Aluminous Hematite: A Mössbauer Study

Stuart A. Fysh[1] and Paul E. Clark[2]
Department of Physics, Monash University, Clayton, Vic. 3168, Australia

Abstract. Aluminous hematites prepared in three different ways have been examined at 300K and 4.2K using the Mössbauer technique. The results indicate significant differences between the behaviour of aluminous hematites that have been subjected to high temperatures ($>600°$ C) and those which have not. The magnitude of the room temperature quadrupole splitting of the former increases with aluminium content, approaching at ~ 16 mole percent substitution the value (-0.22 mm/s) exhibited by all of the low temperature specimens. This variation may be explained qualitatively in terms of a preferential c-axis contraction of the lattice upon incorporation of aluminium, which does not occur unless a c-axis defect structure is removed by subjection of the hematite to high temperatures. The solid solubility limits of high and low temperature hematites (~ 15 mol % and ≥ 19 mol % respectively) also differ, as do the room temperature decreases in hyperfine splitting (-0.82 kOe/mol % Al and -0.86 kOe/mol % Al). At 4.2 K only low temperature hematite exhibits a decrease in hyperfine splitting with increasing Al content (-0.40 kOe/mol % Al). The absolute values of the recoil free fractions of hydrothermally prepared aluminous hematites have been determined at 4.2 K (0.70 ± 0.02 – pure hematite, 0.82 ± 0.02, 14 ± 2 mol % Al substitution) and exhibit a similar increase with Al content to that previously observed for aluminous goethites. The room temperature recoil free fraction of pure hematite has been measured to be 0.64 ± 0.02. The effects of particle size on both hyperfine splitting and recoil free fraction have been investigated.

Introduction

Hematite ($\alpha - Fe_2O_3$) is one of the most commonly encountered forms of iron oxide, and is present to some extent in a wide variety of soil and clay environments. The presence of aluminous hematite in bauxites (Janot and Gibert 1970; Solymár and Jónás 1971) and soils (Schwertmann et al. 1977; Bigham et al. 1978) is now well established, although it is neither as common, nor substituted to the same extent as aluminous goethite. The formation of aluminous hematite has been the subject of numerous studies

(e.g. Muan and Gee 1956; von Steinwehr 1967; Schwertmann et al. 1979).

Because of significant deviations from Vegard's law (Caillére et al. 1960; von Steinwehr 1967; Wolska 1976) and the decreased crystallinity of aluminous hematite (Schwertmann et al. 1979), X-ray diffraction is not an effective tool for analysis of the small quantities of this mineral which may be present in soil and clay samples. Similarly, chemical analysis is not likely to yield reliable results because of the need to pre-extract all other sources of soluble iron and aluminium.

Mössbauer spectroscopy is gaining increased acceptance as a technique for the study of a wide variety of environmental samples. It is particularly suitable for the study of soils and clays as it requires no prior chemical leaching, and is specific for the iron-containing minerals only. As such it is largely unaffected by the presence of other mineral species, and is able to cope with poor mineral crystallinity and low iron concentrations. In order to make quantitative statements about the iron minerals present in a sample on the basis of Mössbauer measurements it is necessary to compare the data with that for standard mineral specimens. In an earlier paper (Fysh and Clark 1982, henceforth referred to as I) we have reported on the preparation and Mössbauer characterisation of aluminous goethite. We present here a similar study of aluminous hematite.

The Magnetic Behaviour of Hematite

Bulk hematite orders antiferromagnetically at $T_N = 956$ K, and is weakly ferrimagnetic between T_N and T_M ($= 260$ K), the temperature of the so-called Morin transition. Below the Morin transition the spins of the Fe^{3+} ions are antiparallel, and make an angle of about $7°$ with the trigonal [111] direction of the rhombohedral unit cell (Morrish et al. 1963). At T_M there is an abrupt spin flip of about $85°$, with the resultant spins lying in the (111) plane, but canted slightly to give rise to the observed weak ferrimagnetism.

Numerous authors have discussed possible mechanisms for the spin flip transition in hematite, and van der Woude (1966) summarises some of this discussion. He concludes that magnetic dipolar and anisotropy terms in the spin Hamiltonian for $\alpha - Fe_2O_3$ favour the spins lying in the c plane and along the trigonal c axis respectively. As temperature increases the second term decreases more rapidly than the first, and at T_M it becomes energetically favourable for a spin flip to take place. The canting of the spins above T_M

[1] *Now at:* BHP Co. Ltd., Central Research Laboratories, P.O. Box 188, Wallsend, N.S.W. 2287, Australia
[2] *Now at:* Department of Applied Physics, Capricornia Institute of Advanced Education, Rockhampton, Q'LD 4700, Australia

is explained as being due to an antisymmetrical spin coupling term in the Hamiltonian.

Mössbauer Spectroscopy of Hematite

Above T_N the Mössbauer spectrum of hematite is a doublet, the single absorption line of the magnetically disordered system being split by the interaction of the nuclear quadrupole moment with the *electric field gradient* (EFG) at the nucleus. Below T_N the onset of magnetic order gives rise to the usual six line spectrum, with the splitting of the outer two peaks being proportional to the magnetic field experienced by the nucleus, H_{int}.

On passing through the Morin transition the Mössbauer spectrum of hematite changes considerably. The magnetic hyperfine splitting is about 7 kOe less for $T > T_M$ than for $T < T_M$ and several conflicting explanations have been given for this. Van der Woude (1966) and Ruskov et al. (1976) both propose that the electronic contribution to the magnetic hyperfine field changes at T_M, but Tobler et al. (1981) claim that this effect is negligible, and that the increase in H_{int} below T_M is due to the shift in orientation of the nuclear moment in the dipolar field.

The quadrupole splitting Δ also changes significantly at T_M with

$$\frac{\Delta_{T > T_M}}{\Delta_{T < T_M}} \approx -0.54 \text{ (Bowen 1979).}$$

In going from $H_{int} \parallel [111]$ to $H_{int} \perp [111]$ the angle between V_{ZZ} (the component of the EFG tensor along the principal axis, [111] for a rhombohedral unit cell) and H_{int} changes by 90°, and $\Delta \perp / \Delta \parallel$ should equal $-1/2$ exactly. The deviation from this value has been attributed by van der Woude (1966) and Ruskov et al. (1976) to slight changes in structural parameters which may accompany the transition.

Tobler et al. (1981) have measured the ratio of the quadrupole splitting above and below T_M to be -0.49, and have calculated this to be equivalent to a spin flip of 86.1°.

Van der Woude (1966) noted that there was no significant change in δ on passing through T_N, other than that which normally accompanies a change in temperature. More recent measurements (Ruskov et al. 1976; Nininger and Schroeer 1978) have revealed a very small discontinuity in δ at T_M, although no clear explanation of this phenomenon has been given.

The hematite present in soil and clay environments is often in a very finely divided state, so that it is appropriate to consider the effects of decreasing particle size on hematite Mössbauer spectra.

Kündig et al. (1966) and Yamamoto (1968) ascertained that T_M decreased with decreasing particle size, and it has been estimated by Nininger and Schroeer (1978) that particles below ~ 200 Å in diameter would not exhibit a Morin transition at al. This decrease in T_M has been explained by Artmann et al. (1965) as being due to the effect of small changes in the lattice constant on the temperature at which the cancellation of the second order magnetic dipolar and spin-orbit anisotropy fields postulated as the cause of the Morin transition becomes energetically favourable. A further cause of decreasing T_M with smaller particle sizes may be the 'pinning' of atomic spins by the surface (Yamamoto 1968; Nininger and Schroeer 1978). Clearly surface atoms constitute a greater fraction of the total as particle size

decreases. An additional consequence of the increasing number of surface ions in small hematite particles has been noted by Kündig et al. (1966). These investigators found that for $T > T_M$ the quadrupole splitting increases with decreasing particle size. Van der Kraan (1973) has shown this effect to be related to the increased EFG experienced by iron nuclei at or near the surface of a crystal.

Mössbauer Effect Studies of Aluminous Hematite

Isomorphous replacement of iron by aluminium in hematite has been observed up to a maximum of ~ 16 mole percent (Muan and Gee 1956; von Steinwehr 1967; Schwertmann et al. 1979).

Srivastava and Sharma (1972) studied the effects of aluminium substitution on the Mössbauer spectrum of hematite between 10 K and 1000 K.

They observed that both T_N and T_M decreased with increasing aluminium content, although T_M decreased more rapidly. In addition, they found that the presence of aluminium in the lattice tended to smear the Morin transition out over a greater range in temperature. Srivastava and Sharma (1972), Krén et al. (1974) and Salugin et al. (1975) obtained conflicting results concerning a decrease in spin flip angle (and hence in $\Delta_{T < T_M}$) with increasing Al content. Povitskii et al. (1978) concluded that these contradictions were the result of different methods of sample preparation, and that to ensure homogeneity it was necessary to co-precipitate iron and aluminium hydroxides prior to ignition.

Besides the temperature of the Morin transition and the spin re-orientation angle, the replacement of iron by diamagnetic atoms is also expected to affect the magnetic field experienced by the nucleus. Srivastava and Sharma (1972) measured the temperature dependence of the magnetic hyperfine splitting of the Mössbauer spectra of both pure and 8 mole percent aluminium substituted hematite, and found that for $0.35 \leq T/T_N \leq 0.9$ the hyperfine field of the latter was less than that of the pure material. More recently Jónás et al. (1980) produced aluminous hematites by calcining synthetic aluminous goethites and found that at room temperature the hyperfine field decreased linearly up to aluminium substitutions of about 20 mole percent, thus supporting earlier Mössbauer measurements (Janot et al. 1971 and Biais et al. 1972) which indicated aluminium replacements of up to ~ 30 percent in hematite. In contrast to the measurements of Srivastava and Sharma (1972), Bigham et al. (1978) reported on Mössbauer studies of several soil clays and observed decreased hyperfine splittings for hematite down to 4.2 K, assumed to be due to aluminium substitution.

We have observed reduced hyperfine splittings for bauxitic aluminous hematite at both room temperature and 4.2 K. Because of the confusion in the literature regarding the behaviour of the hyperfine field of aluminous hematite of 4.2 K, the conflicting reports on Al solubility, and the lack of reliable standard Mössbauer data on this mineral system, the present study was undertaken. The experimental and data analysis techniques employed in this study are the same as those already described in I and only sample preparation details are given here.

Sample Preparation

Three series of aluminous hematites have been prepared. All of the reported chemical analyses were performed by

Comalco staff at the Comalco Research Company laboratories using the techniques described in I.

The first series of aluminous hematites (series 1) were made from unwashed iron-aluminium hydroxides co-precipitated from nitrates with ammonia solution. The hydroxides were dried before firing in a Pt boat at 950° C for 15 h in a constant flow of oxygen. The aluminium nitrate content of the initial solutions was such as to give steps of 2 mole percent Al, ranging from 0 percent through to 20 percent. Several of the specimens (all of which resisted acid dissolution) were analysed by fusing with sodium tetraborate and dissolving in H_2SO_4, but the high losses recorded indicate that the analysis was not reliable. The initial weights of the aluminium and iron nitrates were determined very accurately and the calculated yield after firing always exceeded 97 percent. The small losses showed no dependence on aluminium concentration, indicating that the nitrates were not significantly hydrated. Thus the calculated aluminium content of the initial co-precipitate has been used as a measure of lattice aluminium replacement in these hematites.

A second series of aluminous hematites (series 2) were prepared by firing synthetic aluminous goethites at 590° C for 2 h in a Pt boat. The preparation and Mössbauer characterization of these goethites have previously been described in I.

A third series of aluminous hematites (series 3) was prepared hydrothermally at 250° C. Unwashed co-precipitated hydroxides containing between 0 and 24 mole percent Al were dried and then aged in a Pt beaker for 12 h in 10^{-3} M KOH. Schwertmann et al. (1979) have shown that improved hematite crystallinity is achieved under slightly alkaline ageing conditions. The aged product was decanted and boiled in 5 M KOH for one hour to remove any aluminium hydroxide phases formed. The hematite was then washed by successive decantations with hot deionized water and dialysed against running distilled water for two weeks. Following this the samples were dried and crushed prior to chemical and Mössbauer analysis.

In order to examine the effects of particle size on the Mössbauer spectrum of pure hematite several attempts were made to synthesize very fine pure hematite by boiling a hydroxide precipitated from a pure ferric nitrate solution held at $\sim 95°$ C. The resulting iron oxide always contained some goethite. Pure fine particle hematite was eventually synthesized using the method given by van der Kraan (1972), in which the initial goethite nuclei produced in the above procedure are removed prior to hematite crystallization.

Variation of 300 K and 4.2 K Spectral Parameters with Al Substitution

In this section all of the results regarding the 300 K and 4.2 K spectral parameters are presented and discussed. In the following section the effects of particle size are considered, and in the final section the results of the recoil free fraction measurements are given.

300 K Spectra

Series 1 Hematites. The room temperature spectra of the high temperature hematites all exhibit a well resolved mag-
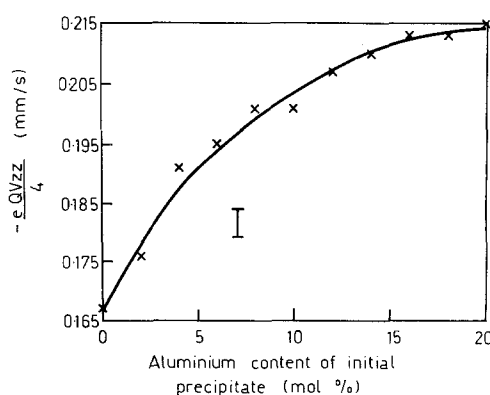

Fig. 1. Variation of quadrupole splitting at room temperature with aluminium content for the series 1 hematites. The error bar represents the estimated experimental uncertainty associated with each measurement
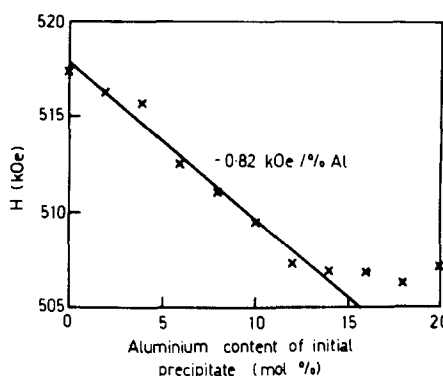

Fig. 2. Variation of magnetic hyperfine field at room temperature with aluminium content for the series 1 hematites

netically split subspectrum together with, for the aluminous specimens, a very small ($<1\%$ of total area) central doublet. The central doublet area increases slightly with aluminium content, and is presumably due to small quantities of ferric iron present in the lattice of Al_2O_3 not incorporated into the hematite.

The isomer shifts of the series 1 hematite spectra are constant to within the error of determination, with a value of 0.36 ± 0.01 mm/s relative to α-Fe at room temperature. The variation of hematite quadrupole splitting with aluminium content is shown in Fig. 1. The variation of $\Delta_{300\ K}$ with aluminium substitution has not been previously reported, and in fact Srivastava and Sharma (1972) state that $\Delta_{T > T_M}$ is independent of aluminium content. The measured dependence of the magnetic hyperfine field on aluminium content is shown in Fig. 2. The equation describing the least squares fit to all the data below 15 mole percent Al is:

$$H_{int} = 517.9 - 0.82\ (\%\ Al)\ kOe.$$

Series 2 Hematites. The room temperature spectra of the series 2 hematites were not quite as sharply resolved as those of series 1. All of the spectra exhibit some line asymmetry, and were fitted with 2 magnetically split subspectra constrained to have the same δ, Δ and halfwidths (see for
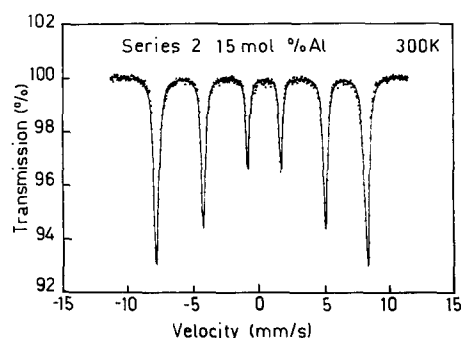
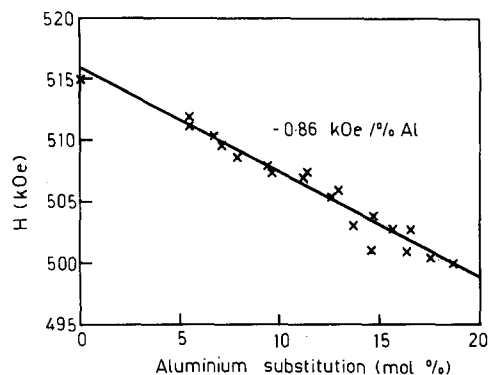Fig. 3. Room temperature Mössbauer spectrum of the series 2 hematite containing 15 mole percent Al

Fig. 5. Mössbauer spectrum at 4.2 K of pure hematite from series 1

Fig. 4. Variation of magnetic hyperfine field at room temperature with aluminium content for the series 2 hematites

spectra have not been included in calculation of the aluminium dependence of the hyperfine field, and are not further considered. As an accurate analysis of their iron content was available, however, several members of this series which exhibited only a six-line spectrum have been employed for recoil free fraction determinations.

4.2 K Spectra

Series 1 Hematites. The isomer shift of all of the 4.2 K series 1 spectra was $+0.49\pm0.01$ mm/s. Interestingly, even for the pure end member of the series some of the hematite ($\sim 15\%$ of the total) remained above the Morin transition at 4.2 K. The spectrum of this specimen is shown in Fig. 5, and it seems likely that the poor statistics of the spectra in at least some of the earlier studies reported may have precluded the observation of this type of behaviour. The size of the fraction above T_M increases to about 35 percent for the 8 mole percent aluminium sample. Spectra of this variety were fitted with two magnetically split subspectra constrained to have the same δ, linewidths and intensity ratios. For 10 mole percent aluminium and beyond there is no Morin transition down to 4.2 K for any detectable fraction of the hematite. This is in agreement with Kren et al. (1974), who noted that the Morin transition was not exhibited down to 6 K by hematite containing 10.2 mole percent aluminium. The quadrupole splitting of the outer (below T_M) subspectra of the series 1 hematites decreases from $+0.36$ mm/s (0% Al) to $+0.22$ mm/s (8 mol % Al). This is consistent with earlier observations (Srivastava and Sharma 1972) and is due to an increase in the angle the spin makes with the [111] direction (Kren et al. 1974). The value of Δ for the inner subspectra decreases from -0.18 mm/s (for all of the samples containing up to 8 mol % aluminium) to -0.16 mm/s for the most aluminous sample. Unfortunately, overlap of the subspectra tends to decrease the accuracy of the determination of Δ. Nevertheless, the hematite for which $T_M < 4.2$ K definitely does not exhibit the increase in Δ with aluminium content seen at 300 K but, if anything, a slight decrease.

The variation of hyperfine splitting with aluminium content for the series 1 hematites at 4.2 K is shown in Fig. 6. To within the error of determination there is no significant decrease in the hyperfine field as aluminium content increases.

example Fig. 3). The asymmetry is most probably due to *superparamagnetic* (SPM) relaxation effects which are discussed further in a later section. Presumably this relaxation, which is a result of reduced particle size, is not exhibited by the series 1 hematites because they have developed a greater degree of crystallinity. The isomer shifts of these spectra are the same as those of the series 1 hematites, but the quadrupole splittings are, to within the error of determination, constant with respect to aluminium concentration. The value of Δ (-0.22 mm/s) is about equal to the maximum value achieved for the most aluminous series 1 hematites. The variation of the hyperfine splitting of the outer magnetically split subspectrum is shown as a function of aluminium content in Fig. 4, and the line of best fit is described by:

$$H_{int} = 515.9 - 0.86 \,(\% \text{ Al}) \text{ kOe}.$$

The rate of decrease is quite similar to that for the series 1 hematites, but surprisingly the hyperfine field is observed to continue to decrease up until the maximum aluminium substitution of 19 mole percent.

Series 3 Hematites. The spectra of most of these specimens contained a small doublet superimposed on the magnetically split hematite spectrum. In view of the considerable difficulty experiences by other workers in removing aluminous phases from hematites produced in a similar manner (Schwertmann et al. 1979), it is likely that this doublet is due to iron present in such phases, which have resisted the 5 M KOH treatment. Because of the uncertainty associated with the aluminium content of these specimens the
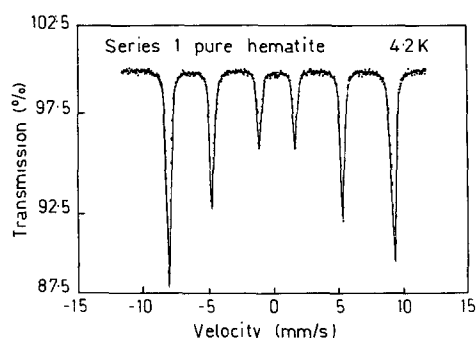
Series 2 Hematites. As for series 1, the isomer shift of the series 2 hematites is constant at $+0.49\pm0.02$ mm/s. Once
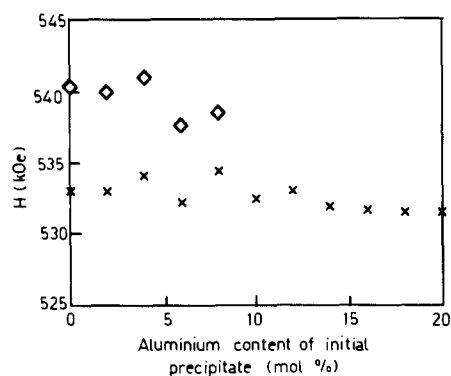
Fig. 6. Magnetic hyperfine field at 4.2 K for the series 1 hematites as a function of aluminium content
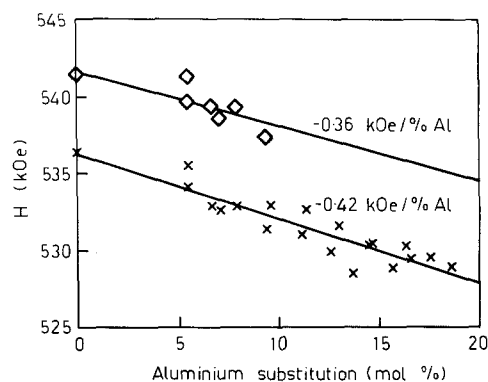

Fig. 7. Magnetic hyperfine field at 4.2 K for the series 2 hematites as a function of aluminium content

again all of the hematites containing less than ~ 9.5 mole percent Al exhibit two subspectra, with the quadrupole splitting of the outer one decreasing from $+0.39$ mm/s (0 mol % Al) to $+0.34$ mm/s (9 mol % Al). These values are consistently greater in magnitude than those for the corresponding members of series 1, i.e. there is a smaller decrease with increasing aluminium content. The quadrupole splitting of the inner subspectra, and of those for which the entire specimen remains above T_M at 4.2 K remains constant at -0.20 ± 0.01 mm/s. The behaviour of the hyperfine splitting with aluminium content is also significantly different to that of the series 1 hematites, as can be seen from Fig. 7. There is a substantial decrease in magnetic field as the aluminium content of the hematites increases. Despite the scatter in the data, which is largely due to the difficulty of resolving the two subspectra, the rate of decrease of the splittings of both appears to be approximately equal at about -0.4 kOe/percent Al. The smaller of the zero aluminium hyperfine field values for this series of hematites is quite different to that of series 1: 536 kOe compared to 533 kOe.

Discussion

There are three particularly interesting features of the results presented here, viz – the apparent difference in the solid solubility limits of aluminium in hematite for the first two series, and their differences in the variation of ΔH_{int} at both 300 K and 4.2 K. Each of these points are now considered.

Solid Solubility Limit of Al in Hematite –
Comparison with the Results of Jonas et al. (1980)

It the study referred to earlier, Jónás et al. (1980) obtained

$$H_{int} = 509 - 1.45 \ (\% \ Al) \ kOe \ at \ 300 \ K$$

for hematites prepared by calcining synthetic aluminous goethites at 550° C. The room temperature hyperfine splittings of both of the pure hematites in the present study (517 ± 1 kOe and 516 ± 1 kOe for series 1 and 2 respectively) are much closer to the accepted value of 516.6 kOe (Stevens et al. 1980) than is that of Jónás et al. At first it may appear that the explanation for both the lower value of the pure hematite splitting and considerably greater decrease in magnetic field with aluminium content is that their specimens were of a particularly fine particle size. Reduced particle size may lead to the observation of a decreased hyperfine splitting. This effect has been discussed previously (in I), and will be further considered later. Such effects may account for the data of Jónás et al. but it is worth noting that some of the aluminous goethites calcined in the present study were particularly finely divided (see I) and yet have not shown such a high level of reduction in magnetic splitting. The goethite having the lowest X-ray determined particle size (mean crystalline dimension in [111] direction = 210 Å) that was used to prepare the aluminous hematite here had an aluminium content of 15 mole percent. It can be seen from Fig. 4 that this specimen has a room temperature hyperfine splitting only marginally less than that predicted by the line of best fit. In the light of this result the measurements of Jónás et al. do not appear to be able to be explained as being solely due to particle size effects, although no alternative explanation is apparent.

The decrease in hyperfine splitting for series 2 hematites containing greater than ~ 16 mole percent aluminium seems to indicate that the aluminium originally present in the goethite structure has remained there throughout the dehydration. Jónás et al. (1980) have presented X-ray analyses of the aluminious hematites they examined, and claimed that these showed a solid solubility limit of 13–14 mole percent, despite the decreased hyperfine field for specimens containing greater quantities of aluminium. In an earlier paper Solymár and Jónás (1971) presented the same data, and suggested that as no separate aluminium phase was detected with X-rays, the excess aluminium must be present in an X-ray amorphous state. However, inspection of their hematite lattice spacing data (see Fig. 8) shows that the single data point (for each of the four crystal planes measured) at a substitution of ~ 15 mole percent does not deviate significantly from the linear decrease in the other points. Their interpretation of this point as evidence for a solid solubility limit of 13–14 mole percent must be regarded as very doubtful.

If aluminium is in fact present in the hematite lattice of calcined goethites in concentrations greater than 16–17 percent, then it seems likely that further calcination of such samples at sufficiently high temperatures may result in the migration of excess aluminium from the lattice to form a second phase. In order to investigate this possibility, samples of a series 2 hematite containing 16 mole percent aluminium were fired at 900° C and 1,100° C for 2 h. The result in both cases was a narrowing of the spectral lines and an increase in hyperfine field from 503 ± 1 kOe to 508 ± 1 kOe. This would seem to indicate that at high
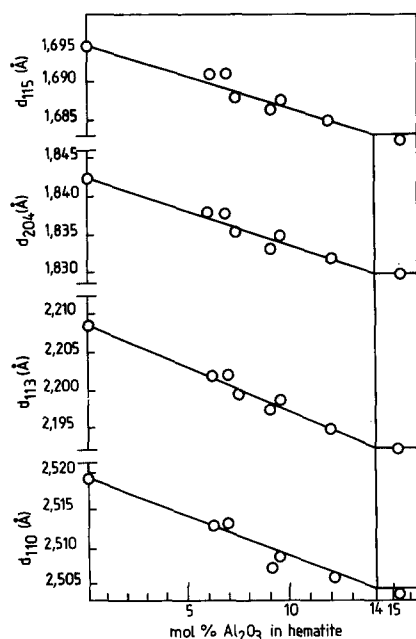
Fig. 8. Lattice spacings of aluminous hematite, taken from Jónás et al. (1980)

enough dehydration temperatures there is sufficient thermal energy available to activate the migration of aluminium atoms out of the hematite structure, presumably to form a second phase on the surface of individual particles. Nevertheless, if dehydration of goethite is affected at $\leq 600°$ C then hematites containing >15 mole percent aluminium may be produced. No attempts to determine the solid solubility limit for co-precipitated hydroxides fired at such low temperatures have been made here, nor have any been reported previously.

Variation of the Quadrupole Splitting with Aluminium Content

The variation of Δ with aluminium content below T_M has already been mentioned, and explained as being due to changes in the angle between the [111] direction and the Fe^{3+} magnetic moment as non-iron atoms enter the lattice. Svab and Kren (1979) have also observed a similar change in spin orientation, as yet unexplained, for a number of other different cation impurities in hematite. The variation with aluminium content of Δ at room temperature is somewhat more difficult to explain. Kren et al. (1974) have measured the angle (θ) between the nuclear magnetic moment and the [111] direction for aluminous hematites prepared in a similar manner to those in series 1 here, and found it to remain constant at 90° up to substitution of 10.2 mole percent Al. The only possible mechanism for a change in Δ, other than θ varying, is for V_{ZZ} to change. Muir and Wiedersich (1966) noted that the room temperature quadrupole splittings of different samples of commercially available high purity $\alpha - Fe_2O_3$ varied between -0.24 and -0.19 mm/s. In order to explain these results Artman et al. (1968) presented calculations which show that very slight changes in the positions of iron and oxygen in the hematite unit cell may lead to considerable changes in the EFG at the iron site. Von Steinwehr (1967) has shown that the lattice contraction of hematite upon incorporation of alu-

minium deviates from Vegard's law. For the range of compositions considered here all of the crystal dimensions contract less rapidly than predicted, but the effect is much less pronounced in the **c** direction, i.e. as aluminium is introduced into the lattice c/a decreases. In the light of the calculations of Artman et al. (1968) it seems very likely that this inhomogeneity in the lattice contraction causes the observed changes in $\Delta_{300\ K}$ for the series 1 hematites. The lack of such an effect at 4.2 K is not immediately understandable, but it seems quite likely that the small relative changes in atomic position required to significantly influence Δ could easily result from various lattice directions having slightly different rates of thermal contraction for the aluminous samples.

Rather more confusing is the total lack of variation in Δ with aluminium content for the series 2 hematites. Muir and Wiedersich (1966) noted that the value of Δ exhibited by a given sample of $\alpha - Fe_2O_3$ was strongly dependent on the thermal history of the specimen. Heat treatment at $\sim 1,050°$ C lowered the quadrupole splittings of the samples by about 15 percent, although neither the isomer shift nor hyperfine splitting were significantly affected. Von Steinwehr (1967) has briefly discussed the effects of dehydration temperature on the lattice parameters of pure hematite. The data presented shows a decrease in the c dimension as the firing temperature increases up to about 900° C, and thereafter an increase. The other dimensions are relatively unaffected. Thus it seems that hematites which have not been subjected to temperatures in excess of $\sim 800-900°$ C may possess some sort of defect structure, largely associated with the **c** direction. Since the increase in $\Delta_{300\ K}$ in the series 1 hematites has been attributed to a small decrease in the c/a ratio, it seems quite likely that the slight increase in c/a at high firing temperatures reported by Von Steinwehr accounts for the decrease in Δ reported by Muir and Wiedersich (1966). Because the series 2 hematites were subjected to a temperature of only 590° C they have remained 'disordered' in the **c** direction, and have retained a high quadrupole splitting even in the unsubstituted lattice.

A further indication of the nature of the proposed **c**-axis ordering in hematite may be gained from the work of Francombe and Rooksby (1959). Their X-ray analysis of goethite prior to and after dehydration led them to suggest that a structural sub-unit $(Fe(OH)_2)$ common to both goethite and hematite is inherited (in dehydroxylated form) by hematite formed from goethite. Upon heating goethite to $\sim 270°$ C the X-ray lines of the sub-unit remain sharp, but those of the hematite superstructure which appear at this temperature are only diffuse. They remain this way up until about 600° C, where the superlattice ordering is completed.

This superlattice ordering is in the **c** direction only, the **a** direction of the hematite having a structure coherent with that of the goethite. Schwertmann et al. (1977) have investigated differential disorder in soil hematites by X-ray analysis, and have proposed that in forming hematite directly from aluminous ferrihydrite (essentially co-precipitated iron-aluminium hydroxides) the aluminium prevents **c**-axis superlattice ordering. They have detected this disorder in soil hematites, and note an earlier study (Perinet and Lafont 1972) in which a similar phenomenon was observed in bauxitic hematite. Thus even in hematites where goethite is not the precursor it appears that **c** axis disorder may be present if the lattice has not been subjected to high ($\geq 700°$ C) tem-

peratures. Further, Mössbauer spectroscopy is able to determine whether or not this disorder is present from the room temperature value of the quadrupole splitting.

Variation of the Magnetic Hyperfine Splitting with Aluminium Content

In order to attempt to explain the different behaviour of the hyperfine splittings of the first two series of hematites it is necessary to consider the effects of magnetic dilution on the processes giving rise to the magnetic field at the nucleus in a little more detail.

The dipolar field contribution has been calculated by Tobler et al. (1981) to be ~ 6.5 kOe for $T < T_M$. Diamagnetic dilution by χ percent will decrease this by $\chi/100 \times 6.50$ kOe (Kittel and Abrahams 1953) so that for 15 mole percent substituted hematite the maximum possible decrease in H_{int} due to H_{dip} is ~ 1 kOe. This effect, plus the decrease ($\ll 1$ kOe at 4.2 K) in splitting because of the reduction in T_N with increasing aluminium content account for the very slight decrease in H_{int} seen for the aluminous series 1 hematites at 4.2 K (see Fig. 6).

Clearly neither of these processes give rise to a magnetic field reduction of the magnitude of that exhibited by the series 2 hematites. In fact such a reduction may be explained as being due to changes in the Fermi contact contribution to the magnetic hyperfine field. Early investigations of the effects of neighbouring magnetic ions on the hyperfine field of a magnetic ion revealed the presence of a supertransferred field component (Owen and Taylor 1966, Huang et al. 1966, 1967). These investigations showed that spin transfer from one metal ion to another via the ligand (referred to as superexchange) may produce contributions to the contact term of the order of 10 kOe/magnetic neighbour. Van der Woude and Sawatzky (1971) and Coey and Sawatzky (1971a) have shown that the reduction in the superexchange interaction which accompanies diamagnetic replacement in ferrites and oxides accounts for almost the entire decrease in the hyperfine splitting which results from substitution in such systems.

Whether or not a particular ligand bond is suitable for superexchange spin transfer depends on the bond angle and length (e.g. Goodenough 1963). Superexchange in hematite is via the O^{2-} p electrons. Transfer of these electrons into the unoccupied iron 4 s and 3 d orbitals results in overlap distortions of the iron s orbitals. The unbalanced spin density caused by this overlap, plus that from the now partially filled 4 s orbital results in a contact supertransferred hyperfine field, which is zero for neighbouring diamagnetic cations.

For the corundum structure of $\alpha-Fe_2O_3$ there are 4 superexchange pathways (Goodenough 1963; Bertaut 1965), and the various exchange constants have been estimated from both Mössbauer (Coey and Sawatzky 1971a) and neutron diffraction (Samuelsen and Shirane 1970) measurements. According to Coey and Sawatzky (1971a), at $T = 20$ K (effectively $T = 0K$ because of the high T_N of hematite) the supertransferred hyperfine field in Rh substituted hematite is measured to be 7.8 kOe/nearest neighbour, assuming a 6 nearest-neighbour model. From Coey and Sawatzky (1971b) the number of nearest neighbours Z' for χ percent diamagnetic substitution is:

$$Z' = \frac{\chi}{100} \cdot Z$$

where Z is the number of nearest neighbours in the pure crystal. Thus a decrease of 7.8 kOe/nearest neighbour corresponds to:

$7.8 \times \frac{6}{100}$ kOe/mole percent substitution

$= 0.47$ kOe/mole percent.

This value is in reasonable agreement with that measured for the series 2 aluminous hematites at 4.2 K.

Although the low temperature aluminium dependence of the magnetic splitting of the series 2 hematites can be fairly readily understood on the basis of a reduction in supertransferred hyperfine filed, clearly that of the first series cannot be explained in this way.

If the differing magnetic splitting dependences of the two series is due to differences in the exchange processes in each, then some indication of such a difference would be expected to be seen in the magnitudes of the splittings of the two pure hematites. The $T_M < 4.2$ K zero aluminium splitting for the second series (536 ± 1 kOe) is about 3 kOe greater than that for the first series (533 ± 1 kOe). In addition the magnetic splittings of natural Australian iron ore hematites (presumed to be of the 'low temperature' disordered variety) which were completely below T_M at 4.2 K have been observed to be as high as 544 ± 1 kOe (Fysh and Ostwald 1982). The increased hyperfine field of the pure series 2 hematite is rather surprising in that hematite produced from goethite is expected to exhibit a vacancy structure. Wolska (1981) has shown that hematites produced hydrothermally (and this would be expected to apply to those obtained from goethite) often have a water content of ~ 3 percent which persists up to about 1,000° C, and that inclusion of aluminium in the lattice increases this water content. The replacement of O^{2-} ions by OH^- ions results in Fe^{3+} vacancies in order to maintain charge neutrality. Such vacancies should lead to a reduction in magnetic splitting, rather than an increase as observed here. Thus the increase in the magnetic splitting of the pure series 2 hematite over that for the series 1 hematite is not understood, and certainly provides no clue as to the behaviour of the magnetic splitting of the first series at 4.2 K. It seems quite likely that the lack of a reduction in magnetic splitting for the series 1 aluminous hematites will only be understood when more direct measurements of the exchange constants in ordered and disordered hematite are made.

Up until this point only the low temperature magnetic behaviour of hematite has been considered. At $T \gg 0K$ the behaviour is expected to become somewhat more complicated because of the different temperature dependence of the hyperfine field in different environments. Coey and Sawatzky (1971b) have considered the temperature dependence of substituted systems in the molecular field approximation. Because sites with a smaller number of iron nearest neighbours order at a lower temperature (hence the reduction in T_N for aluminous hematites) they are expected to exhibit a smaller magnetic splitting at a given $T < T_N$. Thus the increase in the reduction of splitting/mole percent Al compared to that at 4.2 K for the series 2 hematites is a result of the reduction in T_N. The relationship remains linear because of the high value of T_N, even for the most aluminous hematite, and the relatively small concentration range. A non-linear relationship between magnetic hyperfine field and aluminium replacement due to the reduction

of T_N has been observed for aluminous goethites at 77 K (see I); T_N for goethite is ~ 550 K less than that of hematite.

Because it is about equal in magnitude to the change in magnetic splitting with aluminium content of the series 2 hematites, it seems unlikely that the observed hyperfine splitting dependence for the series 1 hematites at room temperature is entirely a consequence of the reduction in T_N. In fact the variation of hyperfine field with aluminium concentration observed for the series 1 hematites in the present study is fairly consistent with that reported by Srivastava and Sharma (1972), viz a decreased hyperfine splitting at some temperature intermediate between T_N and OK, but not as T approaches zero. If in fact the range of temperature for which decreased hyperfine fields are observed is that given by Srivastava and Sharma 1972 ($0.35 \leq T/T_N \leq 0.9$) then reduced splittings would only be measured at 300 K if $T_N \approx 850°$ C. This is only the case for substitutions ≥ 15 mole percent (Srivastava and Sharma 1972), indicating that the value of 0.35 is somewhat too high. Srivastava and Sharma also noted that a reduction in magnetic splitting in an intermediate temperature range was not able to be explained by molecular field theory. The fairly small change in the number of magnetic nearest neighbours in aluminous hematite does not produce a sufficient reduction in the molecular field to account for the decrease. Instead they suggested that the observed behaviour was similar to that calculated by Lines (1970) in a random phase Green's function approximation to the solution of the full spin Hamiltonian. The change in spin anisotropy energy required to reproduce the lowering of the magnetization curve for the aluminous hematite in an intermediate temperature range is in fact consistent with the observed trend of a decrease in T_M/T_N. Although the calculation of Lines (1970) does give qualitative agreement with the observed behaviour of the hyperfine field, the present results indicate considerable structural dependence of the hyperfine splitting in aluminous hematite, the theoretical basis for which remains unexplained.

Particle Size Dependence of the Hyperfine Parameters

The Mössbauer spectrum of finely divided hematite may be affected by superparamagnetic behaviour (e.g. Bean and Livingston 1959) of the individual microcrystals. This sort of behaviour is also exhibited by goethite and was discussed in I, although the term *superantiferromagnetism* was incorrectly used to describe it there. The SPM nature of the series 2 hematites at room temperature has already been mentioned, and such behaviour is commonly encountered in finely divided soil and clay hematites. Application of low temperatures is often necessary in such cases, as the inevitable presence of a range of particle sizes results in a spread of SPM relaxation rates, and the observation of asymmetrically broadened spectra which are often difficult to interpret.

Even when a SPM specimen exhibits a six line spectrum, some reduction in magnetic splitting may be observed due to decreased particle size. This phenomenon has been attributed to small fluctuations of the magnetization of SPM particles about their easy direction (Mørup et al. 1976), and to the reduced hyperfine field experienced by the nuclei at the surface of small particles (Govaert et al. 1976). We have shown (in I) that the effects of particle size on goethite hyperfine splitting are negligible at 77 K and below, at least
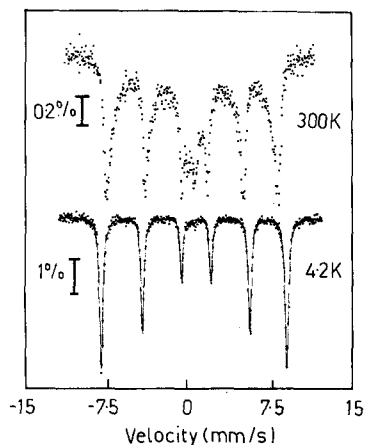

Fig. 9. Room temperature and 4.2 K Mössbauer spectra of fine particle hematite

for particles ≥ 200 Å in diameter. In order to gain some indication of the importance of the effect in hematite, very fine particles of hematite were synthesized in the manner already described.

Chemical analysis revealed that after drying at 110° C the sample retained a water content of 21 weight percent. The room temperature and 4.2 K spectra of the specimen are shown in Fig. 9. By comparison of the data with that of van der Kraan (1972) it would appear that the mean particle diameter is in the range 80–110 Å, as would be expected from the preparative method employed. The room temperature spectrum exhibits considerably relaxed behaviour. Satisfactory fits to this spectrum could not be obtained with either the relaxational model of Blume and Tjon (1968), or a combination of up to 4 discrete magnetically split subspectra, because of the wide range of particle sizes (and hence relaxation times) present. Numerous other workers have fitted such spectra, obtained for a variety of iron oxides, by including the baseline curvature as a fitting parameter. This is clearly not a realistic representation of the data, and experimental set-ups which result in baseline curvature for all spectra, thus often obscuring relaxed behaviour, are totally unsuitable for the quantitative study of fine iron oxides.

There is a reduction of a factor of 5 between the outer line intensity of the 300 K and 4.2 K spectra. The low intensity of the former results in a greater scatter of the data, despite the fact that the spectrum contains $\sim 4.2 \times 10^6$ counts/channel compared with only $\sim 1.7 \times 10^6$ counts/channel for the 4.2 K spectrum, and is largely due to the broadening of the spectral lines. The recoil free fraction of the specimen at 4.2 K has been measured for comparison with that of less fine hematite (see following section). The splitting of the room temperature spectrum is estimated to be 30 ± 4 kOe less than that of well crystallized pure hematite at this temperature. At 4.2 K the difference is reduced to 4 ± 1 kOe, and the entire specimen remains above the Morin transition. Clearly considerable care must be taken in interpreting reductions in the hyperfine field of hematite as being purely due to isomorphous replacement. Where possible it is preferable to take spectra at both room temperature and some reduced temperature so that some indication of the effects of particle size on the splitting can be gained. At least in this way a more realistic estimate of the uncertainty associated with a measurement of the degree of isomorphous replacement can be made.

Recoil Free Fraction Measurements

Two methods have been employed to make recoil free fraction measurements in the present study. The first, which has already been described (see I) relies on the measurement of the change in Mössbauer linewidth with specimen thickness. The rate of change for a given material is proportional to f, the recoil free fraction of the ^{57}Fe present. The second method requires only one measurement (as opposed to at least five for the first), but does not give such a high degree of accuracy. In this case known masses of the hematite and an aluminous goethite having a known recoil free fraction are combined and the spectrum of the composite sample taken. From the relative areas derived from a fit of the data a value for the recoil free fraction of the hematite can be calculated. Thickness overlap effects have been ignored in this procedure, and this is reasonable because:

(1) The relative areas were calculated on the basis of the outer spectral lines only, for which there is not considerable overlap.

(2) The mass of each of the oxides has been chosen such that the areas of each subspectrum are roughly equal.

(3) There is considerable separation of the outer lines from the other more central lines of the spectrum.

(4) The overall specimen is thin, so that the outer lines have a thickness parameter $t_A < 1$.

Nevertheless, the error of determination is estimated to be greater than twice that associated with the first method.

The recoil free fraction of pure hydrothermally produced hematite (series 3) has been measured by the first method at both room temperature and 4.2 K. The room temperature hyperfine splitting (510 ± 1 kOe) of this hematite indicates that it is finely divided, although the spectra were very well fitted by a single magnetically split subspectrum. At 4.2 K the magnetic splitting had a value of 543 ± 1 kOe, indicating no significant particle size effects. The variation of linewidth for the inner, middle and outer pairs of lines in the 6 line spectrum are shown at both temperatures in Fig. 10a, b. The gradients of the three lines give independent estimates of the recoil free fraction, but the lines are not coincident because of minor sample inhomogeneities which affect the lines with larger splitting to a slightly greater extent. The recoil free fractions derived are 0.64 ± 0.02 and 0.70 ± 0.02 at 300 K and 4.2 K respectively. The increase at lower temperatures reflects a stiffening of the lattice i.e. decreased availability of low energy phonons which are available to be thermally excited. It is interesting to compare these values with those previously measured (in I) for goethite; 0.65 ± 0.05 at 300 K and 0.69 ± 0.02 at 4.2 K. These values are equal to within experimental error, presumably because of the similarity of the local environment in the two structures.

The recoil free fraction of the fine hematite sample previously referred to was measured at 4.2 K by the second method, to give a value of 0.67 ± 0.05. While it may be tempting to identify the slight decrease compared with that of pure hematite with the 'softening' of the lattice because of its hydration, the similarity between the pure hematite and goethite values at this temperature makes this an unlikely explanation. If the decrease is in fact significant at all then it is most probably related to the hematite particle size (see I for further discussion of the effects of particle size on recoil free fraction).
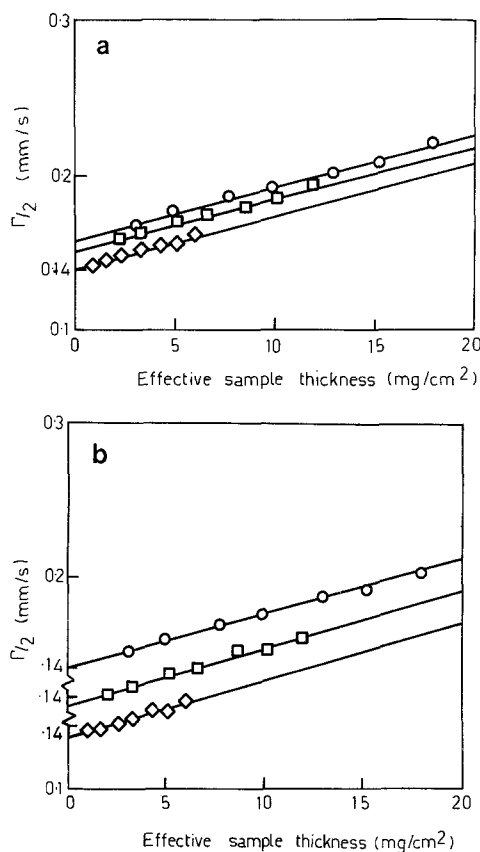

Fig. 10a, b. Variation of linewidth (HWHM) for the inner, middle and outer pairs of lines in the Mössbauer spectrum of pure hematite at (a) 300 K and (b) 4.2 K

As has already been mentioned, the chemical analysis required for f determinations was only available for the hydrothermally produced (series 3) hematites, and this has greatly restricted the range of aluminium compositions available. Further, the uncertainty associated with estimating the actual lattice aluminium content of these specimens introduces substantial error into the determination. For this reason the recoil free fraction of only two aluminous hematites have been measured, and both of these have aluminium substitutions in the range 14 ± 2 mole percent. Samples having lower aluminium contents but remaining either entirely above or below T_M at 4.2 K were not available within this series of hematites.

Recoil free fraction measurements were made by the two methods previously outlined, one being applied to each specimen. The variation of linewidth with specimen thickness is shown in Fig. 11, and the greater broadening of the outer lines relative to that in pure hematite can be seen by comparison with Fig. 10. This is due to the presence of the aluminium, which leads to a greater range of local environments, and has also been observed (in I) to occur in aluminous goethites. The recoil free fractions derived for the two specimens are 0.82 ± 0.02 (using first method) and 0.85 ± 0.05 (using second method). These values are equal to within experimental error, as are the respective hyperfine splittings of the two specimens.

An increase in recoil free fraction with aluminium substitution is also exhibited by aluminous goethite (see I) and the present results for pure and 14 mole percent substituted hematite are shown superimposed on the goethite variation
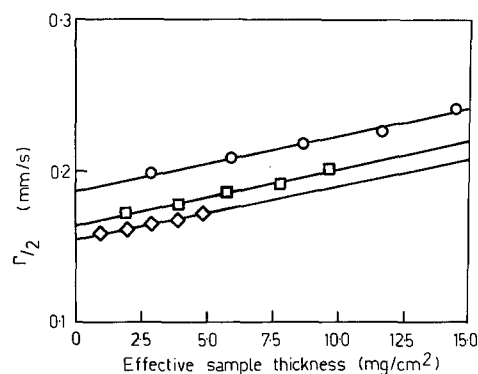
Fig. 11. Variation of linewidth (HWHM) at 4.2 K with specimen thickness for hematite with 14 mole percent Al substitution
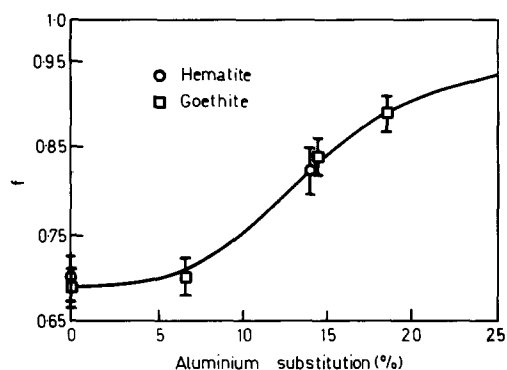

Fig. 12. Comparison of measured recoil free fractions for aluminous goethite and aluminous hematite at 4.2 K. The line is only intended to represent the data, and has no particular functional form, although it is clear that the increase in f must level out beyond ~ 20–25 mole percent substitution

in Fig. 12. To within the error of determination the points lie on the same representative curve, although clearly considerably more measurements are required before the equivalence of the variations is established. The variation of f with aluminium replacement has already been discussed (in I) and the two major reasons for the increase identified as:

(1) decreased lattice reduced mass, leading to an increase in the frequency of the phonon modes, and

(2) stiffening of the lattice because of the reduction in bond length that accompanies replacement.

The present results do not assist in further differentiating between these possible causes for an increase in f as the decrease in reduced mass is the same for both hematite and goethite, as are the relative rates of bond length decrease/mole percent Al (assuming Vegard's law is obeyed).

Conclusion

The present study has given new evidence for a c-axis structural ordering in hematite at temperatures in excess of 600° C, and shown that the extent of this ordering is affected by lattice aluminium content. In addition, the low temperature magnetic properties of the ordered and disordered states have been investigated. It appears that there are considerable differences in the exchange mechanisms operating in the two states, at least as $T \to 0K$. Further measurements of the exchange constants of hematite in the ordered and disordered states are called for, and may

provide some further insight into the influence of aluminium replacement on the lattice structure. The data given in the present study is suitable for determination of the degree of aluminium replacement in hematite specimens, although the parallel influence of particle size on hyperfine splitting indicates the need for caution in interpreting such results. A further use of the effects of high temperature ageing on the low temperature magnetic splitting may lie in the application of the technique to the investigation of the thermal history of natural hematite samples. Thus well crystallized samples which exhibit decreased hyperfine splitting at room temperature but not at 4.2 K may be inferred to have been subjected to elevated temperatures for some period of time. Measurements of the room temperature quadrupole splitting of low aluminium substituted or pure specimens may yield similar results, with values significantly below -0.21 mm/s indicating c-axis ordering.

Another aspect of this study which indicates the need for further investigation is the results concerning the low temperature variation of recoil free fraction with aluminium content. With an increase of about 15 percent in the recoil free fraction taking place upon dilution of the lattice by 14 mole percent, it is quite clear that the use of Mössbauer spectroscopy for quantitative analysis requires particular attention to be paid to the measurement of recoil free fractions. This sort of dependence is probably present for the majority of solid solution systems which have been investigated with the Mössbauer effect, and yet seems to have received little or no attention in previous studies.

References

Artman JO, Murphy JC, Foner S (1965) Magnetic anisotropy in antiferromagnetic corundum-type sesquioxides. Phys Rev 138:912–917

Artman JO, Muir AH, Wiedersich H (1968) Determination of the nuclear quadrupole moment of Fe^{57} from $\alpha - Fe_2O_3$ data. Phys Rev 173:337–343

Bean CP, Livingston JD (1959) Superparamagnetism. J Appl Phys Suppl 30:120–129

Bertaut EF (1965) Theory of solid solutions (1-x) $Cr_2O_3 \cdot xFe_2O_3$ with helical spin configuration. Proc Int Conf on Magnetism, Nottingham, 1964. Institute of Physics and the Physical Society, London, pp 516–523

Biais R, Bonnemayre A, de Gramont X, Michel M, Gibert H, Janot C (1972) Etude des substitutions Al − Fe dans des oxydes et hydroxydes de synthése. Préparation de diaspore ferrifére. Bull Soc Fr Mineral Crystallogr 95:308–321

Bigham JM, Golden DC, Bowen LH, Buol SW, Weed SB (1978) Iron oxide mineralogy of well-drained Ultisols and Oxisols: I. Characterization of iron oxides in soil clays by Mössbauer spectroscopy, X-ray diffractometry, and selected chemical techniques. Soil Sci Soc Am J 42:816–825

Blume M, Tjon JA (1968) Mössbauer spectra in a fluctuating environment. Phys Rev 165:446–456

Bowen LH (1979) Mössbauer spectroscopy of ferric oxides and hydroxides. Mössbauer Eff Ref Data J 2:76–94

Cailliére C, Gatineau L, Hénin S (1960) Préparation a basse température d'hématie alumineuse. CR Acad Sci 250:3677–3679

Coey JMD, Sawatzky GA (1971a) A study of hyperfine interac-

tions in the system $(Fe_{1-x}Rh_x)_2O_3$ using the Mössbauer effect. J Phys C 4:2386–2407

Coey JMD, Sawatzky GA (1971b) The Mössbauer spectra of substituted systems – local molecular field theory. Phys Status Solidi B 44:673–680

Francombe MH, Rooksby HP (1959) Structure transformations effected by the dehydration of diaspore, goethite and delta ferric oxide. Clay Miner Bull 4:1–14

Fysh SA, Clark PE (1982) Aluminous goethite: A Mössbauer study. Phys Chem Minerals 8:180–187

Fysh SA, Ostwald J (1982) Mössbauer investigations of Australian iron ore mineralogy. Mineral Mag (submitted)

Goodenough JB (1963) Magnetism and the chemical bond. Interscience, New York

Govaert A, Dauwe C, De Sitter J, De Grave E (1976) On the surface contribution to the line profile of small particles of goethite. J Phys (Paris) Colloq 37:C6-291–292

Huang NL, Orbach R, Šimánek E (1966) Contribution to the hyperfine field from cation-cation interactions. Phys Rev Lett 17:134–136

Huang NL, Orbach R, Šimánek E, Owen J, Taylor DR (1967) Cation-cation interaction contributions to the hyperfine interaction. The "supertransferred hyperfine interaction". Phys Rev 156:383–390

Janot C, Gibert H (1970) Les constituants du fer dans certaines bauxites naturelles étudiées par effet Mössbauer. Bull Soc Fr Mineral Crystallogr 93:213–223

Janot C, Gibert H, de Grammont X, Biais R (1971) Étude des substitutions Al−Fe dans les roches latéritiques. Bull Soc Fr Mineral Crystallogr 94:367–380

Jónás K, Solymár K, Zöldi J (1980) Some applications of Mössbauer spectroscopy for the quantitative analysis of minerals and mineral mixtures. J Mol Struct 60:449–452

Kittel C, Abrahams E (1953) Dipolar broadening of magnetic resonance lines in magnetically diluted crystals. Phys Rev 90:238–239

van der Kraan AM (1972) Thesis, Delft

van der Kraan AM (1973) Mössbauer effect studies of surface ions of ultrafine $\alpha - Fe_2O_3$ particles. Phys Status Solidi A 18:215–226

Krén E, Molnár B, Sváb E, Zsoldos E (1974) Neutron diffraction study of the $(1-x)\ \alpha - Fe_2O_3 - \alpha - Al_2O_3$ system. Solid State Commun 15:1707–1710

Kündig W, Bömmel H, Constabaris G, Lindquist RH (1966) Some properties of supported small Fe_2O_3 particles determined with the Mössbauer effect. Phys Rev 142:327–333

Lines ME (1970) The quadratic-layer antiferromagnet. J Phys Chem Solids 31:101–116

Morrish AH, Johnston GB, Curry NA (1963) Magnetic transition in pure and Ga doped $\alpha - Fe_2O_3$. Phys Lett 7:177–178

Mørup S, Topsøe H, Lipka J (1976) Modified theory for Mössbauer spectra of superparamagnetic particles: Application to Fe_3O_4. J Phys (Paris) Colloq 37:C6-287–290

Muan A, Gee CL (1956) Phase equilibrium studies in the system iron-oxide – $\alpha - Al_2O_3$ in air and at 1 Atm. O_2 pressure. J Am Ceram Soc 39:207–214

Muir AH, Wiedersich H (1966) Mössbauer study of e^2qQ in $\alpha - Fe_2O_3$ and the quadrupole moment of Fe^{57m}. Bull Am Phys Soc 11:770–771

Nininger RC, Schroeer D (1978) Mössbauer studies of the Morin transition in bulk and microcrystalline $\alpha - Fe_2O_3$. J Phys Chem Solids 39:137–144

Owen J, Taylor DR (1966) Zero-point spin deviation in antiferromagnets. Phys Rev Lett 16:1164–1166

Perinet G, Lafont R (1972) Sur la présence d'hématite alumineuse désordonée dans des bauxites du Var. Comptes Rendus 274:272–274

Povitskii VA, Salugin AN, Baldokhin YV, Makarov EF, Elistratov NV (1978) Spin re-orientation in hematite $(\alpha - Fe_2O_3)$ with Al impurity. Phys Status Solidi B 87:K101–104

Ruskov T, Tomov T, Georgiev S (1976) Mössbauer investigation of the Morin transition in hematite. Phys Status Solidi A 37:295–302

Salugin AN, Povitskii VA, Filin MV, Elistratov NV, Pis'marov AF (1975) Mössbauer spectroscopic investigation of spin reorientation in the system $(1-c)\ Fe_2O_3 - c\ Al_2O_3$. Sov Phys Solid State 17:1179–1180

Samuelsen EJ, Shirane G (1970) Inelastic neutron scattering investigation of spin waves and magnetic interactions in $\alpha - Fe_2O_3$. Phys Status Solidi 42:241–256

Schwertmann V, Fitzpatrick RW, Le Roux J (1977) Al substitution and differential disorder in soil hematites. Clays Clay Min 25:373–374

Schwertmann U, Fitzpatrick RW, Taylor RM, Lewis DG (1979) The influence of aluminium on iron oxides. Part II. Preparation and properties of Al-substituted hematites. Clays Clay Miner 27:105–112

Solymár K, Jónás K (1971) A goethite racsaba beepült Al-tartalom vizsgálata és jelentösége a magyar bauxitokban. Kohasz Lapok 104:226–235

Srivastava JK, Sharma RP (1972) Magnetic dilution effects on Morin phase transition in hematite. Phys Status Solidi B 49:135–146

von Steinwehr HE (1967) Gitterkonstanten und System – (Al, Fe, Cr)$_2O_3$ und ihr Abweichen von der Vegardregel. Z Kristallogr 125:377–403

Stevens JG, Stevens VE (eds) (1980) Mössbauer Eff Ref Data J 3:99

Svab E, Kren E (1979) Neutron diffraction study of substituted hematite. J Magn Magn Mater 14:184–186

Tobler L, Kündig W, Savić I (1981) Investigation of the Morin transition in $\alpha - Fe_2O_3$ by the Mössbauer effect. Hyperfine Int 10:1017–1022

Wolska E (1976) Über die Koexistenz der Aluminium- und Eisen-(III)hydroxide und Oxide. Monatsh Chem 107:349–357

Wolska E (1981) The structure of hydrohematite. Z Kristallogr 154:69–75

van der Woude F (1966) Mössbauer effect in $\alpha - Fe_2O_3$. Phys Status Solidi 17:417–432

van der Woude F, Sawatzky GA (1971) Hyperfine magnetic fields at Fe^{57} nuclei in ferrimagnetic spinels. Phys Rev B 4:3159–3165

Yamamoto N (1968) The shift of the spin flip temperature of $\alpha - Fe_2O_3$ fine particles. J Phys Soc Jpn 24:23–28