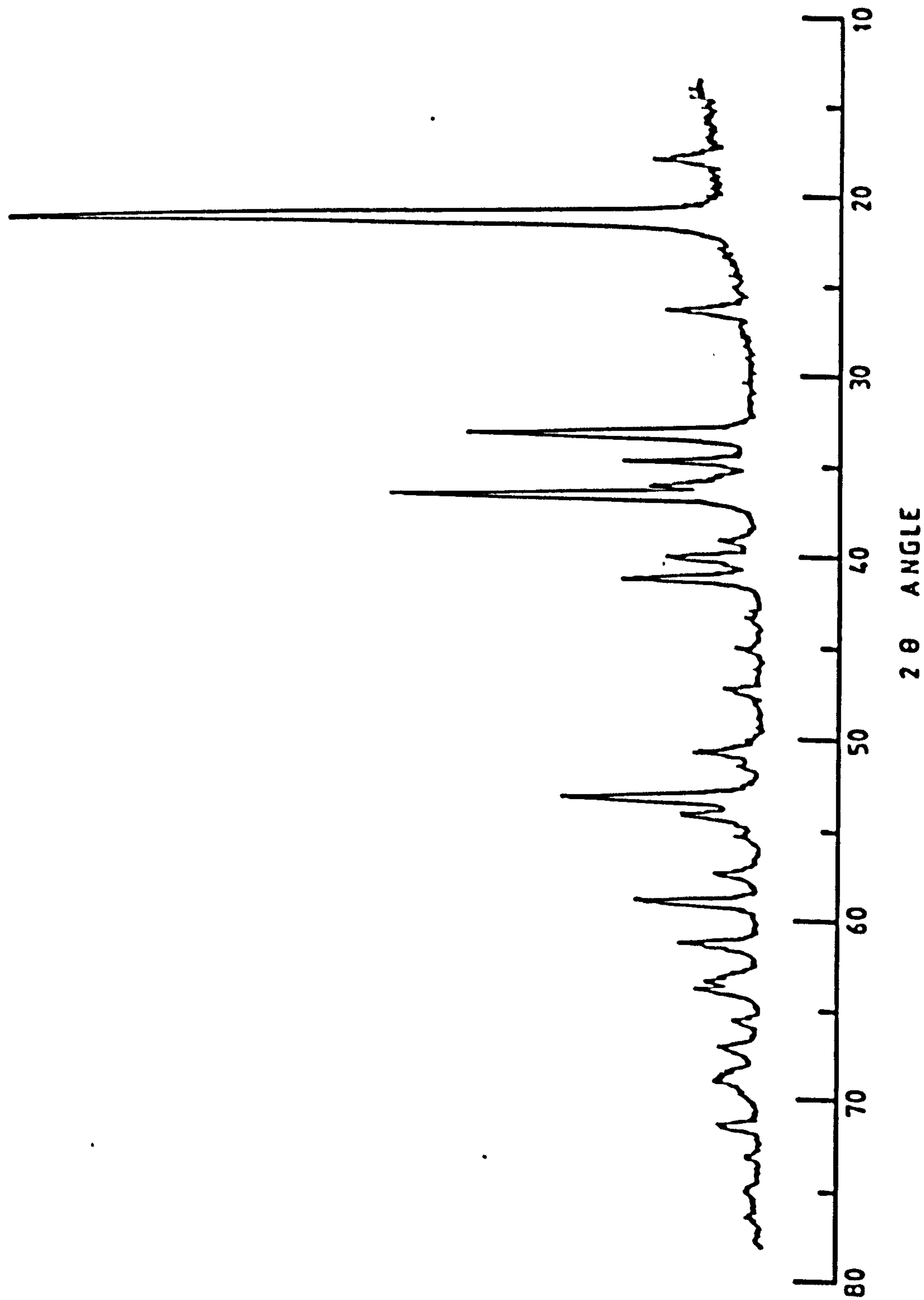


Figure 5.22 XRD pattern of nickel-bearing synthetic goethite. Cu K α radiation.

quite small ($<0.5 \mu\text{m}$) but, as seen below, they did not show superparamagnetic behaviour which indicated that the crystallites were greater than about 18 nm.

Mössbauer effect results

Mössbauer effect spectra of the nickel-bearing synthetic goethites were obtained at room temperature and at liquid nitrogen temperatures. The spectra were very similar to the spectrum of the pure mineral (Figure 5.23).

The Mössbauer spectrum showed that samples which assayed more than 1.36% Ni were not single phase in spite of the fact that the XRD results indicated that they were. These samples showed in addition to the goethite spectrum, two doublets, one ferric and one ferrous, which indicate either the presence of a second phase or of an anomalous goethite. Specimens showing these features were rejected.

Computer fits of the spectra were carried out. The room temperature spectra were found to contain more than a single magnetic pattern and could only be fitted by a combination of two or more sites with decreasing magnetic field and increasing linewidths. These spectra did not yield the necessary accuracy in the fitted parameters for the values to show any systematic behaviour with nickel content.

The low temperature spectra, on the contrary, could be fitted by a single site magnetically split pattern and the derived magnetic hyperfine fields had sufficient accuracy for comparison of the different goethites. Table 5.17 and Figure 5.24 show the measured magnetic hyperfine field as a function

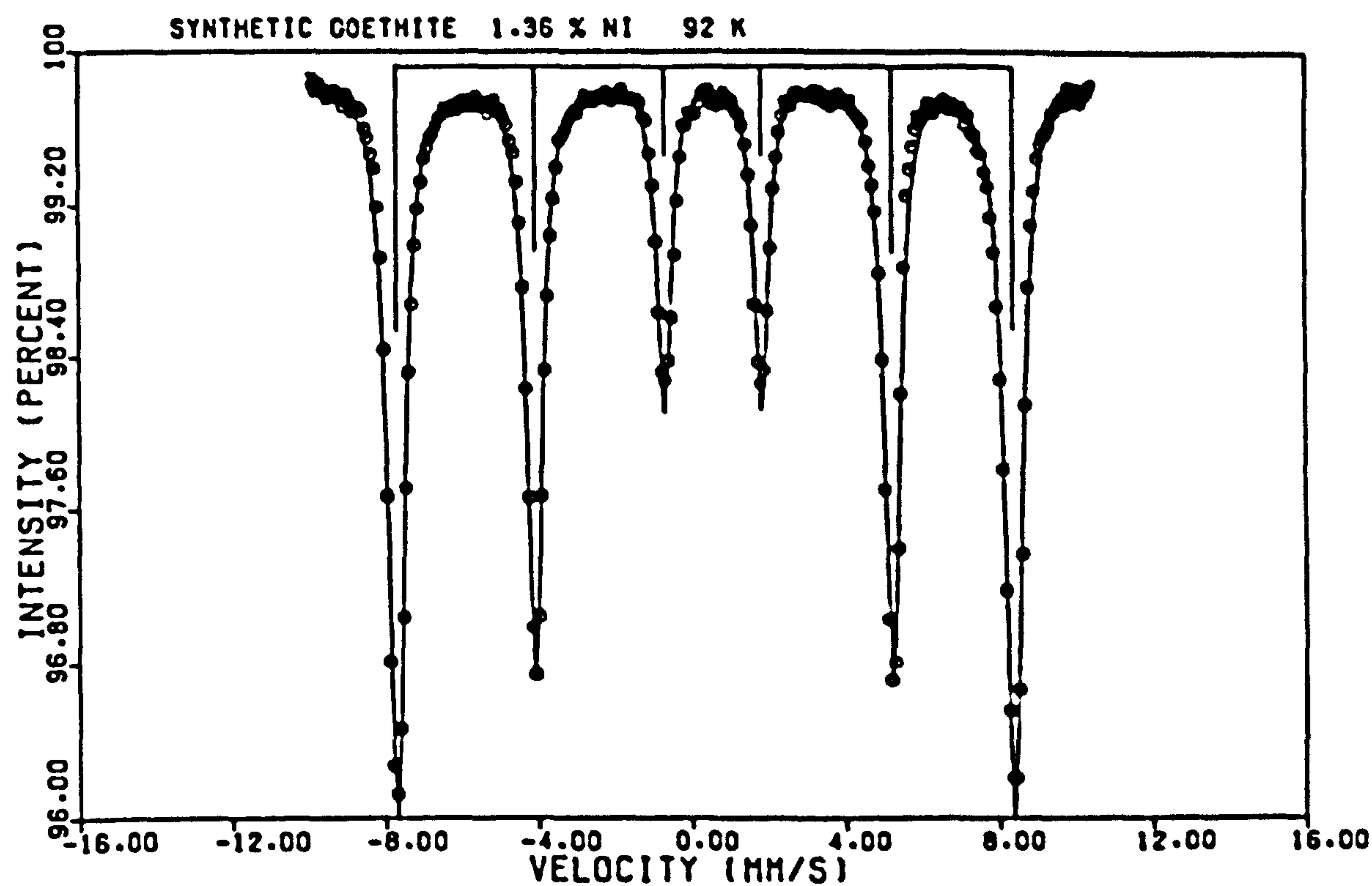
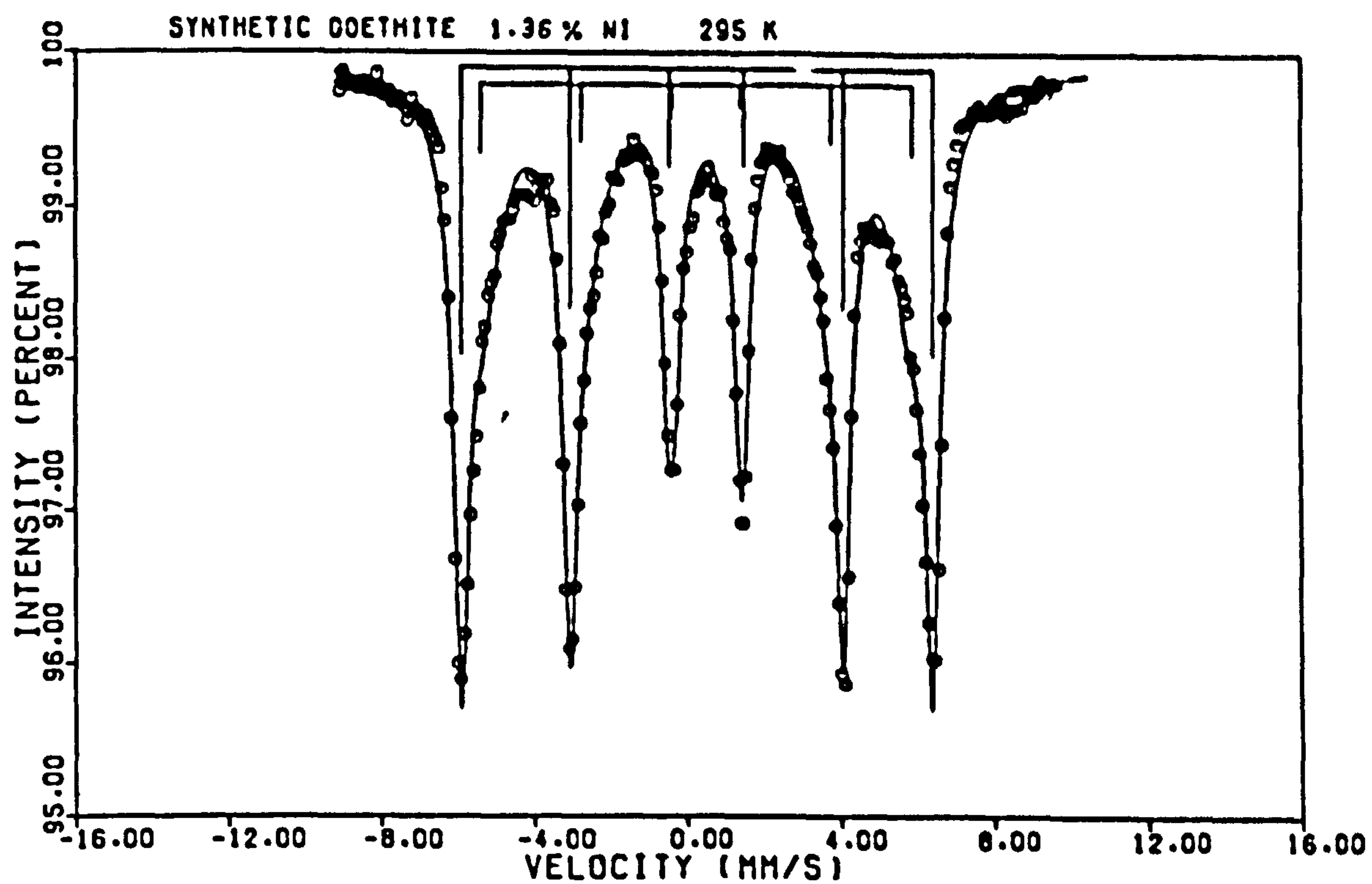


Figure 5.23 Fe^{57} Mössbauer effect spectra in nickel-bearing synthetic goethite.

Table 5.17 Magnetic hyperfine field at Fe^{57} nuclei in nickel-bearing synthetic goethites at liquid nitrogen temperatures

Nickel Content (Ni as % of Fe)	H (Tesla) ± 0.09	Temperature (°K)
0.0	50.4 ⁺	77
0.84	49.97	90
1.10	49.75	85
1.36	49.82	92
1.74*	49.59	80

* Sample supplied by W. Schellmann

⁺ Forsyth, et al. (1968).

Table 5.18 Comparison of the average Fe-Ni proximity between nickel contained on the surface and nickel contained in the bulk for hypothetical small particles of goethite. (Ni as 1.5% of Fe assumed)

Ni CONTAINED IN THE BULK	Ni CONTAINED IN THE SURFACE		
	Goethite particle size (nm)	Ni-Ni distance (nm)	Proportion of Fe within 0.5 nm of Ni atom (%)
Fe-Ni distance = 0.5 nm	5.0	1.55	27
Ni-Ni distance = 1.26 nm	10.0	1.1	14.3
	15.0	0.9	9.7
Fe atoms per Ni atom = 66.6	30.0	0.63	5.0
	60.0	0.45	2.5
goethite unit cells per Ni atom = 16.6	120.0	0.32	1.2

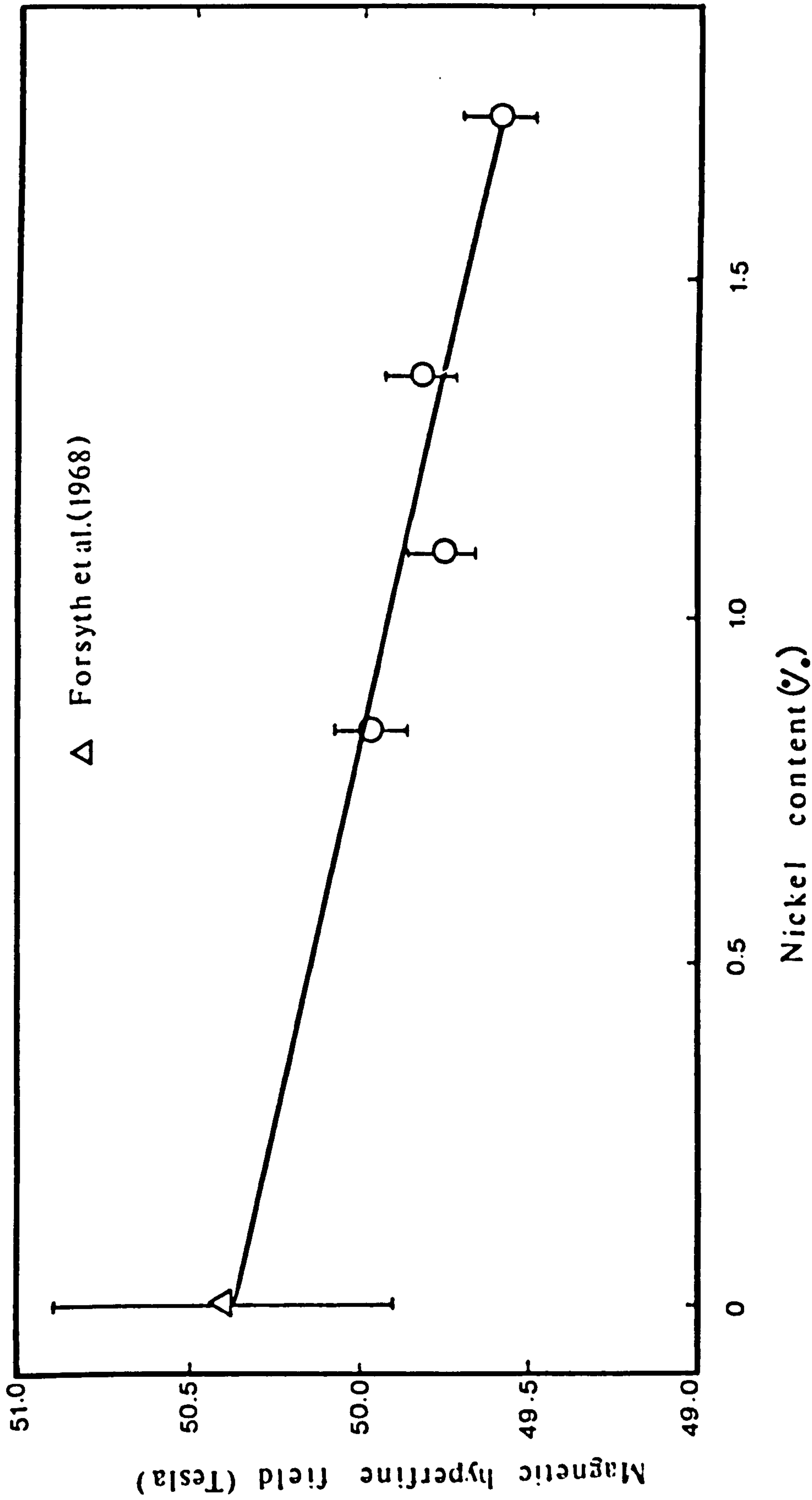


Figure 5.24 Magnetic hyperfine field at Fe⁵⁷ nuclei as a function of Ni content (Ni as % of Fe) in Ni-bearing synthetic goethites. Errors are purely statistical.

of nickel content derived from the low temperature spectra. The results show a small decrease of the magnetic hyperfine field as a function of nickel content and suggest that some, at least, of the nickel is in sufficient proximity to the Fe atoms to affect the hyperfine field. These results can be used to decide whether the nickel is contained in the bulk of the material or chemisorbed on the surface of crystallites. To this end the proximity of nickel atoms to iron atoms was estimated under the following two conditions: 1) 1.5% nickel contained with a uniform distribution in the bulk of goethite. 2) the same proportion of nickel uniformly contained on the surface of goethite crystallites. Under the first condition the average Fe-Ni distance is of the order of 0.5 nm and is independent of the goethite particle size. With nickel adsorbed uniformly on the surface of goethite particles both the surface area per nickel atom, and the average Fe-Ni distance depend on the size of the particles. Since in this instance the average Fe-Ni does not have much meaning, a calculation was made, for different particle sizes, of the proportion of Fe atoms which are within 0.5 nm of the surface (the average Fe-Ni distance for goethite in the bulk). The particle sizes were chosen in the range found for goethite in the Ni-laterites (5 to 30 nm). Table 5.18, containing the results, shows that the proportion of Fe atoms within 0.5 nm of a Ni atom is only between 5 and 27% when the Ni is adsorbed on the surface. Hence it is unlikely that Ni on the surface can significantly change the magnetic hyperfine field of Fe atoms.

Although the calculations of Table 5.18 are only approximate they suggest that nickel is in fact contained in the bulk of the goethite.

Natural nickel bearing goethite contains other elements as well as nickel. Therefore the decreased magnitude of the magnetic hyperfine field detected in the natural laterite samples cannot be used for a semiquantitative estimation of the nickel contained in the goethite of these deposits without further study of the problem.

The fact that it has only been possible to incorporate nickel into goethite by oxidation of ferrous hydroxide suggests that this is the mechanism through which a large proportion of the goethite in lateritic deposits is formed.

5.5 Conclusions

The results of the study by ordinary methods of determinative mineralogy of the three laterites, provided a wealth of information about these materials as well as indicating the inadequacy of physical methods of mineral concentration in producing mineral concentrates or in significantly upgrading the materials in the valuable elements. This study also confirmed the limitations of these methods of mineral appraisal in providing the information required for establishing the most appropriate chemical processing route for lateritic materials.

The wide-line nuclear magnetic resonance experiments showed the feasibility of obtaining NMR spectra of Al^{27} in a range of aluminium bearing lateritic minerals but also indicated that further work must be carried out in order to fully evaluate the potential of this technique for appraisal of lateritic minerals. Likewise the detection of strong proton NMR signals (shown in Appendix D) in synthetic gibbsite, bayerite and boehmite as well as in nickel antigorite and nickel hydroxide show that further work is required to determine whether such signals are also obtained in natural minerals of lateritic origin. A determination of the proton relaxation time in these compounds would provide an indication of the feasibility of studying bauxite minerals and the nickel silicate minerals by techniques of double resonance.

The zero-field nuclear magnetic resonance experiments performed showed the technique to be capable of providing accurate measurement of the magnetic hyperfine field in pure well crystalline hematite and magnetite in a range of temperatures. The work showed the fundamental importance and influence of the magnetic structure of the compounds in determining whether resonance signals are detected or not. The inability to detect signals from goethite or from hematite and magnetite which occur

in small proportion, in small sizes or with poor crystallinity indicate the limitations of the instrumentation used in providing useful information for the appraisal of lateritic materials.

The piezoelectric resonance signals detected with the Decca NQR spectrometer had a frequency spectrum which is a function of particle size. Hence it would be interesting to find out if the detection of such signals can be used as a technique to establish particle size distributions.

The Mössbauer effect measurements performed showed greater success than the resonance experiments in supplying useful information about the laterite samples. In addition to detailed information about the internal structure of chromite minerals, the technique was shown capable of providing quantitative estimates of the iron minerals contained in laterites as well as the particle size distribution of these minerals in the nanometer size range. This information, as well as the evidence that suggests the presence of nickel in goethite as substitutional or interstitial, are quantities of direct interest in the problem of processing laterites.

This work has not by any means solved the problem of laterite appraisal but has indicated that a combination of old and new techniques of materials study provide some hope of eventually solving this difficult problem.

APPENDIX A

Structure of Al minerals

This appendix briefly describes the crystallographic environment of aluminium atoms in some Al-bearing minerals.

Kaolinite (Grim, R.E. P.58, 1968)

General formula: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$

Structure: Monoclinic. Two-layered hydrous aluminium silicate.

One layer is composed of oxygen tetrahedra with Si atoms in the centres arranged so that the tips point in the same direction. The other layer is composed of oxygen or OH octahedra with Al atoms in the centres. The two layers share a common boundary (Figure A.1).

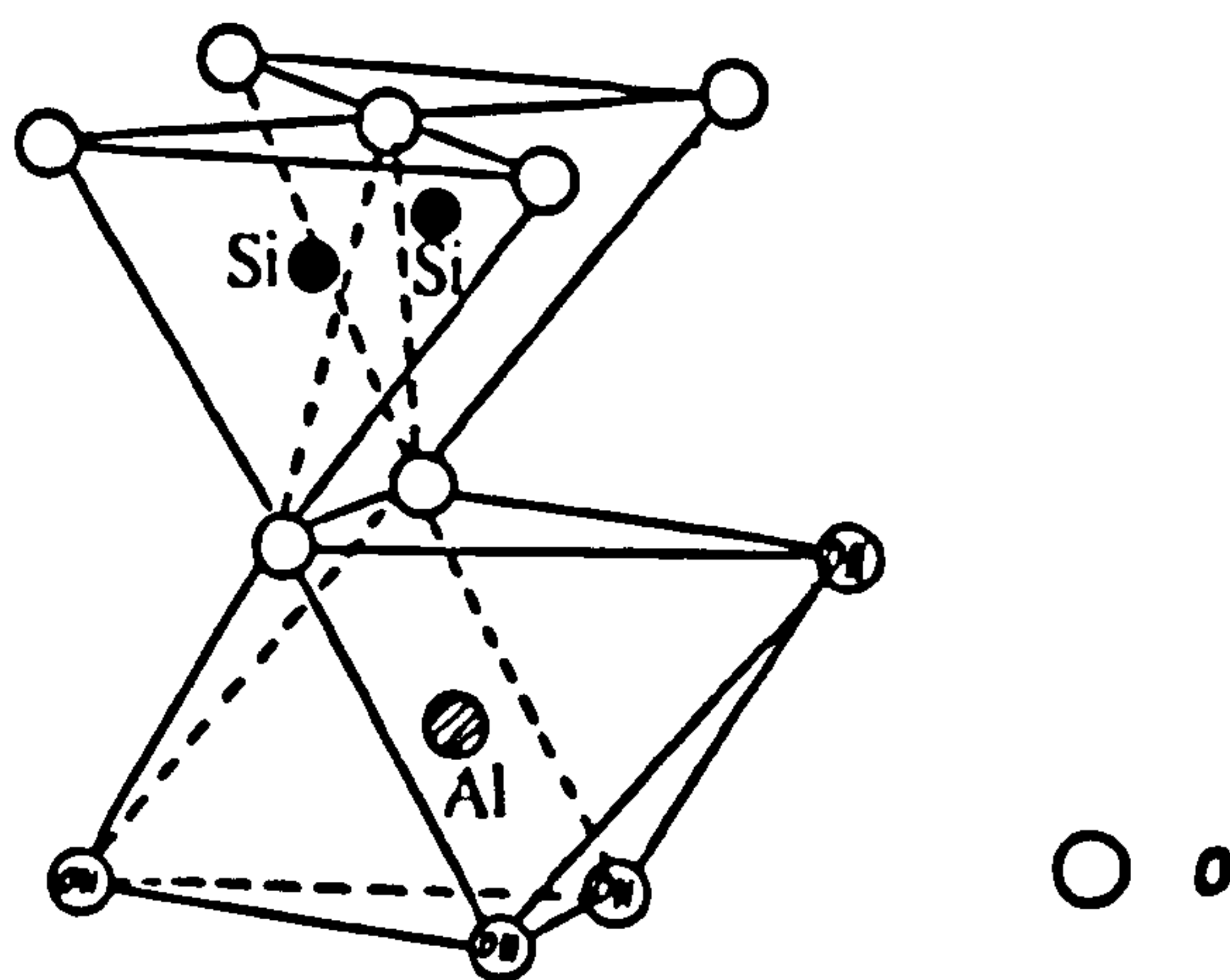


Figure A.1 Al atoms in kaolinite and halloysite

Al symmetry: The Al atoms are in octahedral symmetry with two of the six corners taken by oxygen atoms; and the other four by OH groups.

Kaolinite crystals are made up of kaolinite double layers stacked one over the other.

Halloysite (Grim, R.E. P.71, 1968)

General formula: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 4\text{H}_2\text{O}$

Structure: Halloysite possesses a layered structure which is formed by one double layer of kaolinite and a layer of water repeated over and over.

Al symmetry: The same octahedral symmetry as in kaolinite.

(Figure A.1).

Gibbsite (Hydrargillite) (Wyckoff Vol. 2. P.78, 1964; Vedral, et al. 1974).

General formula: $\alpha\text{-Al}(\text{OH})_3$.

Structure: Monoclinic. Layer structure consisting of linked sheets of the kind of octahedra that occur in close-packing. Each octahedron encloses an Al atom. The sheets of octahedra are stacked in such a way that the oxygen atoms are above each other along the c axis. This placing of the oxygen atoms of different layers one on top of the other is different from the ordering in complete close packing in which oxygens of one layer are placed in the holes of the adjacent layer.

Al symmetry: Octahedral (Figure A.2).

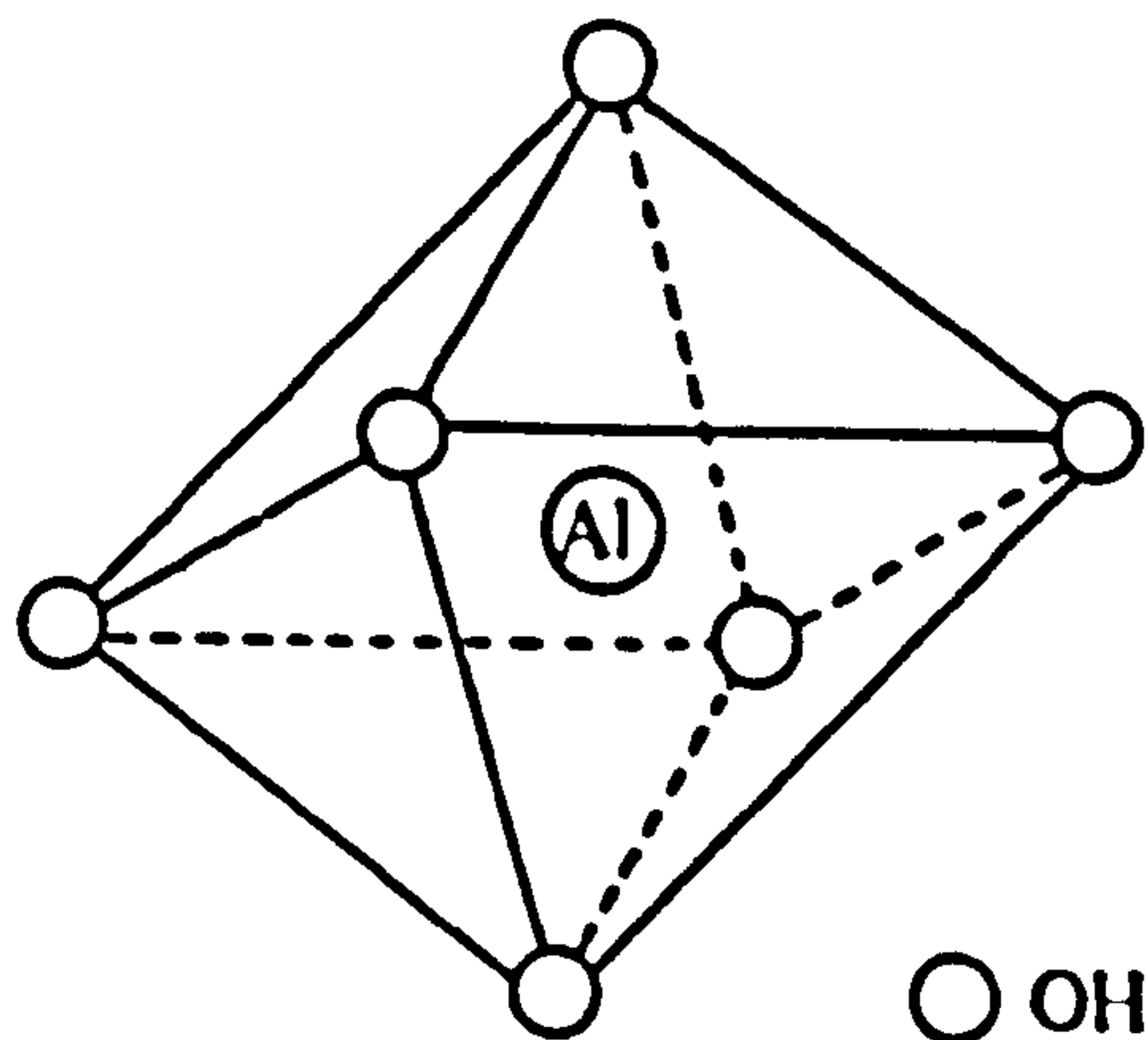


Figure A.2 Al atoms in gibbsite

Boehmite (Wyart, et al 1959; Fripiat, et al. 1967; Vedral, et al. 1974).

General formula: $\beta\text{-Al O OH}$

Structure: Orthorhombic. The structure is built up of well-defined layers parallel to the (100) face. Each layer is made up of octahedra with aluminium atoms in the centres. The octahedra are linked together by sharing corners.

Al symmetry: Octahedral: The octahedra are nearly regular and have four corners occupied by oxygen atoms and two by hydroxyl groups. (This mineral has the same structure as lepidochrosite $\gamma\text{-FeO OH}$).

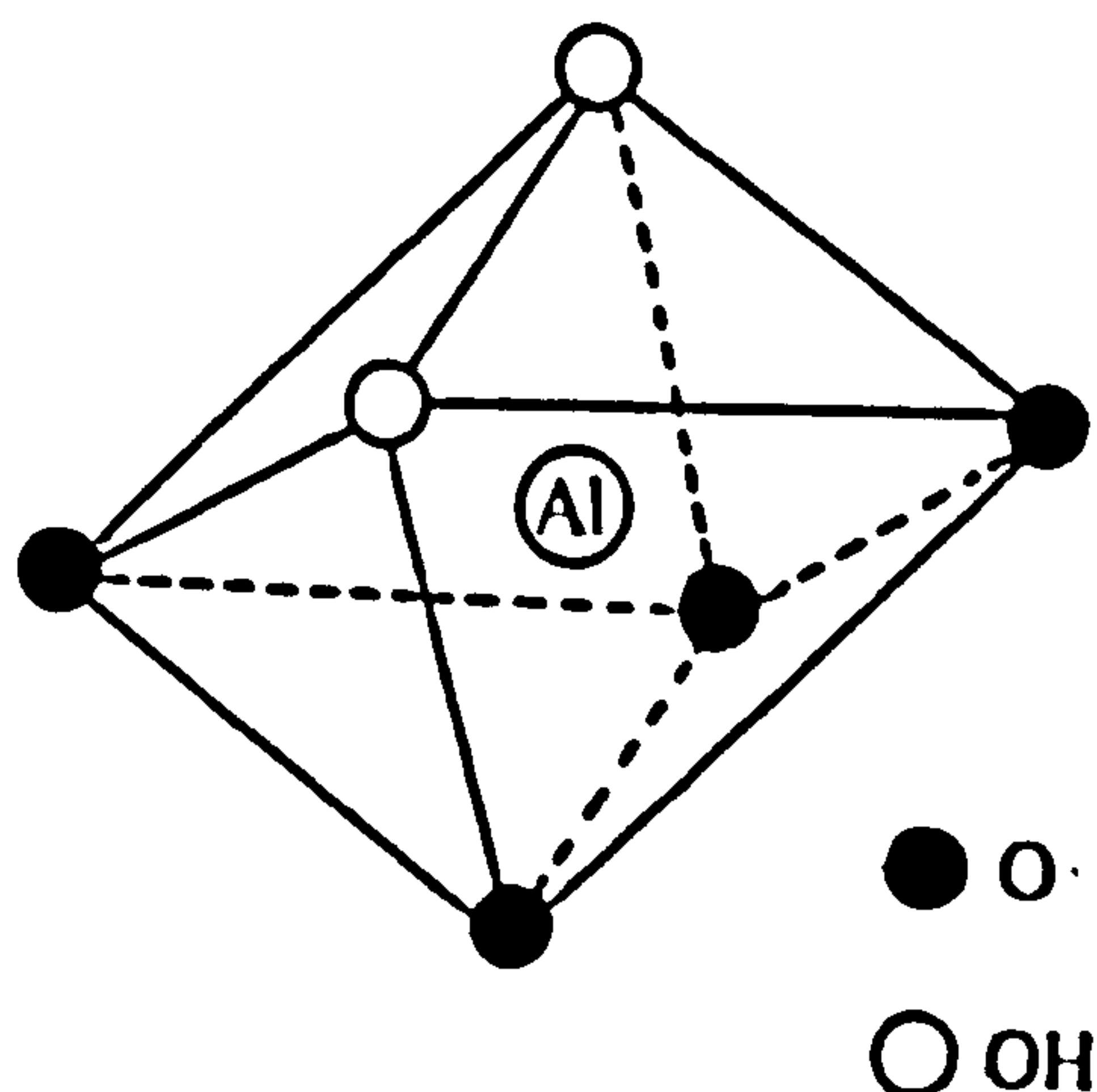


Figure A.3 Al atoms in boehmite

Diaspore (Wyckoff Vol. 1 P.290, 1963)

General formula: $\alpha\text{-Al O OH}$

Structure: Orthorhombic. This mineral has the same structure as goethite $\alpha\text{-Fe O OH}$ which is described in greater detail in Appendix B. Atomic positions in diaspore correspond to an almost perfect hexagonal close packing.

Al symmetry: Octahedral, Al atoms are in the centre of slightly distorted octahedra with four corners occupied by oxygen atoms and two by hydroxyl groups.

APPENDIX B

The structure of goethite

This appendix contains a review of structural information about goethite.

The topics covered include:

- 1) Crystal structure
- 2) Magnetic structure
- 3) Magnetic susceptibility
- 4) Differential thermal analysis (DTA) behaviour
- 5) Structural defects

1) Goethite, Crystal Structure

The goethite unit cell is orthorhombic with dimensions:

$a = 4.587$, $b = 9.937$, $c = 3.015 \times 10^{-1} \text{ nm}$. (Forsyth, et al. 1968). The space group is $Pb\ nm$ and the unit cell contains

4 Fe at $\frac{1}{4} (x, y, \frac{1}{4})$, $\frac{3}{4} (x + \frac{1}{2}, \frac{1}{2} - y, \frac{3}{4})$

with $x = 0.0477$, $y = 0.8539$

4 O_1 in similar positions with $x = .7058$, $y = .1994$

4 O_2 in similar positions with $x = 0.1974$, $y = .0531$

4 H_1 in similar positions with $x = 0.3991$, $y = 0.0876$

With this information it is possible to derive the space coordinates of the atoms in the unit cell. See Table B.1. Figure B.1 shows the unit cell projected in a plane parallel to the a-b plane. The numbering of the atoms is the one given by Forsyth, et al. (1968). All the atoms in the unit cell are located in two planes with $z = \frac{1}{4}$ and $z = \frac{3}{4}$

Table B.1 Coordinates of atoms in the goothite unit cell
derived from data in Forsyth, et al.(1968)

Atom	Coordinates ($\times 10^{-1}$ nm)		
	x	y	z
Fe ₁	4.3682	1.4518	2.2613
Fe ₂	0.2187	8.4852	0.7538
Fe ₃	2.5123	6.4203	2.2613
Fe ₄	2.0747	3.5167	0.7538
O _I	3.2375	1.9814	0.7538
O _I	1.3495	7.9555	2.2613
O _I	0.9440	2.9871	2.2613
O _I	3.4035	6.9499	0.7538
O _{II}	0.9054	0.5276	0.7538
O _{II}	3.6815	9.4093	2.2613
O _{II}	3.1990	4.4408	2.2613
O _{II}	1.3880	5.4961	0.7538
H ₁	1.8307	0.8704	0.7538
H ₂	2.7563	9.0665	2.2613
H ₃	4.1242	4.0980	2.2613
H ₄	0.4628	5.8390	0.7538

The goethite structure described by Forsyth, et al. (1968) is analogous, but somewhat different from the goethite structure described by Wyckoff, Vol. 1, P.290, (1963). The lattice parameters reported by Wyckoff result in a slightly larger, more elongated unit cell but with the same orthorhombic structure. (Wyckoff: $a = 4.64$, $b = 10.0$, $c = 3.03 \times 10^{-1} \text{ nm}$). The positions of the atoms are also slightly different, particularly the location of the hydrogen atoms: Wyckoff assigns the hydrogens to locations next to O_1 sites while Forsyth, et al. assigns the hydrogens to locations next to the O_2 sites.

Pure, well-crystalline natural goethite, as well as synthetic goethite produced by dehydration and ageing of ferric hydroxide in the presence of a solution of alkali hydroxide (Böhm, 1925; Krause, et al. 1932) is acicular. When the crystals are well developed they give goethite a texture described as fibrous. Fibrous goethite is made of crystallites with a very large aspect ratio, the long axis being parallel to the c-axis.

Goethite produced by other methods, particularly by oxidation of ferrous hydroxide does not present this acicular shape. It tends to be pseudomorphous: The particle shape does not change during the oxidation and hence the shape depends on the shape of the ferrous hydroxide particles from which it is derived. This can explain the large variety of crystallite and particle shapes found in natural lateritic goethite when observed optically in polished and thin sections or when observed under the electron microscope (Kuhnel, 1974). Optical examination reveals that lateritic goethite often assumes the shape of other minerals which have been leached or the shape of crevices produced during the laterization process. This and other evidence* suggests that a large proportion of lateritic goethite is formed by oxidation of ferrous hydroxide.

*See discussion in Section 5.4.3.

Well crystalline and poorly crystalline natural goethite, as well as goethite synthesised by the various methods, produce approximately the same XRD pattern. Other properties, discussed below, do not show this consistency.

The crystal structure of goethite may be thought of as being built up of chains of iron and oxygen atoms which align themselves along the c-axis such as those shown in Figure B.2, and the structure may be constructed by arranging these chains in bundles, as shown in Figure B.3.

2) Goethite magnetic structure

It is generally recognised that the internal magnetic structure of goethite is antiferromagnetic. This is based on results of magnetic susceptibility, Mössbauer effect and neutron diffraction measurements.

The magnetic susceptibility measurements (v. Oosterhout, 1965; Banerjee, 1970; Pastrana and Hopstock, 1977) show that goethite has a weak ferromagnetic behaviour with a magnetic susceptibility for powdered samples between $10 - 80 \times 10^{-10}$ (SI). Measurements with single crystals show that the material is magnetically anisotropic: the susceptibility measured parallel to the c-axis is lower (17×10^{-10}) than when measured perpendicular to the c-axis (26×10^{-10}) (v. Oosterhout, 1964, values at 300K). The temperature coefficient of the susceptibility is positive up to about 403°K. All these results are consistent with antiferromagnetic ordering with a Neel temperature of about 403°K.

The Mössbauer effect measurements confirm the existence of a magnetic ordering (Hryniewicz and Kulgawczuk, 1963; v. Oosterhout 1964; Hryniewicz, et al, 1965; Forsyth, et al, 1968) which disappears when the samples are heated to temperatures above the Neel point. The nature of

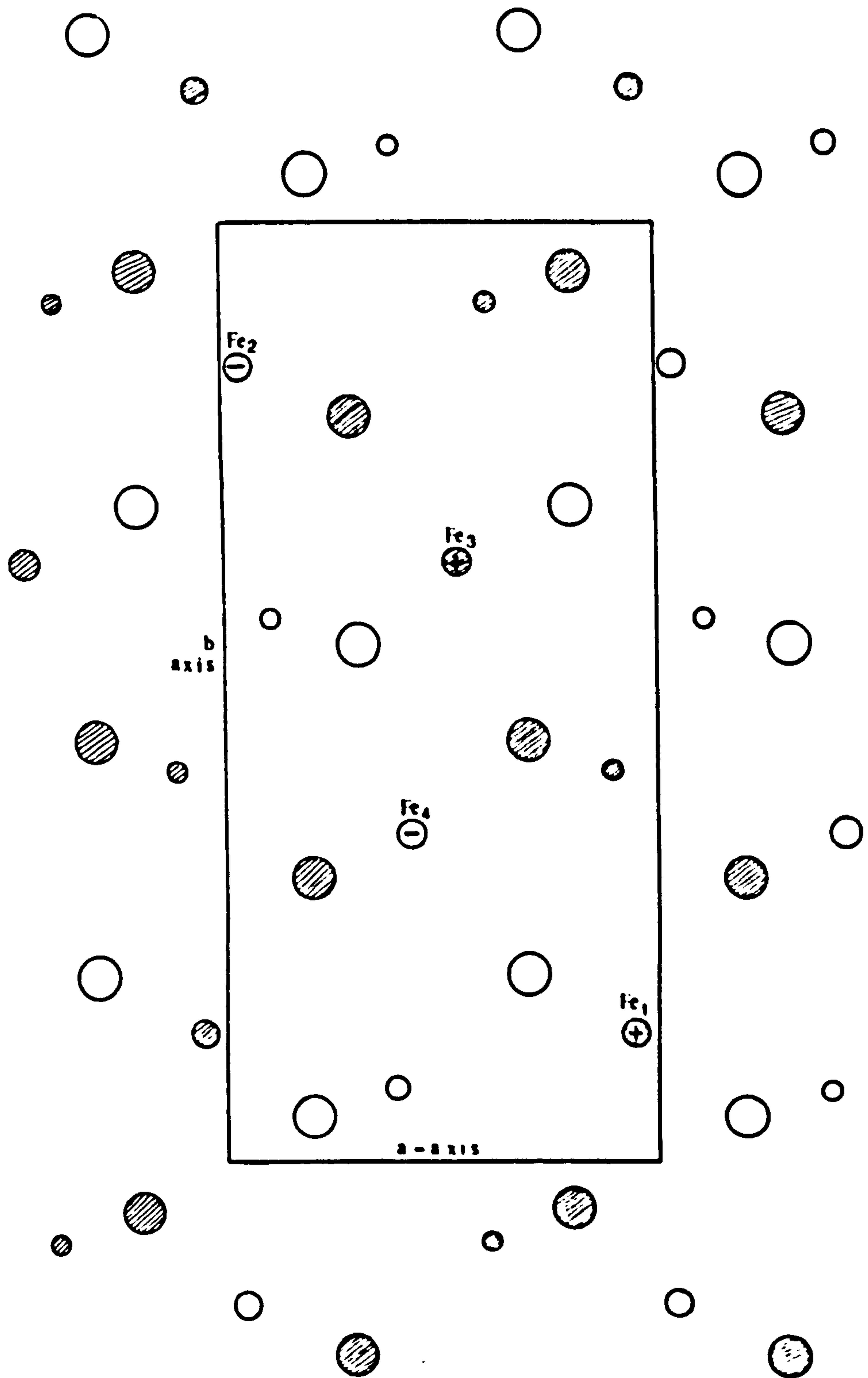


Figure B.1 Projection on the a-b plane of the goethite unit cell. Drawn from data in Forsyth, et al. (1968). Clear circles: atoms in $c = \frac{1}{4}$ plane, shaded circles: atoms in $c = \frac{3}{4}$ plane.

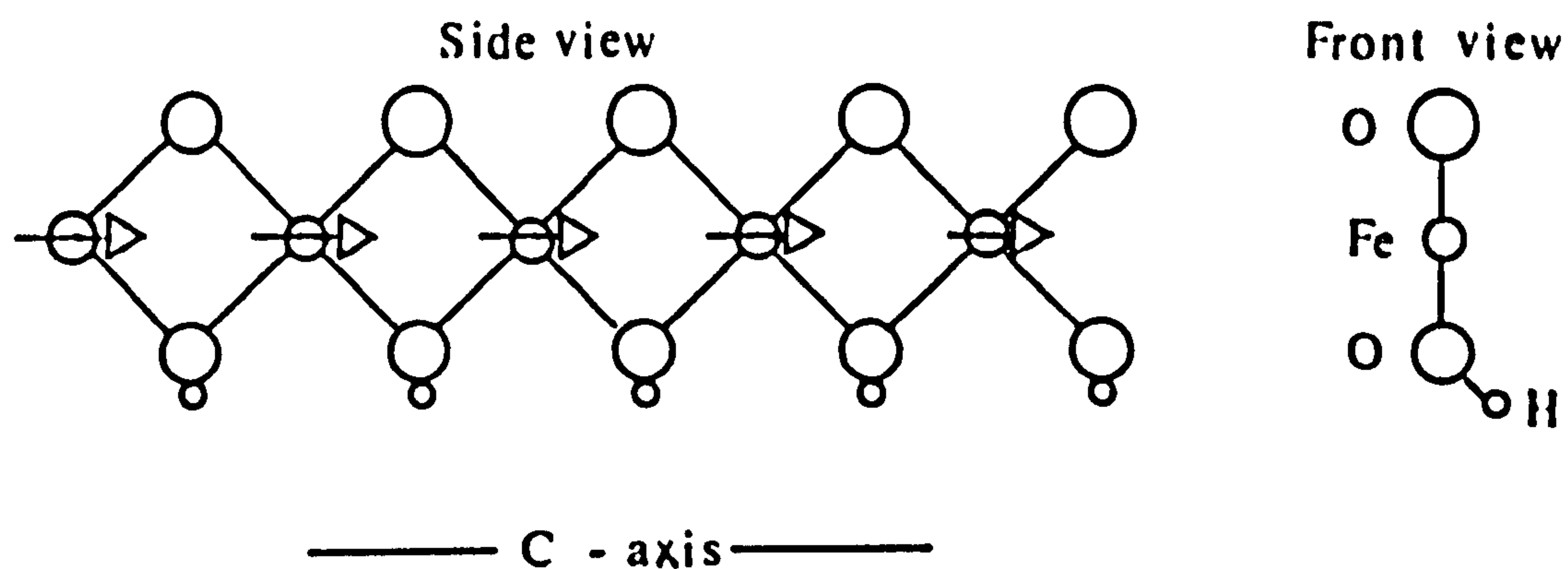


Figure B.2 Fe O OH chain shown in front and side view. The arrows suggest the ferromagnetic ordering of the Fe spin moments.

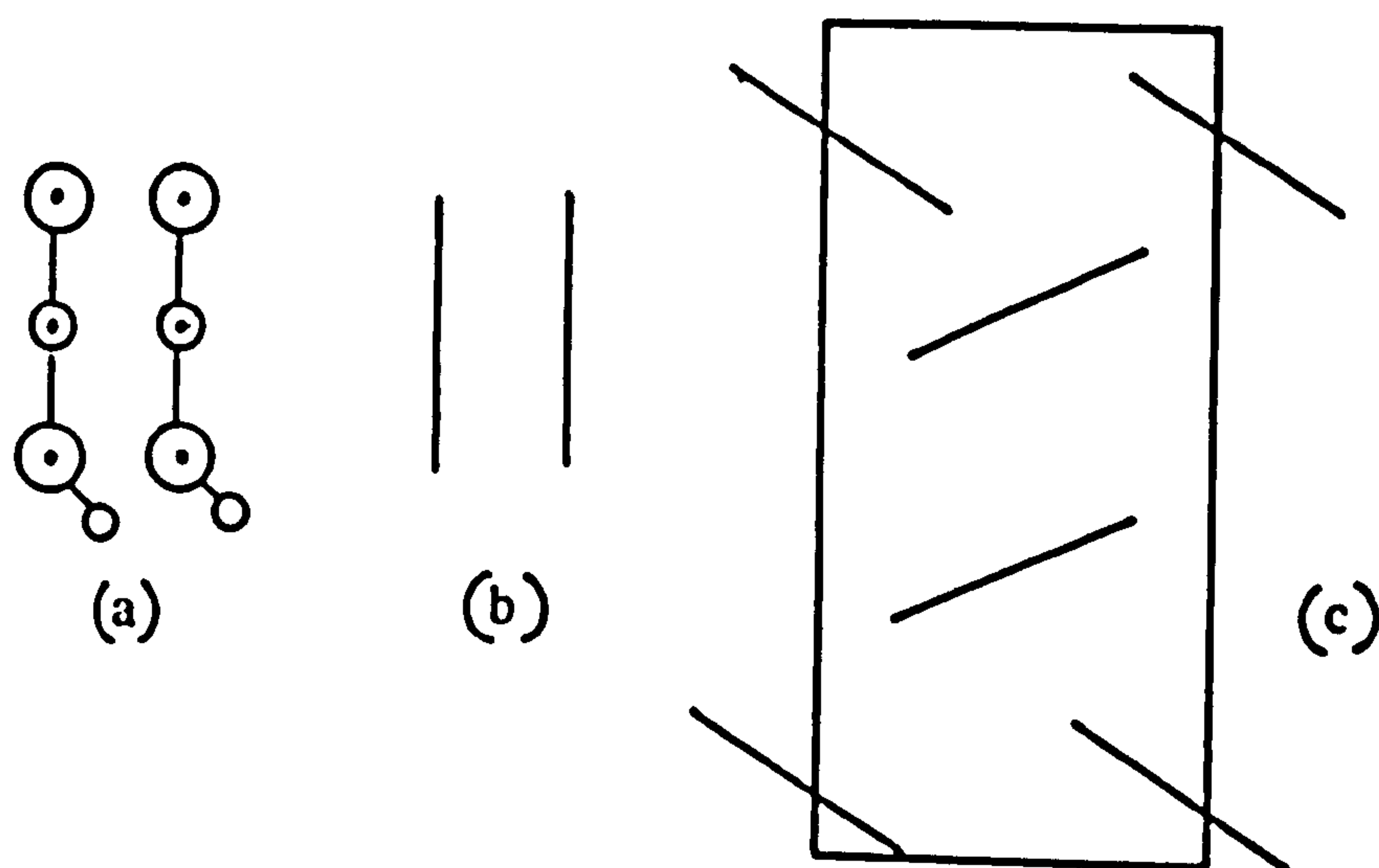


Figure B.3 Schematic diagram showing how the goethite structure may be constructed by "bundling" chains of Fe O OH atoms. a) end view of chain, b) schematic representation of (a), c) schematic structure of the goethite unit cell. (After v. Oosterhout, 1964).

the magnetic ordering has been further clarified by Forsyth, et al. (op. cit.) with Mössbauer effect measurements on a goethite single crystal, and by employing neutron diffraction techniques on powdered samples.

According to the magnetic ordering model proposed by Forsyth, et al, within each O-Fe-OH chain the iron spin moments are parallel to the c-axis and all point in the same direction leading to a ferromagnetic chain (as suggested by the arrows in Figure B.2). Forsyth, et al. attribute this spin ordering to the antiparallel alignment that follows from a strong superexchange interaction between the Fe atoms of different chains, rather than by the interaction between the Fe atoms within each chain. They postulate a strong superexchange interaction coupling $\text{Fe}_1\text{-O-Fe}_4$ and $\text{Fe}_2\text{-O-Fe}_3$ antiparallel with an angle of 124° and Fe-O-Fe distance of $3.88 \times 10^{-1} \text{ nm}$, (Figure B.4) and postulate a weaker superexchange interaction coupling $\text{Fe}_3\text{-O-Fe}_4$ and $\text{Fe}_2\text{-O-Fe}_1$ antiparallel with an angle of 104° and an Fe-O-Fe distance of $4.19 \times 10^{-1} \text{ nm}$ (Figure B.5).

The previous description refers to the coupling between atoms of different chains. With respect to the coupling between atoms in each chain, i.e. the coupling between the Fe atoms along the chains parallel to the c-axis, it is postulated that this coupling is the same as the weak coupling between the Fe_3 and Fe_4 and between Fe_2 and Fe_1 chains. This coupling is twofold: a weak superchange path via two oxygen atoms and a direct Fe-Fe exchange interaction. Both of these lead to antiferromagnetic ordering. Hence, according to this description any one of the four "chains", if isolated, would lose its

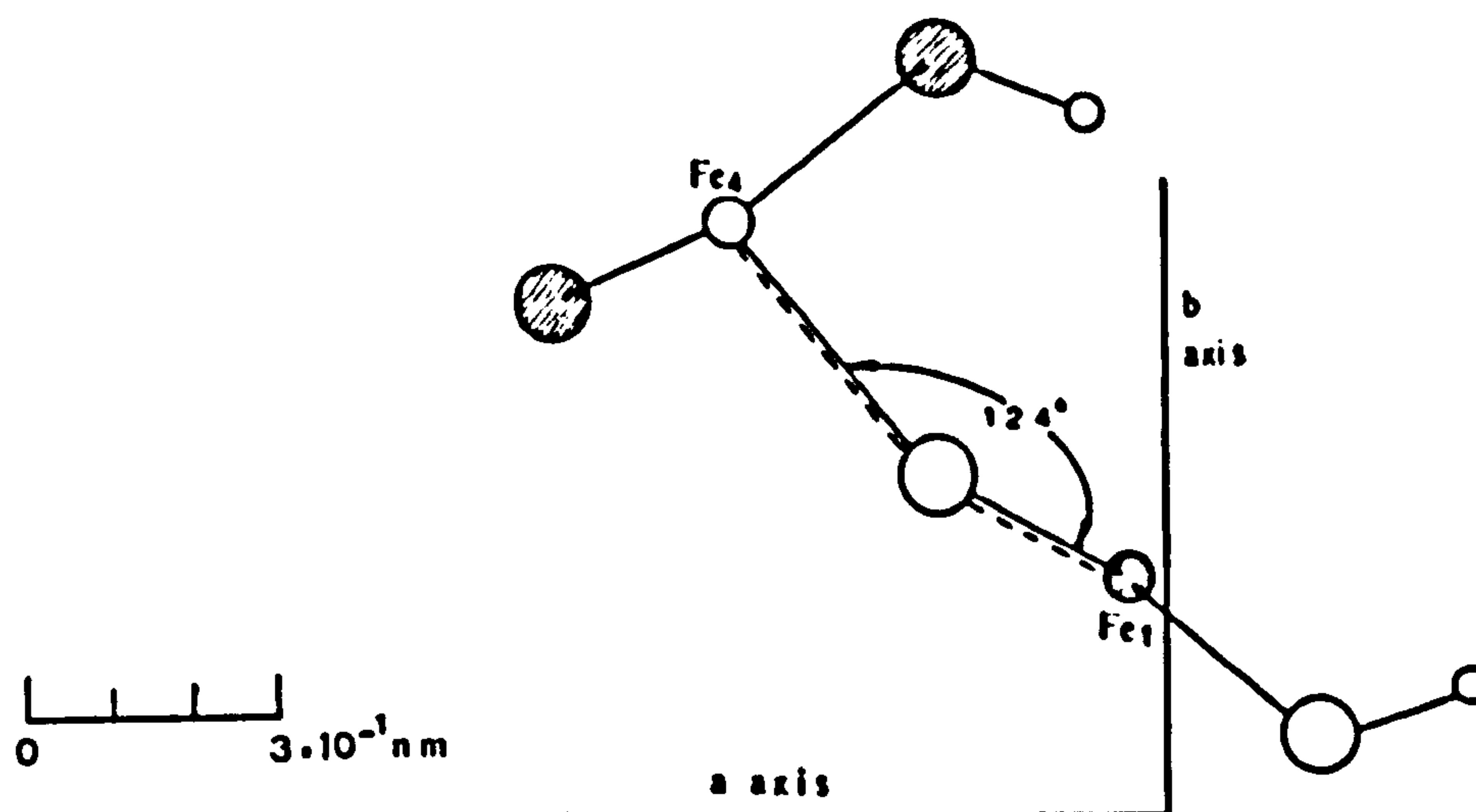
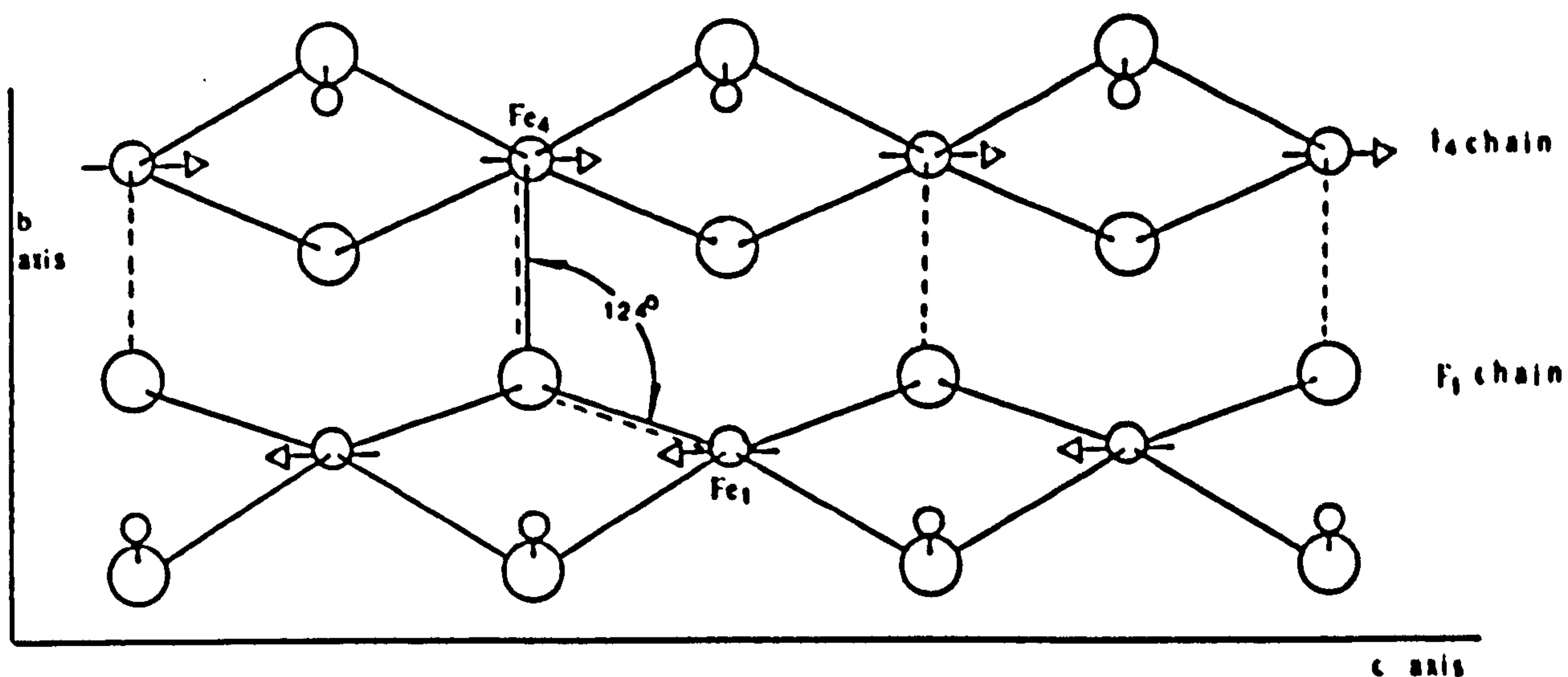


Figure B.4. Two views of the Fe_4 and Fe_1 chains showing the "path" of the strong $\text{Fe}_4\text{-O-Fe}_1$ superexchange interaction in goethite. A similar relationship exists between the Fe_2 and Fe_3 chains.

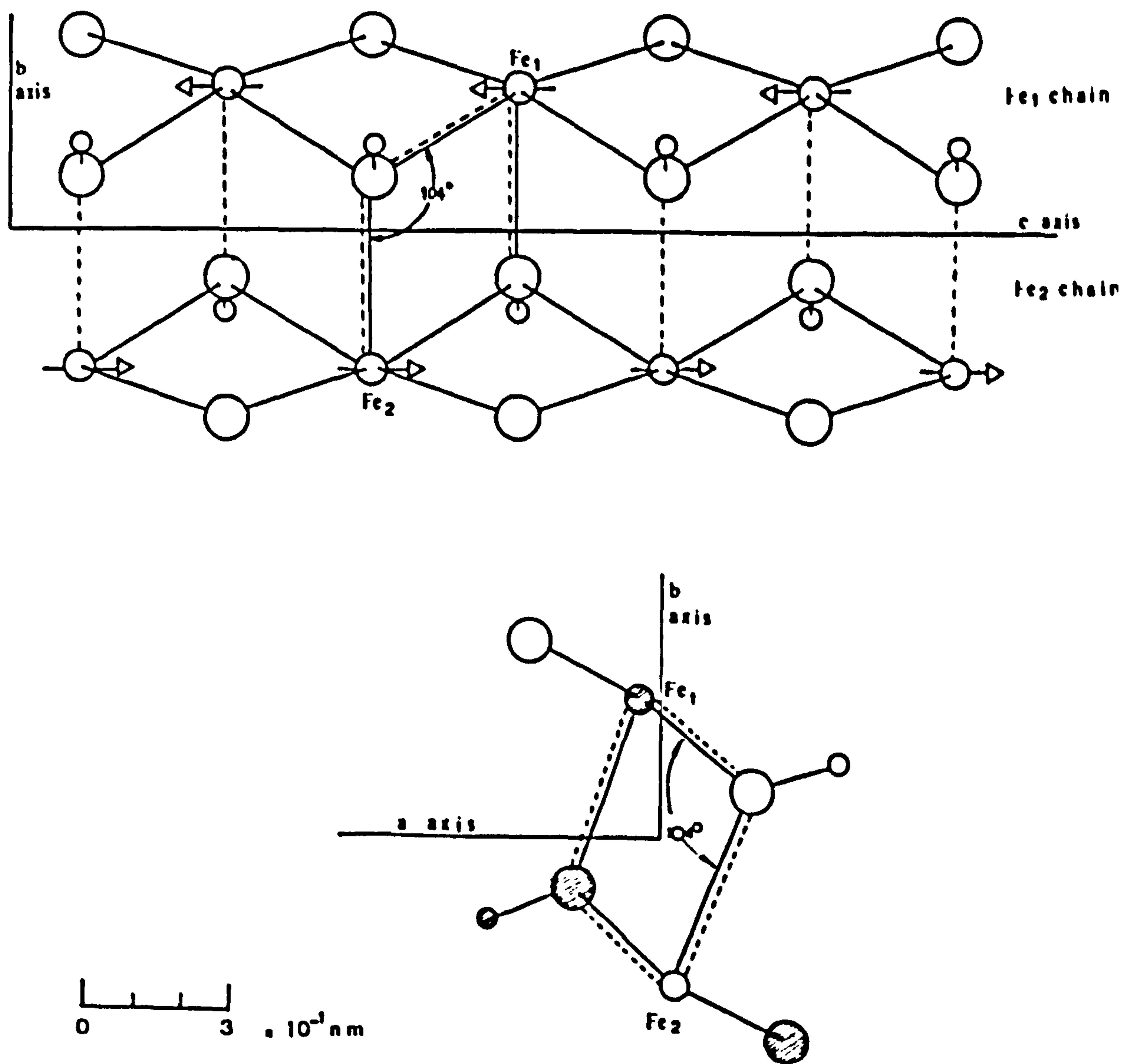


Figure B.5. Two views of the Fe₁ and Fe₂ chain showing the "path" of the weaker Fe₁-O-Fe₂ superexchange interaction in goethite. A similar relationship exists between the Fe₄ and Fe₃ chains.

ferromagnetic ordering and would become antiferromagnetic. This suggests that chains in the surface of a crystallite do not have the same ordering as the chains in the bulk of the crystal. This conclusion does not support the hypothesis that uncompensated ferromagnetic spin ordering in the surface of crystallites explains the weak ferromagnetism observed in goethite. (See discussion below.)

The results of Mössbauer effect measurements in goethite reported in the literature are shown in Table B.2.

3) Goethite, magnetic susceptibility

Measurements of bulk magnetic susceptibility of goethite reported in the literature show a large variability as shown in Figure B.6. Some of these differences are due to the susceptibility being dependent on temperature and applied magnetic field. Consequently, the susceptibility quoted by some authors is indicated as χ_∞ , which is the value extrapolated to infinite magnetic field. In other cases the magnitude of the field is given, while sometimes there is no indication of the magnitude of the field used. Even taking into account these factors, reported values are not very consistent.

The susceptibility of natural goethite specimens seems, on average, to be smaller (around $20\text{--}30 \times 10^{-10}$ SI) than that of synthetic goethite, and, at room temperature, to have a positive temperature coefficient of the susceptibility as expected in an antiferromagnetic material below the Neel point. (Crangle, P.69, 1977). Nevertheless, a negative temperature coefficient has also been observed by V. Oosterhout (1965) in some of his synthetic samples; this coefficient becomes more negative with increasing ageing of the specimen.

Table B.2 Results of Mössbauer effect experiments in goethite reported in the literature. I.S. = isomer shift (with respect to Fe) H = magnetic field, Q.S. = quadrupole splitting (2E).

Temperature (°K)	I.S. (mm/s)	H (Tesla)	Q.S. (mm/s)	No. Sites in source (°K)
408	NR	0	0.6(1)	1 403 1)
291	0.35(5)	38.4(5)	-0.3(1)	1 1)
77	NR	50.4(5)	-0.3	1 1)
4.2	NR	50.4(5)	-0.3	1 1)
Room	NR	38.8	NR	1 2)
Room	0.41	28.2(5) 34.2(7)	6(2)neV $I_1/I_2 = .65(10)$	2 370 3)4)
294	NR	36.5	NR	1 5
Room	NR	36.4	NR	1 6
Room	NR	33.0-37.5	0.29(5)	1 7
Room	NR	38.9(2)	0.26(2)	1 8)
85	NR	50.0(3)	0.26(2)	1 8)
393.3	NR	0	0.38	1 8)
Room	0.37	29.5(1.0) 34.5(1.0)	0.30(5) 0.38(5) (sample 1)	2 9)
82	NR	51.0(1.0)	NR (sample 1)	1 9)
Room	0.38	35.7(1.0)	0.40(5)	1 9)
Room	0.38	37.1(1.0)	0.40(5)	1 9)
82	NR	49.5(1.0)	NR	1 9)
Room	0.38	29.5(1.0) 33.5(1.0)	0.35(5) 0.40(5)(sample 4)	2 9)
Room	0.38	36.0(1.0)	0.40(5)	1 9)
Room	0.42	37.5(1.0)	0.36(5)	1 9)

1) Forsyth, et al. 1968; 2) v. Oosterhout, 1965; 3) Hryniewicz, et al. 1963; 4) Hryniewicz, et al. 1965; 5) Shinjo, 1966; 6) Rositer and Hodgson, 1965; 7) Janot, et al. 1968; 8) van der Woude, et al 1966; 9) Dezsí and Fodor, 1966.

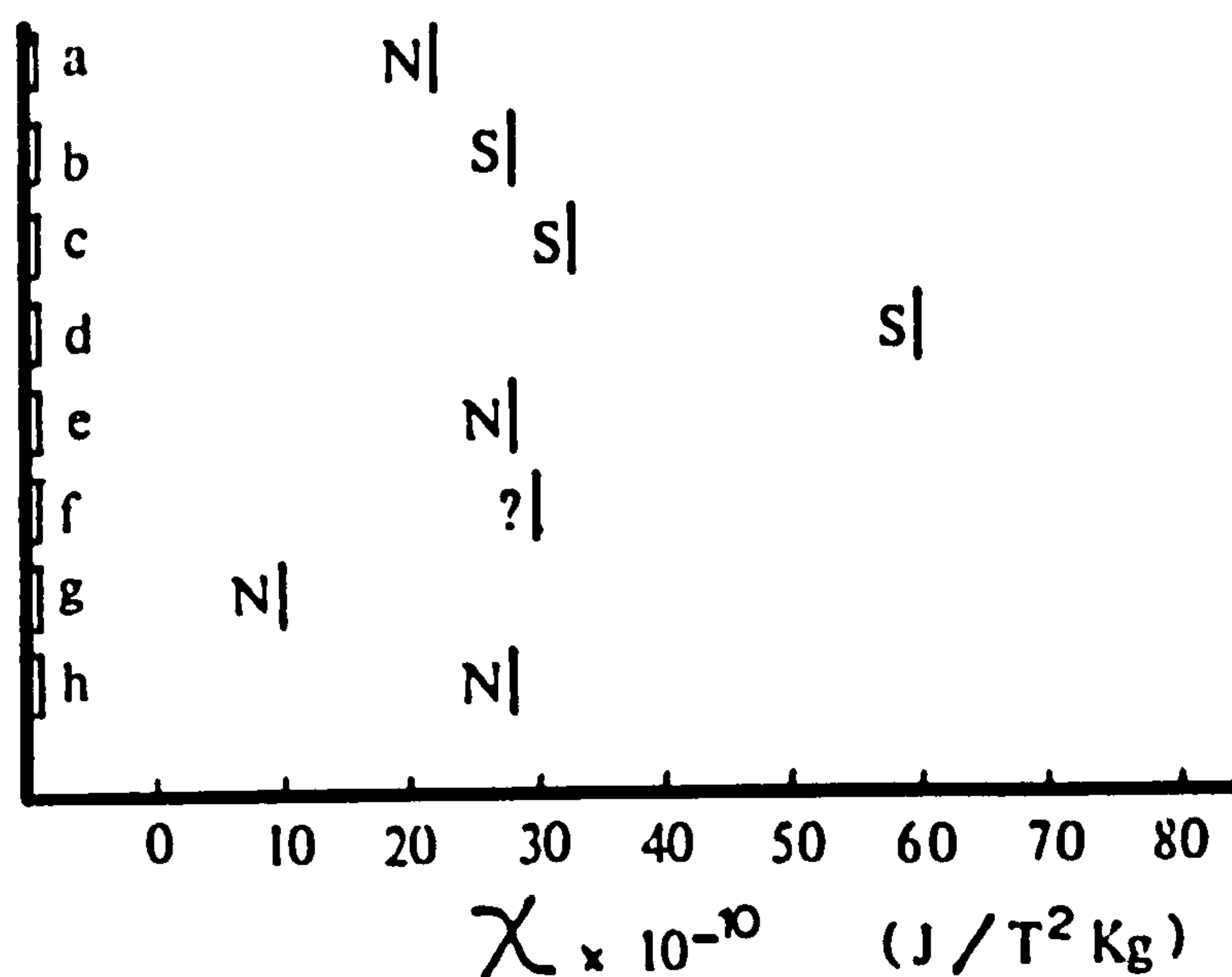


Figure B.6 Magnetic susceptibility of goethite at room temperature. N = natural mineral, S = synthetic. a) v. Oosterhout, 1965; b) op. cit. aged 4h at 120°C; c) op. cit. aged 48h at 120°C; d) Banerjee, 1970; e) Pastrana and Hopstock, 1977; f) Hryniewicz, et al 1963; g) Prasad and Ghildyal, 1975; h) this work.

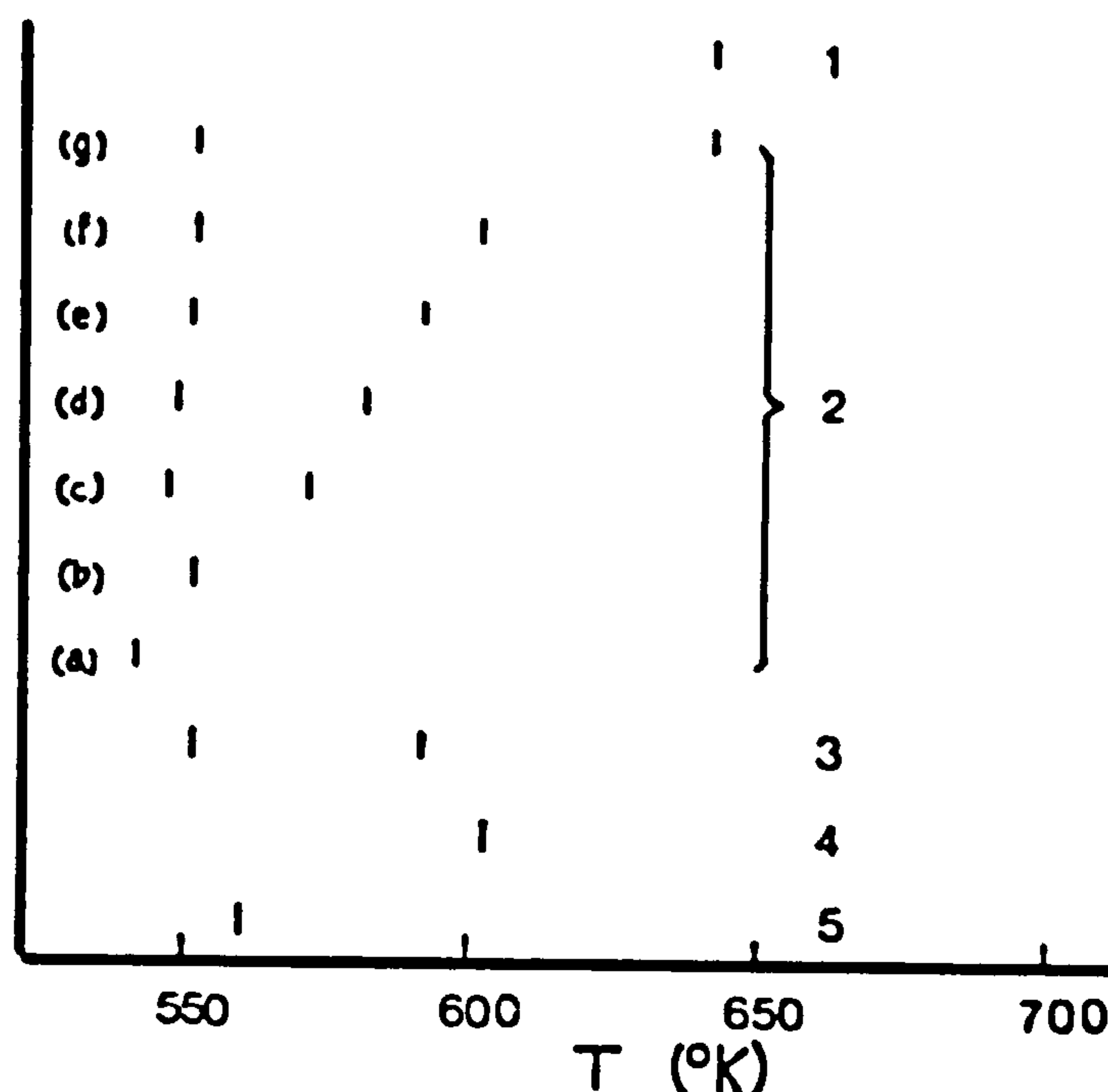


Figure B.7 Dehydration temperatures of goethites of different origin. 1. Mineral from Lostwithiel. 2. Böhm-Krause goethites of different age. (a) 16 hrs. at 25°C, (b) 2 hrs. at 120°C, (c) 4 hrs. at 120°C, (d) 24 hrs. at 120°C, (e) 48 hrs. at 120°C, (f) 3 hrs. at 150°C, (g) 3 hrs. at 150°C, followed by 2 hrs. at 200°C. 3,4. Commercial samples. 5. Synthetic lepidocrocite (After v. Oosterhout, 1965).

In a perfect antiferromagnetic mineral (such as goethite), the perfect spin ordering should result in zero remnant magnetization. Nevertheless, Strangway, et al. (1967) and Banerjee (1970), have observed stable remanent magnetization in natural and in synthetic goethite respectively. Banerjee (op. cit.) also showed that artificial thermoremanent magnetization could be induced in his synthetic goethite samples by heating to above the Neel temperature and then cooling while maintaining the specimens in an applied magnetic field. This treatment is reported to induce a weak ferromagnetic behaviour for all subsequent heating and cooling cycles of the samples. Nevertheless in the same paper Banerjee remarks that this behaviour was not observed under identical conditions with a natural single crystal of goethite from Lostwithiel, Cornwall, England*.

Hryniewicz, et al. (1965) report that accurate measurements of the magnetic susceptibility of their α -Fe O OH samples showed a clear magnetic transition at about 343°K and another less clearly marked transition at about 368°K . These results support their conclusions, deduced from Mössbauer effect measurements, of the presence of two magnetic sublattices in the goethite structure. In spite of the self-consistence of their results it is suspicious that the transition temperatures they found are lower than the usually quoted Neel point for goethite of 403°K .

4) Goethite differential thermal analysis (DTA) behaviour

A variability in the dehydration temperature of goethite similar to the variability observed in the reported values of magnetic

*An unsuccessful attempt to reproduce Banerjee's results with synthetic and natural goethite is reported in this work in Section 5.4.

susceptibility, has been pointed out by V. Oosterhout (1965). (See Figure B.7). According to this author the differences in the dehydration temperatures depend on the method of formation; synthetic goethites having a dehydration temperature dependent on the method of synthesis. Table B.3 shows methods of preparing goethite. Type A goethite (in V. Oosterhout's classification) which are produced by methods a, b and under certain conditions method c (Table B.2) have two dehydration temperatures, approximately 553 and 593°K, while natural and synthetic goethites prepared according to method d show only one dehydration temperature at approximately 605°K.

In spite of the differences in the DTA and magnetic susceptibility results, goethites prepared according to the various methods all show the same behaviour with respect to line positions in X-ray diffraction and only minor differences in infrared and chemical analysis.

5) Goethite. Defective structure

The different types of goethite have been explained as

1) Particle size effects or, 2) A tendency of α -Fe O OH to present a defective crystal structure. The varying behaviour of goethite being the result of different degrees of defectiveness.

The type of defect of the structure leading to particular forms of behaviour is a matter of speculation. One possibility that has been advanced (V. Oosterhout, 1964) is that the chains of ferric ions along the c-axis are interrupted by Fe^{3+} vacancies producing chain terminations. The excess charge is then compensated by hydrogen ions leading to the presence of H_2O molecules and extra OH ions at the site of the vacancies.

Table B.3 Methods of synthesising goethite (after V. Oosterhout, 1965).

- a) Slow oxidation by air of a suspension of ferrous hydroxide
or carbonate in a dilute solution of ferrous sulphate
(Nitschman, 1938).**
- b) Oxidation of a solution of ferrous sulphate with air in the
presence of metallic iron and a suspension of goethite crystal
nuclei (B.I.O.S., 1947, P.47).**
- c) Dehydration of so-called ferric hydroxide in the presence of a
solution of alkali hydroxide (Bohm, 1925; Krause, et al. 1932).**
- d) Large-scale reduction of organic nitro-compounds with metallic
iron, dilute hydrochloric acid and some aluminium chloride
(B.I.O.S., 1947, P.14).**

Greater or lesser numbers of such vacancies lead to a distribution of chain lengths and it is claimed that this can explain qualitatively the extra water content and the existence of a range of dehydration temperatures.

It is difficult to understand why these vacancies should lead to different dehydration temperature if all the Fe ion sites in goethite are equivalent. On the other hand, if the Fe sites are not all equivalent, (two different sites having been demonstrated by the Mössbauer effect of some samples) then not all vacancies are equivalent and it is plausible that different dehydration temperatures are associated with water present in different vacancies.

The magnetic behaviour of goethite has also been attributed to such a defect-ridden structure by Banerjee (1970) and by Stacey and Banerjee, P.40 (1974): At the site of a broken link in the ferromagnetic Fe chain there is an uncompensated spin moment. The random distribution of such uncompensated spin moments results in the observed weak ferromagnetic behaviour, although the goethite as a whole is antiferromagnetic. According to Banerjee (1970), if the specimen is heated to above the Neel temperature and then cooled in an externally applied magnetic field, the randomly oriented moment-carrying links line up along the applied field direction resulting in the net thermoremanent magnetization observed in some natural and synthetic specimens.

A related group of observations and experiments reported by Nalovic (1971) and Nalovic and Pinta (1972a, 1972b) indicate that 1) there is a correlation between a decrease in the crystallinity of iron oxyhydroxides in tropical soils and the total content of 4th transition series elements. (0.6 to 3% total Mn, Cr, V, Co, Ni, Cu;

designated as ΣM) 2) the presence of ΣM elements are found to inhibit the crystallinity of laboratory-prepared oxyhydroxides.

3) Iron oxyhydroxides formed in the presence of ΣM elements result in compounds being formed with a) higher volume, b) higher surface area and porosity and c) higher content of water of hydration.

It would seem plausible that these observations could be explained by the presence of ΣM elements promoting the formation of a highly defective goethite in the synthetic and natural soils reported by Nalovic and Nalovic and Pinta (op. cit.).

APPENDIX C Mineral proportions from Mössbauer spectra

This appendix gives a method for determining the proportions of iron minerals in a mixture. Formulae are derived for the following cases: 1) when the recoil-free fractions of the various minerals are known, 2) when the recoil-free fractions can be assumed to be equal and 3) when the recoil-free fractions are unknown and there is suspicion that they are different. In this last case the formula makes use of data derived from the spectrum of a synthetic mixture of the minerals in the unknown. It is assumed that the spectra obtained have sufficiently high S/N ratio for accurate area measurements to be performed, that they have been obtained with thin Mössbauer absorbers, and that the areas corresponding to each mineral have been identified.

The relative absorption area A of the spectrum of a mineral is proportional to 1) f , the recoil-free fraction, 2) C , the iron concentration in the mineral and 3) P , the relative proportion of the mineral in the absorber. Hence for the i^{th} mineral phase we can write

$$A_i = K f_i C_i P_i \quad \text{C.1}$$

where K is a proportionality constant.

hence

$$P_i = \frac{A_i}{K f_i C_i} \quad \text{C.2}$$

for n minerals summing the relative proportions gives

$$\sum_{j=1}^n P_j = \sum_{j=1}^n \frac{A_j}{K f_j C_j} = (K)^{-1} \sum_{j=1}^n \frac{A_j}{f_j C_j} = 1$$

hence

$$\sum_{j=1}^n \frac{A_j}{f_j C_j} = K \quad \text{C.3}$$

Substituting K in C.2 leads to

$$P_i = \frac{A_i}{f_i C_i} \frac{1}{\sum_{j=1}^n \frac{A_j}{f_j C_j}} \quad \text{C.4}$$

Relation C.4 can be used to calculate the proportion of any mineral if the recoil-free fractions and the iron concentrations of all the minerals are known.

If the recoil-free fractions are unknown but can be considered equal relation C.4 can be used to calculate the mineral proportions making all f values equal to one.

If the recoil-free fractions are unknown and they are suspected to be different from each other the method requires the making of a synthetic mixture of the various minerals with identical weight proportion of each mineral. A thin Mössbauer absorber is made, a spectrum run and analysed and the absorption area of each mineral measured.

Applying equation C.4 to the synthetic mixture; from the way the mixture is prepared

$$P_1 = P_2 = \dots\dots\dots = P_n = 1/n$$

so that

$$\frac{A_1}{f_1 C_1} \left(\sum_{j=1}^n \frac{A_j}{f_j C_j} \right)^{-1} = \frac{A_2}{f_2 C_2} \left(\sum_{j=1}^n \frac{A_j}{f_j C_j} \right)^{-1} = \dots\dots$$

from where

$$\frac{A_1}{f_1 C_1} = \frac{A_2}{f_2 C_2} = \dots\dots \quad \text{C.5}$$

The recoil-free fraction f and the iron concentrations are constants for each mineral hence they can be merged into a single factor: $F_i = f_i C_i$, hence

$$\frac{A_1}{F_1} = \frac{A_2}{F_2} = \dots$$

or for any two components i and j

$$\frac{A_i}{F_i} = \frac{A_j}{F_j} \quad \text{or} \quad \frac{A_i}{A_j} = \frac{F_i}{F_j} \quad \text{C.6}$$

Relation C.4 can be applied to an unknown mixture. Calling X the absorption areas in the unknown and P_i the proportion of the i^{th} component, relation C.4 can be written as

$$P_i = \frac{X_i}{F_i} \frac{1}{\sum_{j=1}^n \frac{X_j}{F_j}} = X_i \frac{1}{\sum_{j=1}^n \frac{F_i}{F_j} X_j}$$

Substituting relation C.6 and re-ordering, results in

$$P_i = \frac{X_i}{A_i} \left(\sum_{j=1}^n \frac{X_j}{A_j} \right)^{-1} \quad \text{C.7}$$

C.7 gives the weight proportion P_i of any mineral in the mixture in terms of the measured absorption areas in the standard mixture (A) and in the unknown mixture (X).

APPENDIX DMiscellaneous NMR spectra

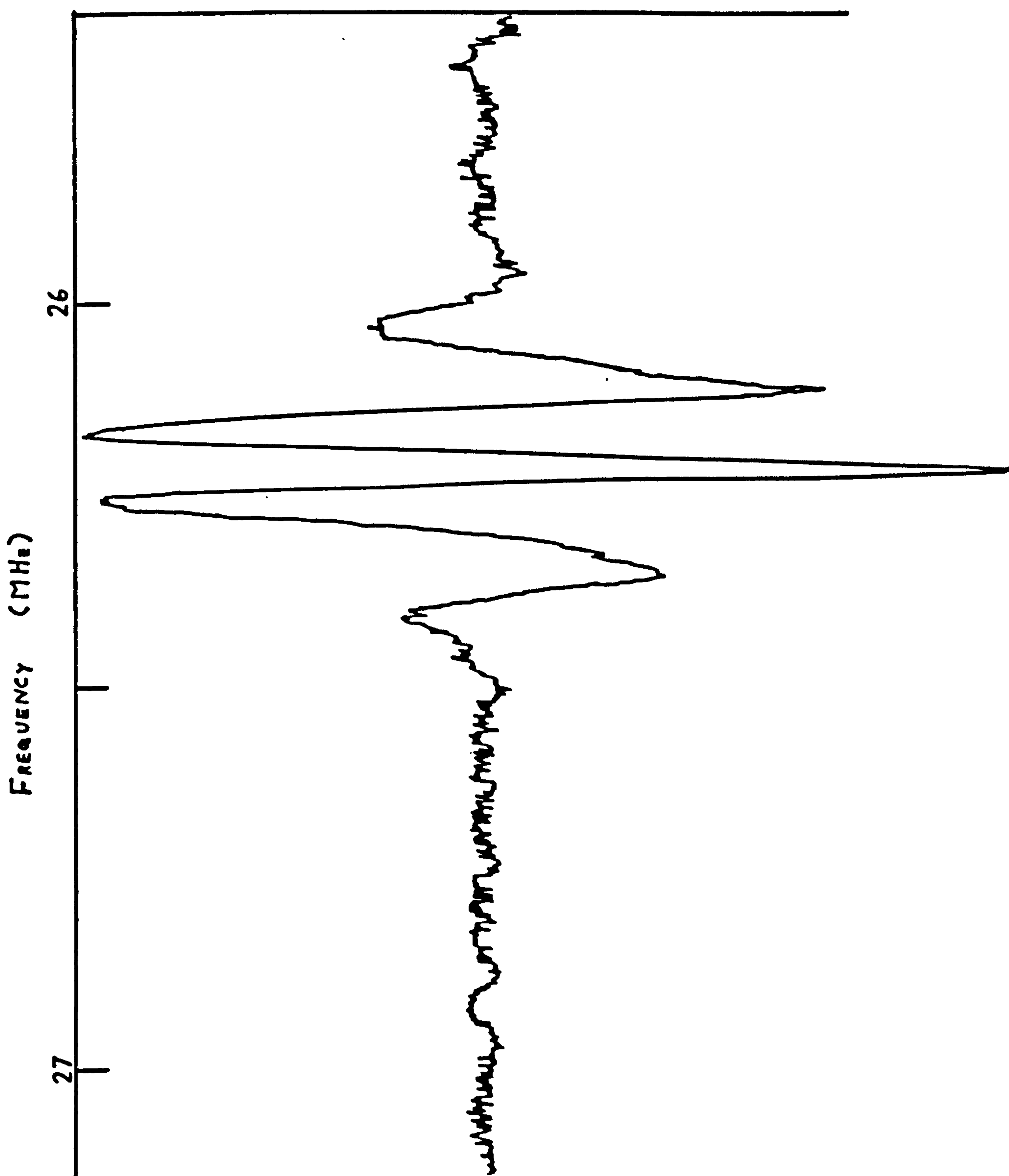


Figure D.1 Zero-field NMR of Ni^{61} in metallic nickel. Resonance frequency 26.212(2) MHz, $T = 290^\circ\text{K}$ linewidth 0.9 MHz. Conditions: RF level 8, CSC 922, amplifier level 7 FM modulation X1, 1, Quench PRF 50 KHz, AGC auto, coherence 5, sweep 256, chart 600/h, 1V, time constant 1 sec. (Decca spectrometer)

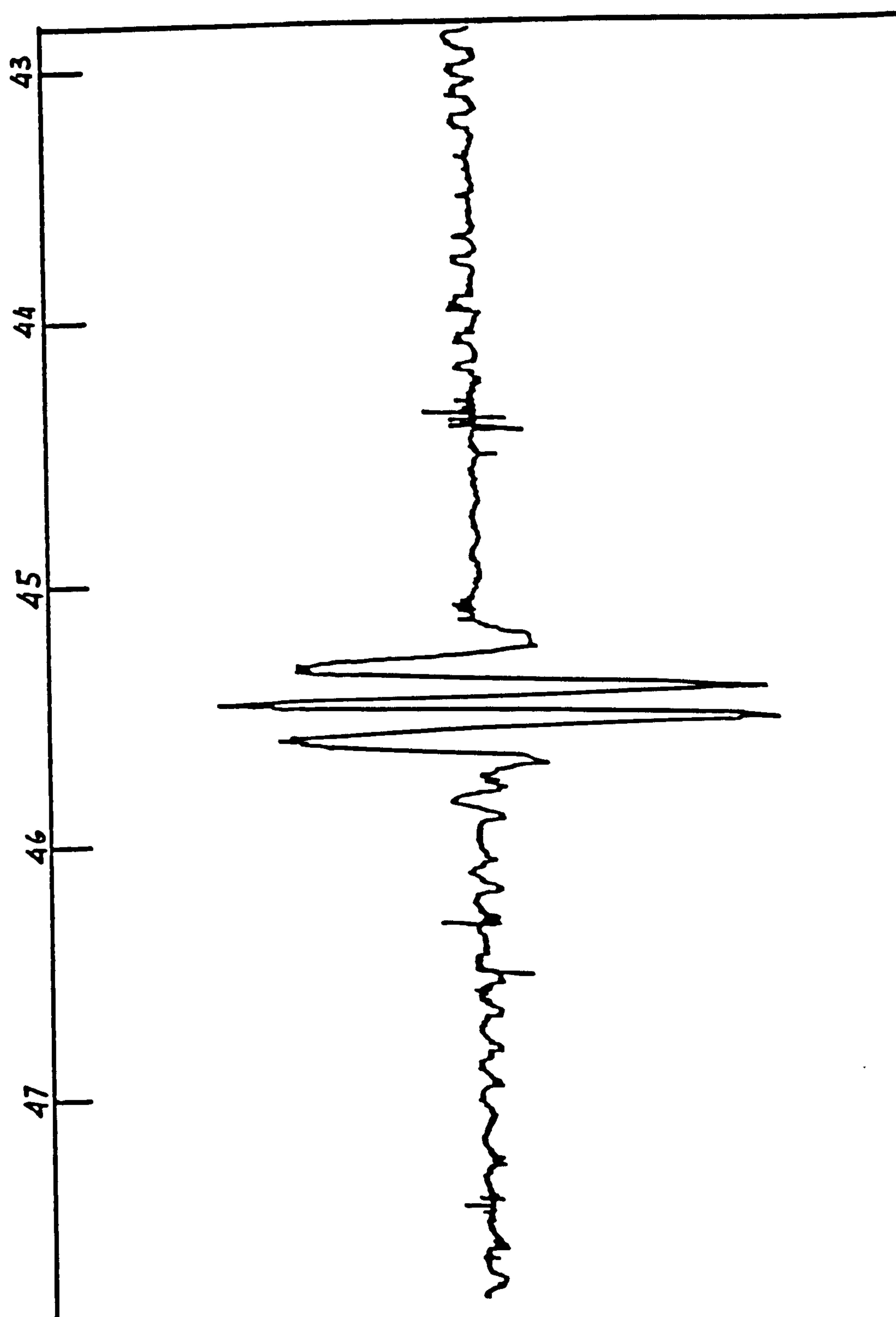


Figure D.2 Zero-field NMR of Fe^{57} in metallic iron. Resonance frequency 45.43(1) MHz, $T = 290^\circ\text{K}$, linewidth = 0.5 MHz. Conditions: RF level 9, CSC = 187, amplifier level 6.5, FM modulation X1,10, quench PRF 50 KHz, AGC auto, coherence 5.5, sweep 512, chart 600/h, 5V, Time constant 0.1 sec. (Decca Spectrometer)

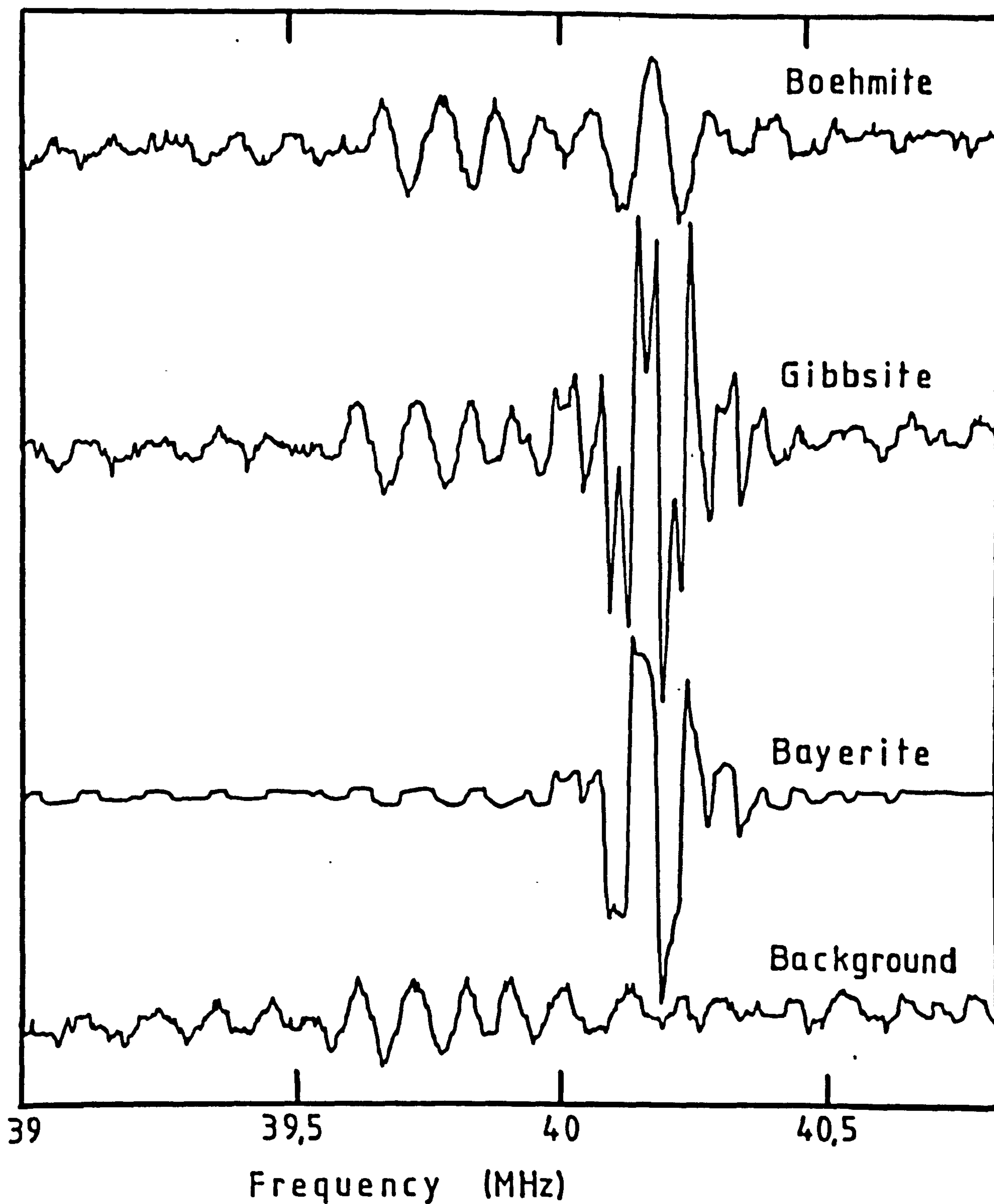


Figure D.3 Proton NMR resonance signals in synthetic aluminium minerals obtained with the DECCA NQR spectrometer in an external magnetic field of 0.9458 Tesla. Conditions: RF level 8, CSC 999, amplifier level 8, FM modulation X1.2, quench PRF 50 KHz lock, AGC auto coherence 5, sweep 256, chart = 600/h, IV, time constant 3s.

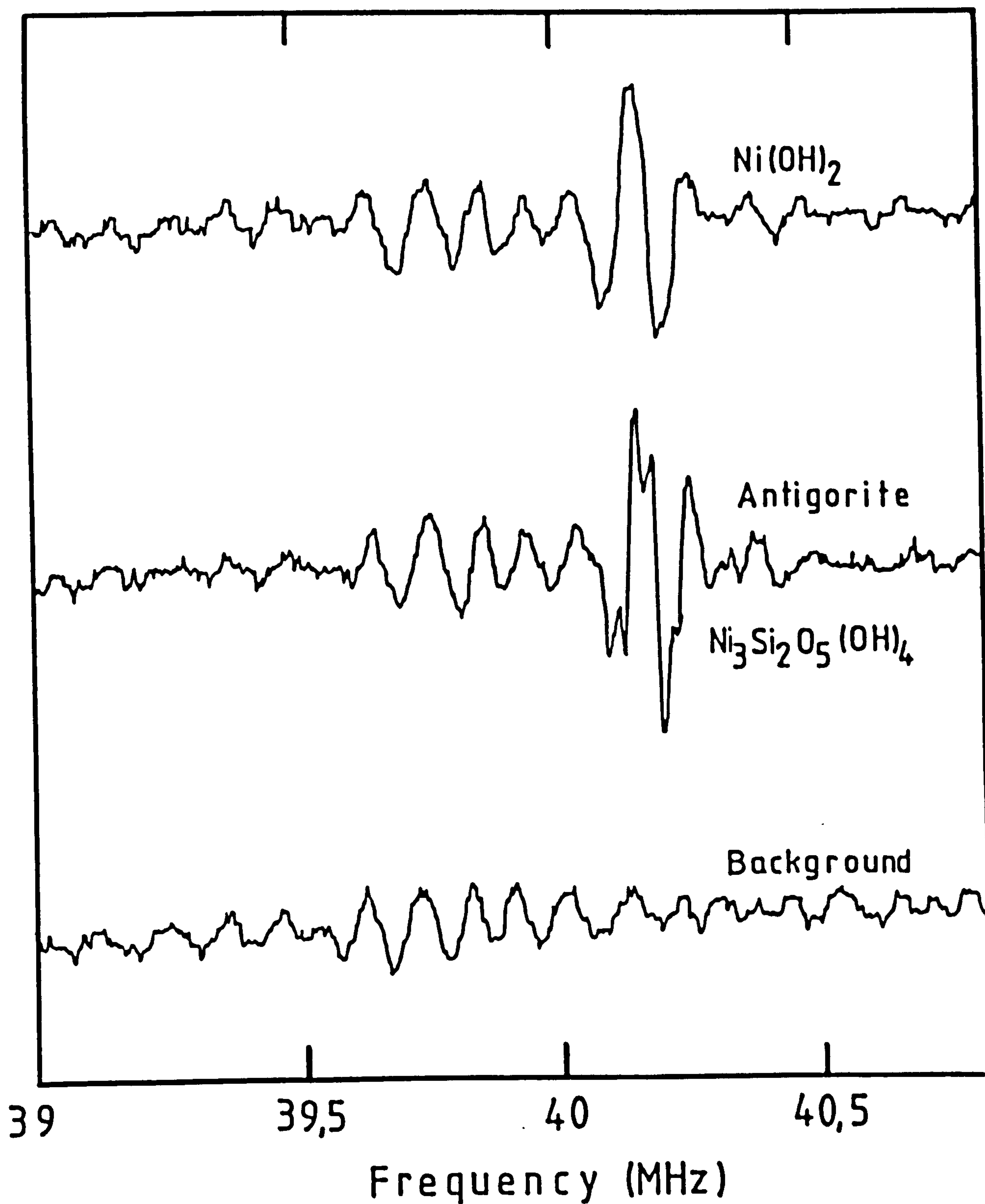


Figure D.4 Proton NMR resonance signals in synthetic nickel compounds obtained with the DECCA NQR spectrometer. Conditions as in figure D.3.

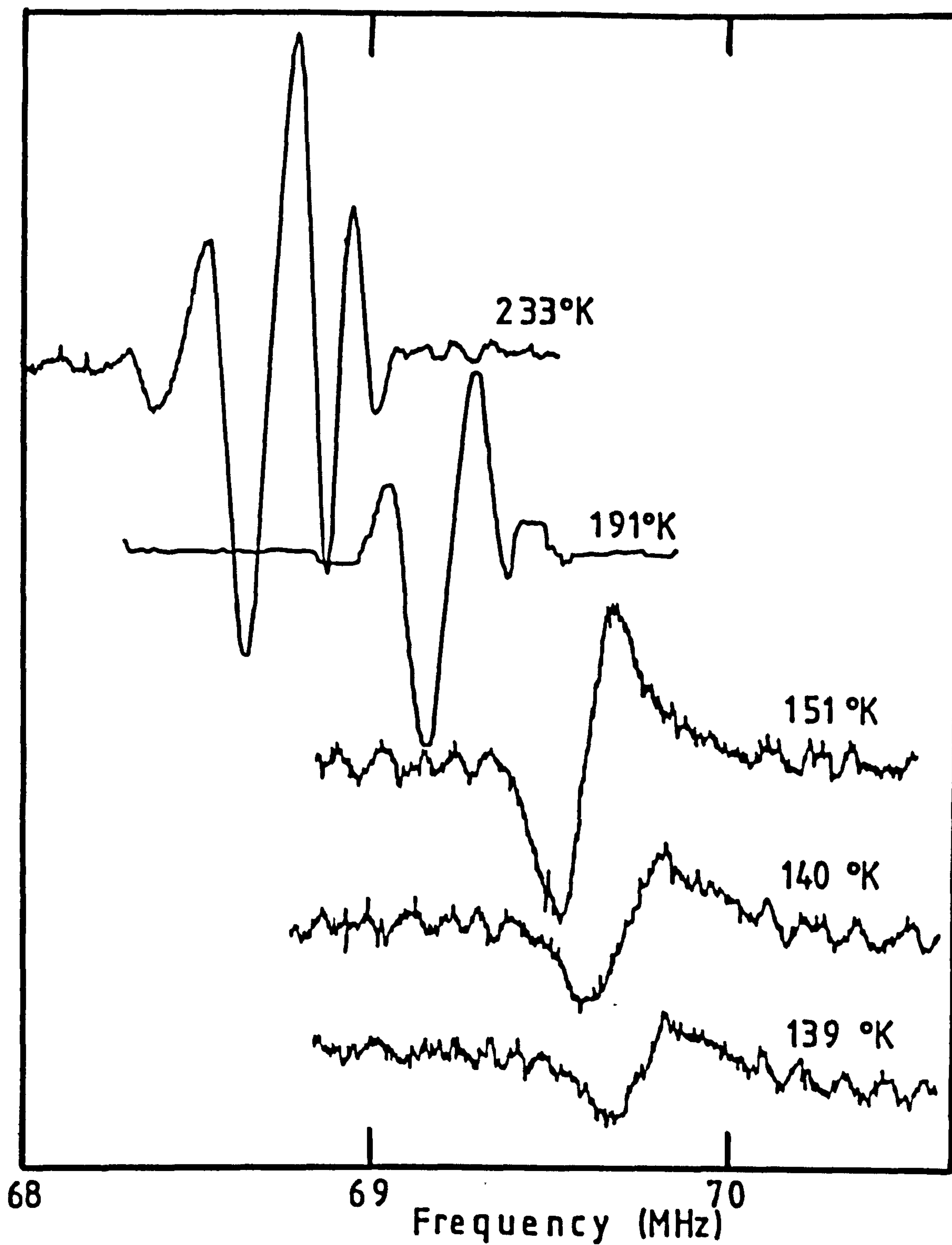


Figure D.5 Fe^{57} resonance signals in magnetite at different temperatures obtained with the Decca NQR spectrometer. Conditions: RF level 10, CSC 213, amplifier level 8.5, FM modulation X1.7, quench PRF 25 KHz variable, AGC auto, coherence 6, sweep 128, chart 600/h, 1V, time constant 3 sec.

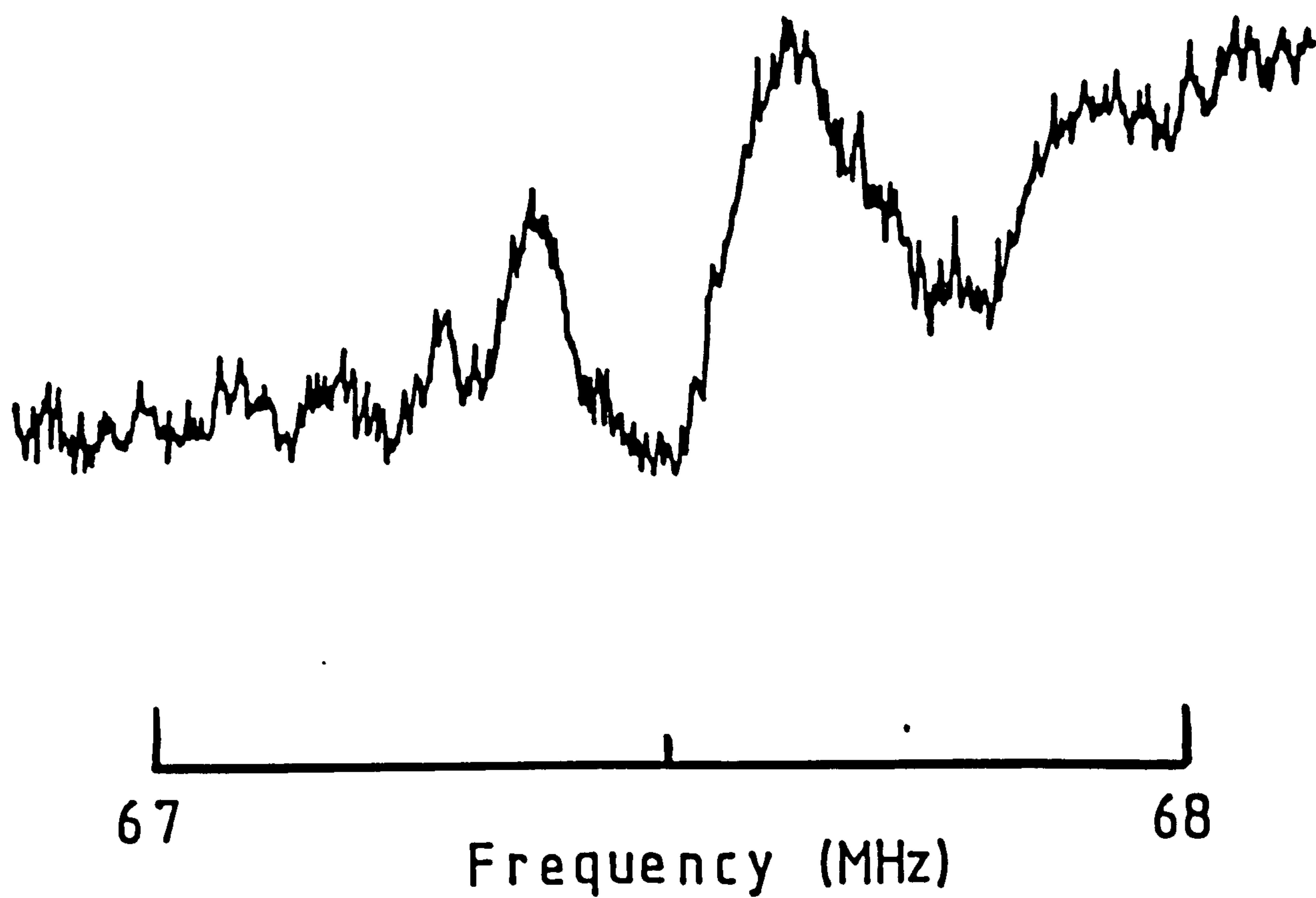


Figure D.6 Fe^{57} resonance signal of magnetite contained in a magnetic fraction of the nickel laterite from Loma de Hierro, Venezuela. $T = 295^\circ\text{K}$. Conditions as in Figure D.5.

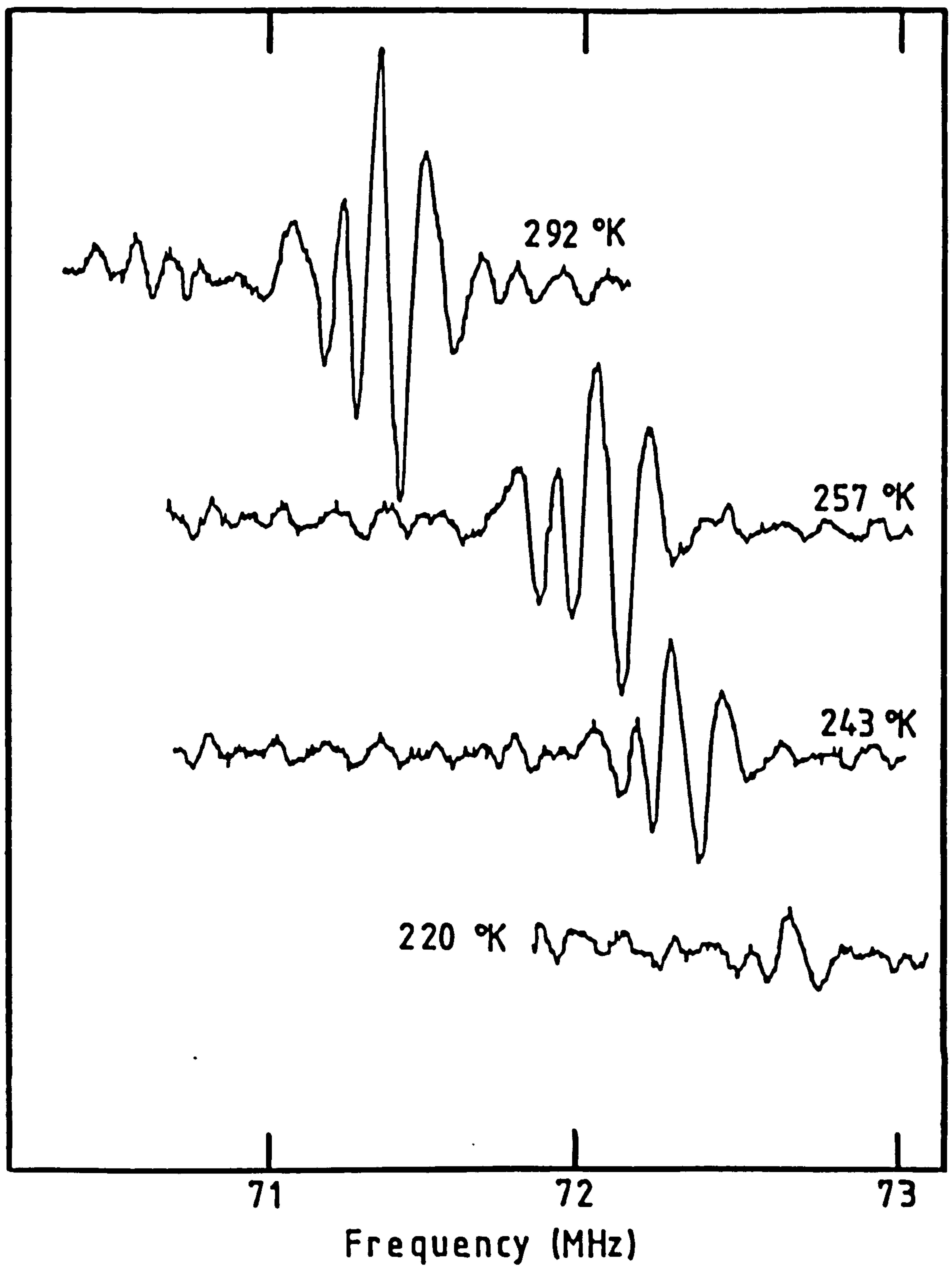


Figure D.7 Fe^{57} resonance signals in hematite at different temperatures obtained with the DECCA NQR spectrometer. Conditions similar to those in Figure D.5.

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