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Aluminium dependence of Mössbauer parameters in goethite and hematite

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Дается критический обзор вариаций мессбауэровских параметров (магнитного сверхтонкого поля, изомерного смещения и квадрупольного расщепления) в зависимости от содержания алюминия, замещающего железо в железных гидроокислах и окислах.

Температура перехода Моурина (T_M) и температура Нееля (T_N) показывают зависимость от количества алюминия в гетите и гематите. Неупругое рассеяние и ширина линий увеличиваются с увеличением содержания алюминия в обоих минералах. Увеличение неупругого рассеяния вызывается уплотнением решетки как результат укорочения связей и уменьшения средней массы решетки с увеличением содержания изоморфного алюминия. Вариации ширины линий зависят от распределения напряженности магнитного сверхтонкого поля. Она уменьшается линейно с увеличением содержания алюминия, что является результатом или пониженного обменного сверхпереноса, или уменьшения размеров частиц, и/или локальных неоднородностей в элементарных ячейках. Изменение в изомерном смещении при замещении железа алюминием пренебрежимо маленькое. Выше T_M величина квадрупольного расщепления не зависит от содержания алюминия, а ниже T_M она варьирует незакономерно. Ее вариации вызываются изменениями угла между с-осью и магнитным моментом Fe^{3+} и/или неравномерным уплотнением решетки вследствие замещения Fe^{3+} Al^{3+}.

Обсуждаются экспериментальные результаты нескольких авторов в связи с указанными явлениями.

Ключевые слова: мессбауэровские параметры, гетит, гематит, алюминий.

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Introduction

The Mössbauer parameters of iron hydroxide and oxide phases are greatly influenced by aluminium substitution on iron site(s) of these phases and such a substitutional effect is well documented in goethite (α-FeOOH) and hematite (α-Fe_2O_3) among the iron hydroxides and oxides, respectively. Although a good number of workers are involved in the Mössbauer studies of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), the effect of aluminium substitution on these two phases is yet to be studied in more details than presented in this review.

Crystal structure of goethite and hematite

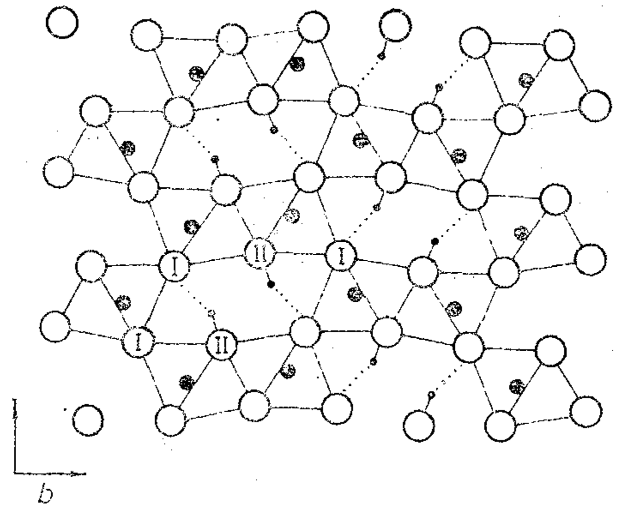
Goethite possesses orthorhombic structure with Fe^{3+} occupying the 4C octahedra of Pbnm space group and are arranged in double rows running parallel to [001] (Fig. 1).

Hematite shows a hexagonal structure in which closed-packed planes of oxygen atoms are stacked along [0001] in which Fe^{3+} occupy the two thirds of the available octahedral sites leading to the production of dioctahedral arrangement. Each oxygen atom shares four iron atoms and each iron atom is surrounded by six oxygen atoms (Fig. 2).

For evaluation of the effects of Al-substitution it seems necessary to study the magnetic behaviour of these minerals.

Magnetic characters of pure goethite and hematite

Goethite orders antiferromagnetically below 393 K(T_N, Neel temperature) and therefore at room temperature a well defined sextet ought to be found.



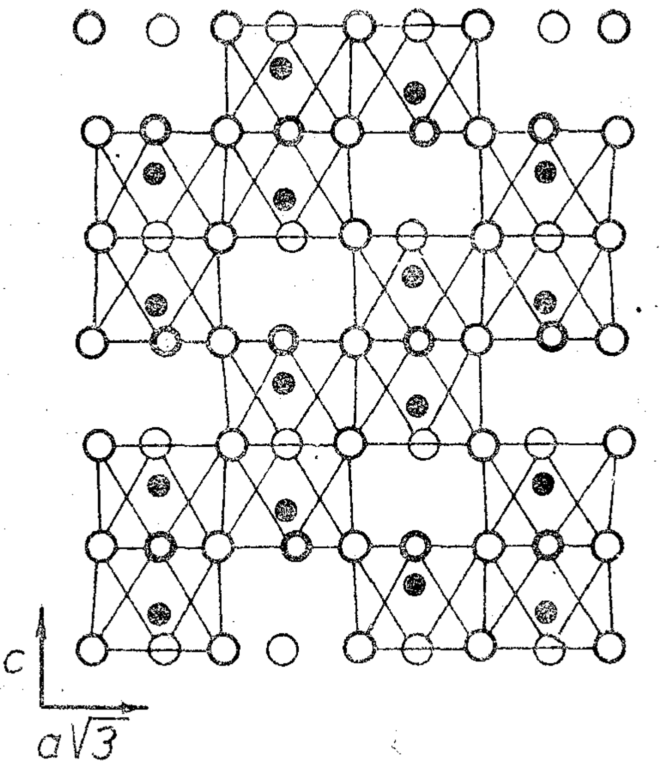


Fig. 1. The goethite structure projected on (001). Oxygen atoms are represented by large open circles, Fe atoms by medium solid circles, and H atoms by small solid circles. Octahedra are outlined by solid lines. Hydrogen bonds are indicated by solid and dotted lines (Eggleton et al., 1988)

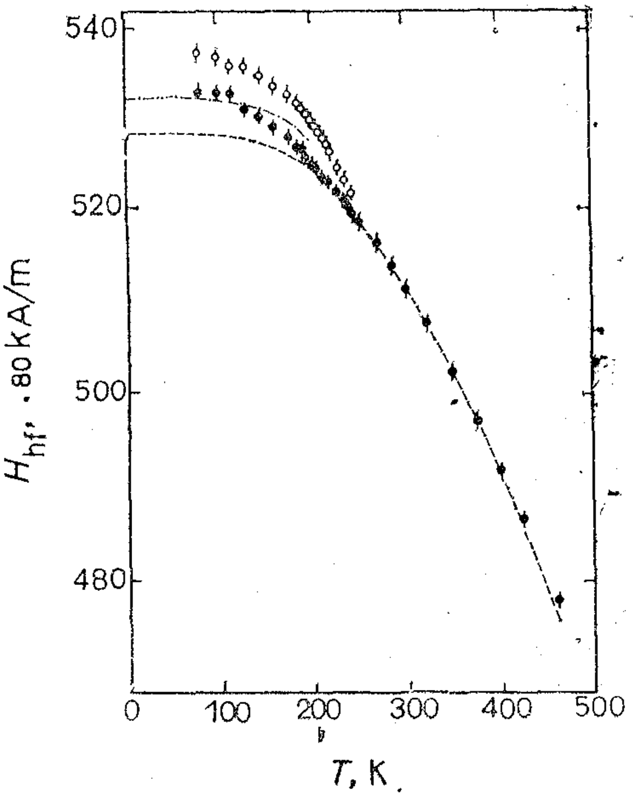
Фиг. 1. Проекция на гьотитовата структура върху (001). Кислородните атоми са дадени с големи празни кръгчета, Fe атоми — със средно големи черни кръгчета, а H атоми — с малки черни кръгчета. С плътни линии са очертани октаедрите. Водородните връзки са показани с плътни и пунктирани линии (Eggleton et al., 1988)

Fig. 2. The hematite structure. Oxygen atoms are represented by open circles, Fe atoms by solid circles. The projection is along $[11\bar{2}0]$: solid circles are in the plane, thin open circles are below the plane, and thick open circles are above the plane of the paper

Фиг. 2. Сгрукгура на хематита. Кислородните атоми са дадени с празни кръгчета, Fe — с черни кръгчета. Проекцията е по $[11\bar{2}0]$: кръгчетата със средна дебелина на линията лежат в равнината на листа, с тънка линия — под нея, а с дебела — над нея

But at room temperature the Mössbauer spectra frequently show a mixture of a doublet and a partially resolved sextet which may be due to the result of superantiferromagnetic relaxation of magnetization (Bean, Livingstone, 1959). In a magnetically ordered substance the magnetization tends to take certain "easy" direction due to crystalline anisotropy. But in case of small-sized particles, as a result of superantiferromagnetic relaxation, it is easy to change this direction with the supply of an external energy (as for example thermal excitation). When the relaxation time is longer compared to Mössbauer transition time (10^{-7} s), a well resolved sextet will be produced whereas a relaxed spectrum results when the relaxation time becomes equal to (or smaller than) the Mössbauer transition time. A range of particle sizes will affect relaxation and may bring about a broadening of the relaxed spectra which would be asymmetrical (Mørup et al., 1976). This effect of superantiferromagnetic relaxation is observed to be reduced at temperatures below 77 K. This relaxation reduces the hyperfine field. Therefore the hyperfine field varies with temperature and below 393 K this change follows the Brillouin function (Van der Woude, Dekker, 1966) (Fig. 3).

Of the trivalent iron oxides hematite has the highest saturation hyperfine field (H(O)=54, 2T) as well as the highest Neel temperature (T_N=956 K, below which it is magnetically ordered). Below 260 K (T_M, Morin transition



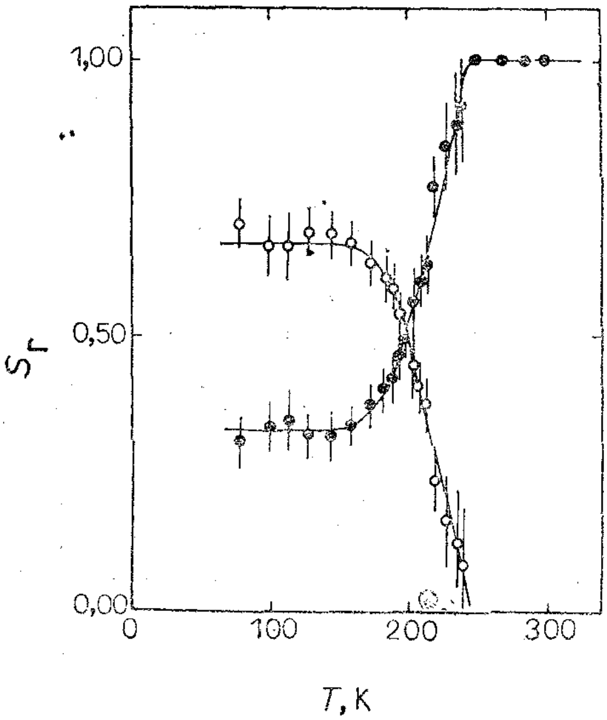


Fig. 3. ^{57}Fe magnetic hyperfine fields for the weakly ferromagnetic (●) and antiferromagnetic (○) spin structures (-.-.-. — Brillouin curve fitted to data below 160 K; - - - —Brillouin curve fitted to data above 245 K, De Grave et al., 1983)

Фиг. 3. Магнитни свръхфини полета за слабоферомагнитните (●) и антиферомагнитните (○) спинови структури на ^{57}Fe (-.-.-. — Брилюенова крива, подбрана за данните под 160 K; - - - — Брилюенова крива, подбрана за данните над 245 K, De Grave et al., 1983)

Fig. 4. Temperature dependence of the relative contribution of the weakly ferromagnetic (●) and antiferromagnetic (○) fractions (De Grave et al., 1983)

Фиг. 4. Температурна зависимост на относителното участие на слабата феромагнитност (●) и на антиферомагнитността (○) (De Grave et al., 1983)

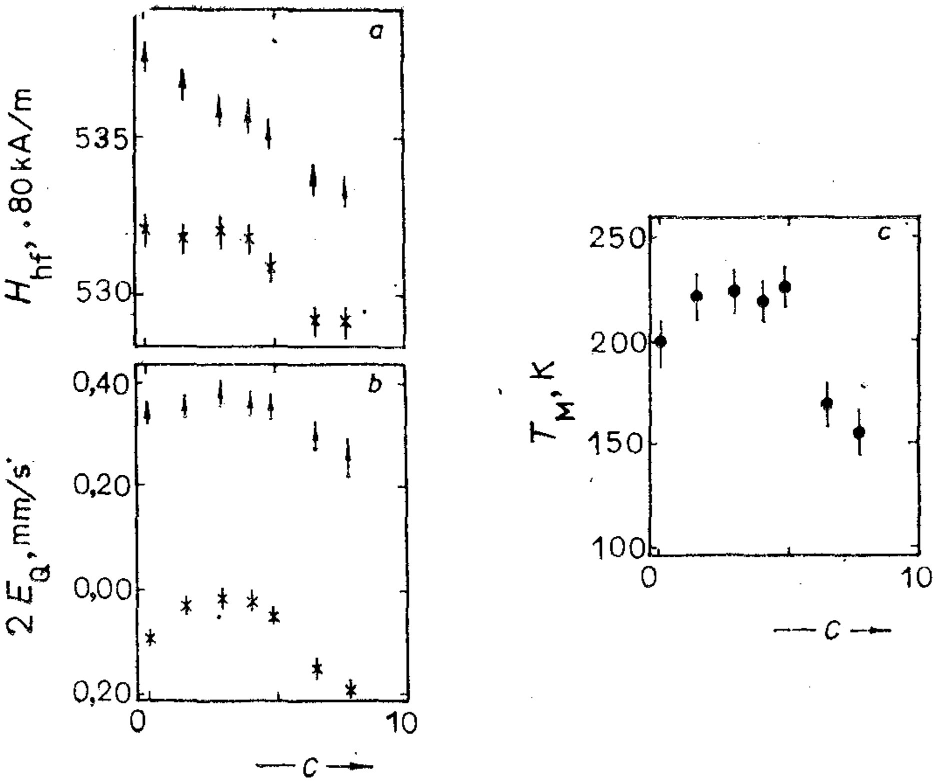


Fig. 5. Low temperature saturation values of the magnetic hyperfine fields *(a)*, of the quadrupole splitting *(b)* and of Morin transition temperature *(c)* of α-(Fe$_{1-C}$Al$_C$)$_2$O$_3$ plotted as a function of the Al-substitution (▲ — AF phase, × — WF phase; De Grave et al., 1988a)

Фиг. 5. Стойности на насищане при ниска температура на магнитните свръхфини полета *(a)*, на квадруполното разцепване *(b)* и на температурата на прехода на Моурин *(c)* за α-(Fe$_{1-C}$Al$_C$)$_2$O$_3$ като функция от съдържанието на Al (▲ — фаза AF, × — фаза WF; (De Grave et al., 1988a)

temperature) hematite behaves as antiferromagnetic in which the spins (of Fe^{3+}) are antiparallel with slight canting (~7°) with the trigonal [111] direction (Morrish et al., 1963). At T_M the spins undergo a sudden 90° flip and become perpendicullar to the trigonal [111] axis with slight canting and thus behave as ferrimagnetic (Fysh, Clark, 1982b).

The magnetic dipolar moments cause the spins to align along the *C*-plane but the magnetic anisotropy favours the spins to be aligned along the *C*-axis (Van der Woude, 1966). With increasing temperature the influence of anisotropy decreases rapidly (Fig. 4) and at 260 K (T_M) spin flip causes the spins to be oriented along the *C*-axis. But antisymmetrical spin coupling in the spin Hamiltonian causes a slight canting of the spin resulting in a weak ferrimagnetism.

Mössbauer spectra of pure phases

Above 393 K (Neel temperature) goethite gives paramagnetic doublet which is produced by the interaction of quadrupole moment with electric field gradient and a quadrupole splitting of 0,5 mm/s (Van der Woude, Dekker, 1966; Forsyth et al., 1968). Below this temperature it is antiferromagnetic, generating a six line spectrum. At room temperature it has a magnetic hyperfine field of 38,2 T; its saturation hyperfine field is 50,6 T.

Hematite, identically, shows a paramagnetic doublet above 956 K (Neel temperature), below which magnetic ordering causes splitting of this doublet into a six line spectrum. While passing through Morin transition temperature (260 K) changes of Mössbauer spectra are noted. A small change of isomer shift (δ) within this transition has been reported by Ruskov et al. (1976) and Nininger, Schroeer (1978) although some earlier workers (Van der Woude, 1966) showed that it does change a little. The quadrupole splitting within this transition changes and follows the relation (Bowen, 1979)

$$\frac{\Delta\; T>T_M}{\Delta\; T<T_M} \approx 0{,}54.$$

Mössbauer spectra of aluminous phases

In the oxides and hydroxides of iron, Fe^{3+} (0,67 Å) may be isomorphously substituted by Al^{3+} (0,57 Å). Fe^{3+} has five $3d$ electrons with five Bohr magneton magnetic moments in the high spin state and thus behaves as a paramagnetic ion whereas electronic structure of Al^{3+} is similar to neon (Ne) and therefore it is diamagnetic. Therefore such a substitution has a considerable effect on the magnetic properties and as a result on the Mössbauer parameters. Al-substitution (Al_s) also changes the Morin transition temperature (De Grave et al., 1982, 1983, 1988b) and the effect in hematite is shown in Fig. 5 *c*.

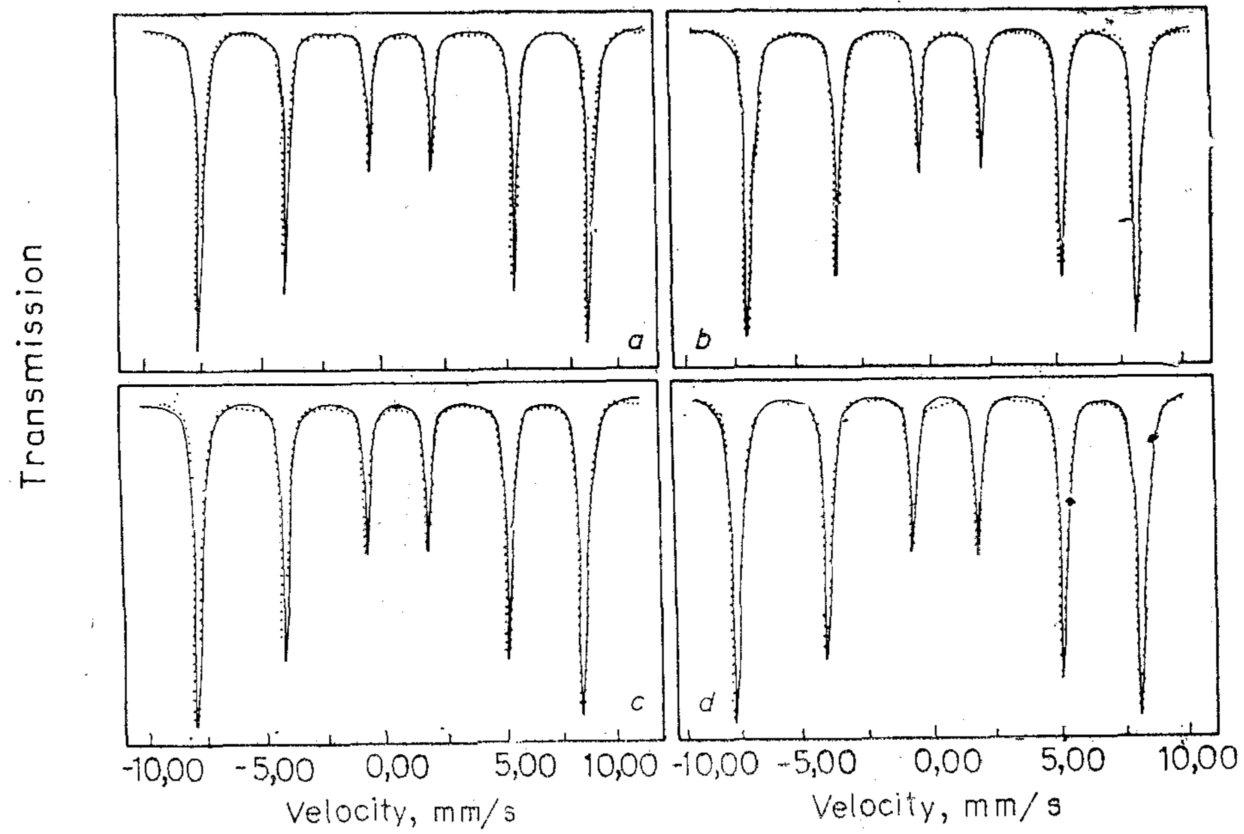


Fig. 6. The Mössbauer spectra of Al-goethites at 4,2 K with Al-substitutions of *a*—0,00 *b*—0,05, *c*—0,09 and *d*) 0,12 (Murad, Schwertmann, 1983)

Фиг. 6. Мьосбауерови спектри на Al-гьотити при 4,2 K и стойности на заместващия Al: *a* — 0,00, *b* — 0,05, *c* — 0,09 и *d* — 0,12 (Murad, Schwertmann, 1983)

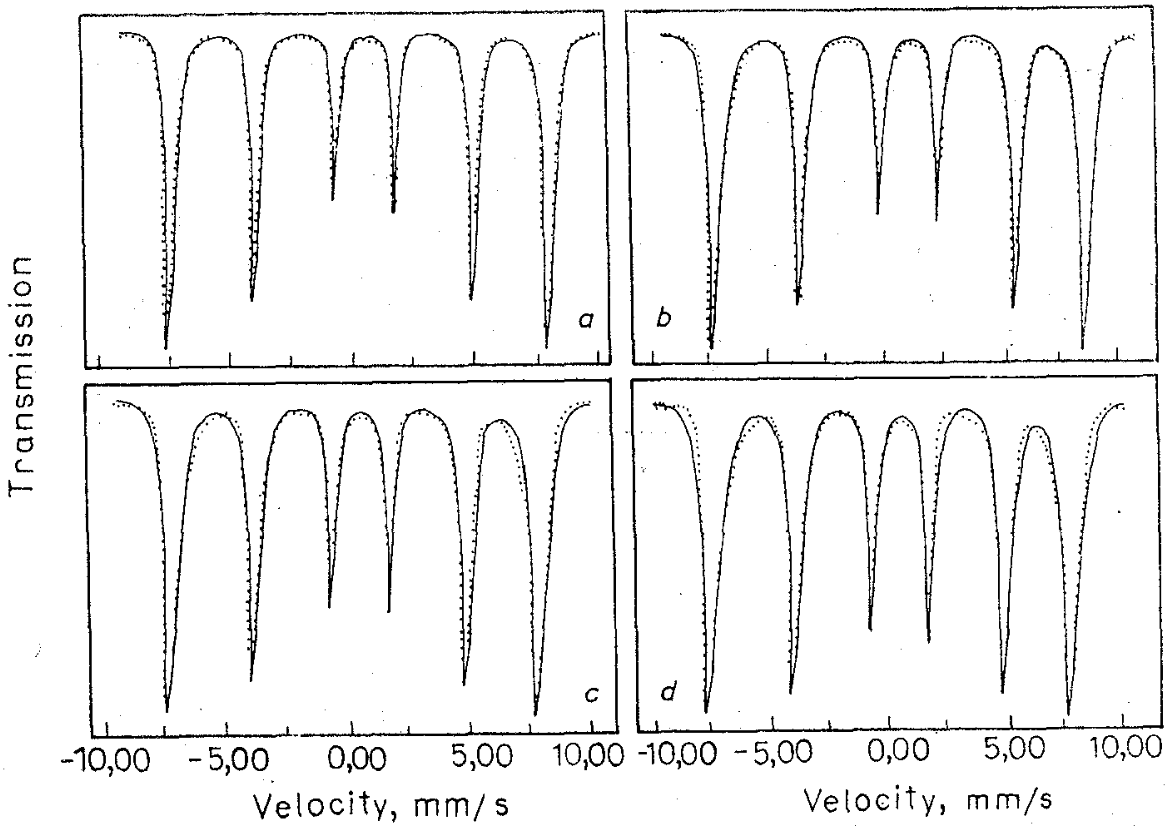


Fig. 7. The Mössbauer spectra of Al-goethites at 125 K with Al-substitutions of: *a* — 0,00, *b* — 0,05, *c* — 0,09 and *d* — 0,12 (Murad, Schwertmann, 1983)

Фиг. 7. Мьосбауерови спектри на Al-гьотити при 125 K и стойности на заместващия Al от *a* — 0,00 *b* — 0,05, *c* — 0,09 и *d* — 0,12 (Murad, Schwertmann, 1983)

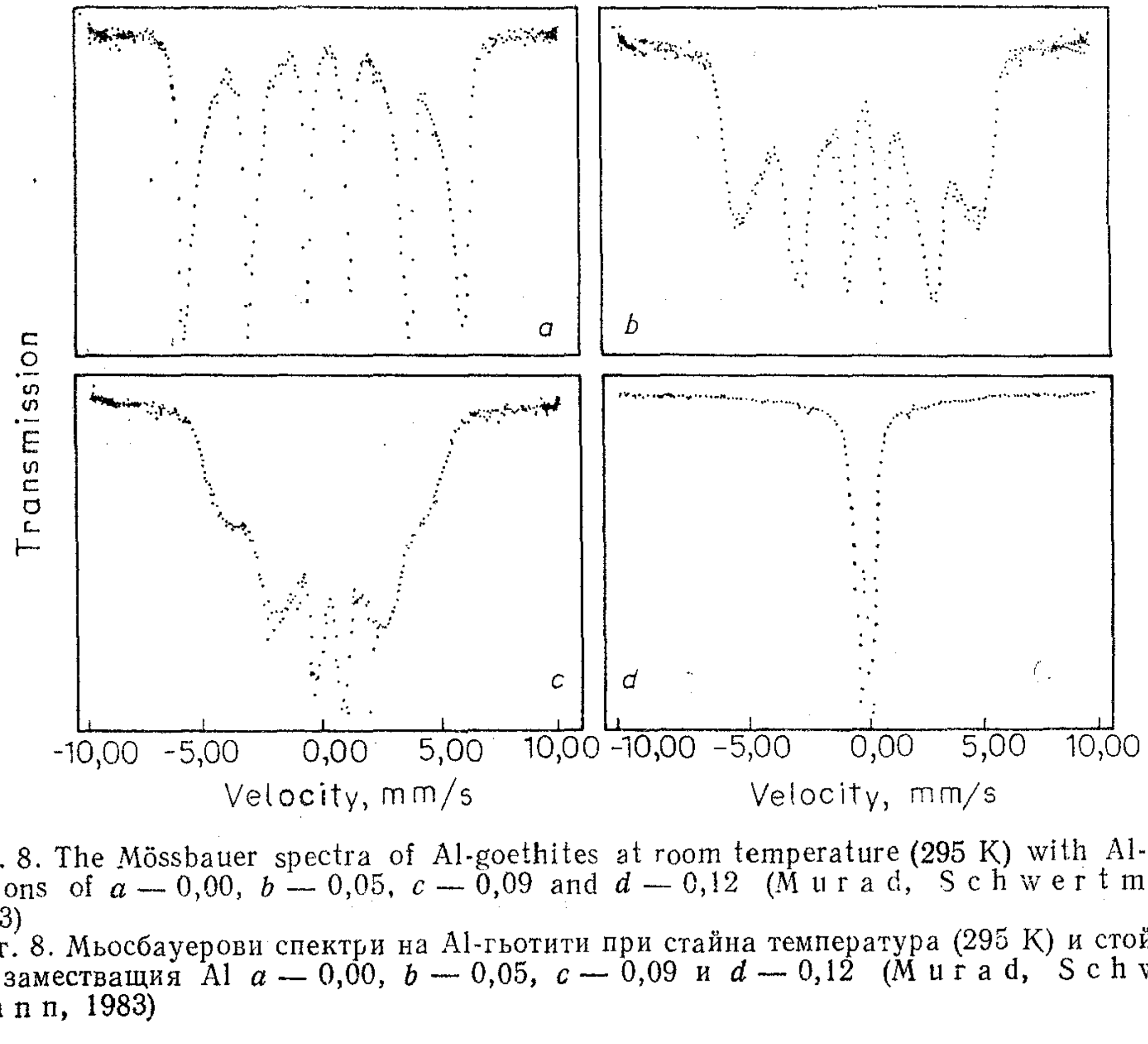


Fig. 8. The Mössbauer spectra of Al-goethites at room temperature (295 K) with Al-substitutions of *a* — 0,00, *b* — 0,05, *c* — 0,09 and *d* — 0,12 (Murad, Schwertmann, 1983)

Фиг. 8. Мьосбауерови спектри на Al-гьотити при стайна температура (295 K) и стойности на заместващия Al *a* — 0,00, *b* — 0,05, *c* — 0,09 и *d* — 0,12 (Murad, Schwertmann, 1983)

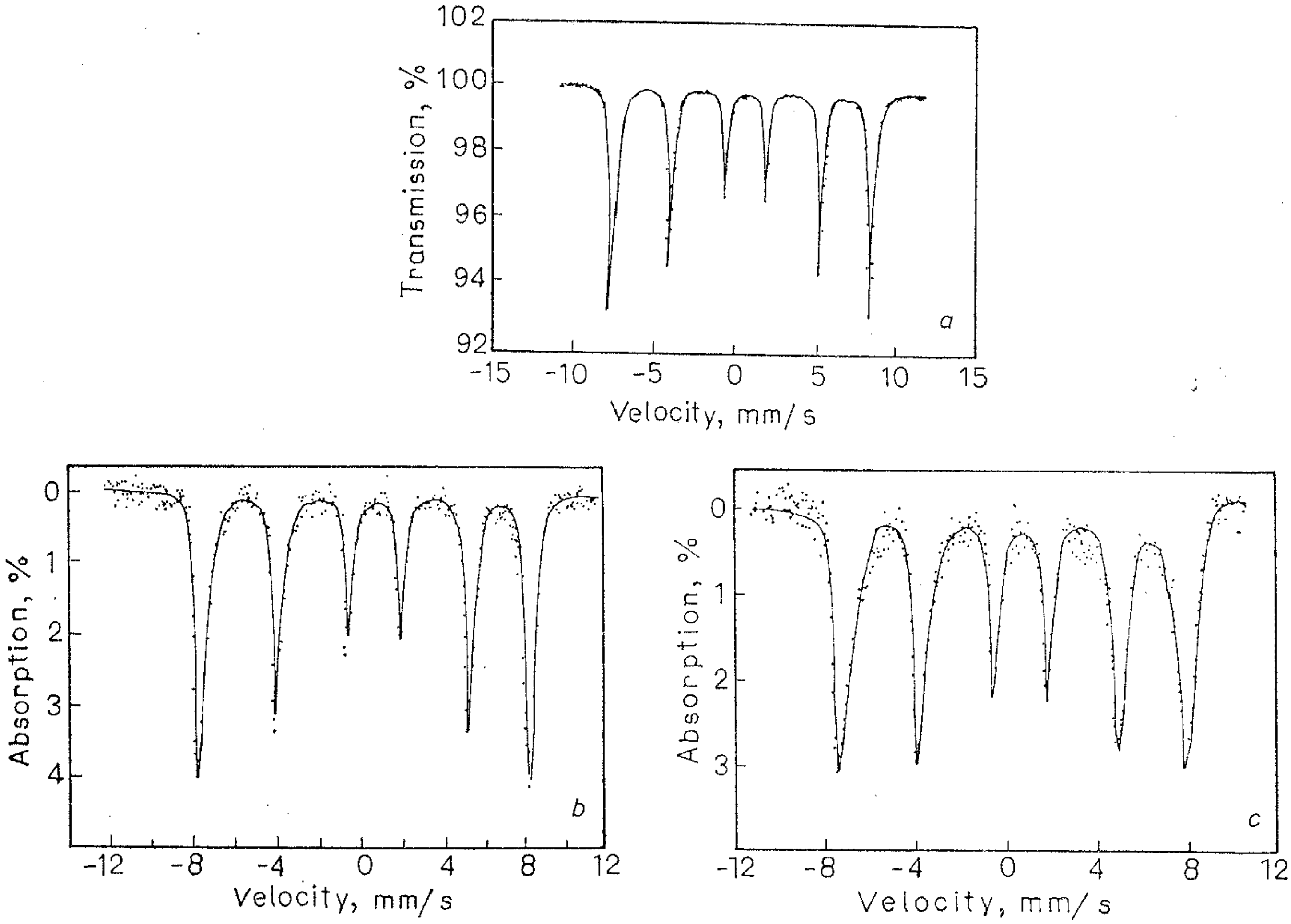


Fig. 9. Mössbauer spectra of Al-hematites at room temperature for *a* — 15 mol. % Al_s (Fysh, Clark, 1982b); *b* — 17,1 mol % Al_s (De Grave et al., 1982b) and *c* — 28,2 mol.% Al_s (De Grave et al., 1982b)

Фиг 9. Мьосбауерови спектри на Al-хематити при стайна температура за *a* — 15 mol. % Al_s (Fysh, Clark, 1982b); 17.1 mol.% Al_s (De Grave et al, 1982 *b*) и *c* — 28,2 mol.% Al_s (De Grave et al., 1982b)

In goethite this type of aluminium substitution takes place to an extent of 33 mol. % (Murad, Schwertmann, 1983) and in hematite approximately 16 mol. % (Muan, Gee, 1956; Von Steinwehr, 1967; Schwertmann et al., 1979) or 32 mol. % (De Grave et al., 1982b). The effects of Al-substitution on the Möessbauer spectra of goethite are shown in Fig. 6 at 4,2 K, in Fig. 7 at 125 K and in Fig. 8 at room temperature. The similar effects in hematite are shown in Fig. 9 at room temperature and in Fig. 10 at 4,2 K.

The variation of magnetic properties with aluminium substitution is important in hematite. At 77 K hematite with less than 4 mol. % Al_s is antiferromagnetic with the spins nearly parallel to [111]. But for greater than 8 mol. % Al_s at that temperature it behaves as weakly ferromagnetic. Inbetween 4—8 mol.% Al_s both antiferromagnetic and weakly ferromagnetic phases remain present but in varying proportions (De Grave et al., 1983).

The percentage of Al_s may be determined by two important techniques: 1) XRD, and 2) Mössbauer spectroscopy.

As Al^{3+} has lower ionic radius than Fe^{3+}, aluminous phase has lower unit

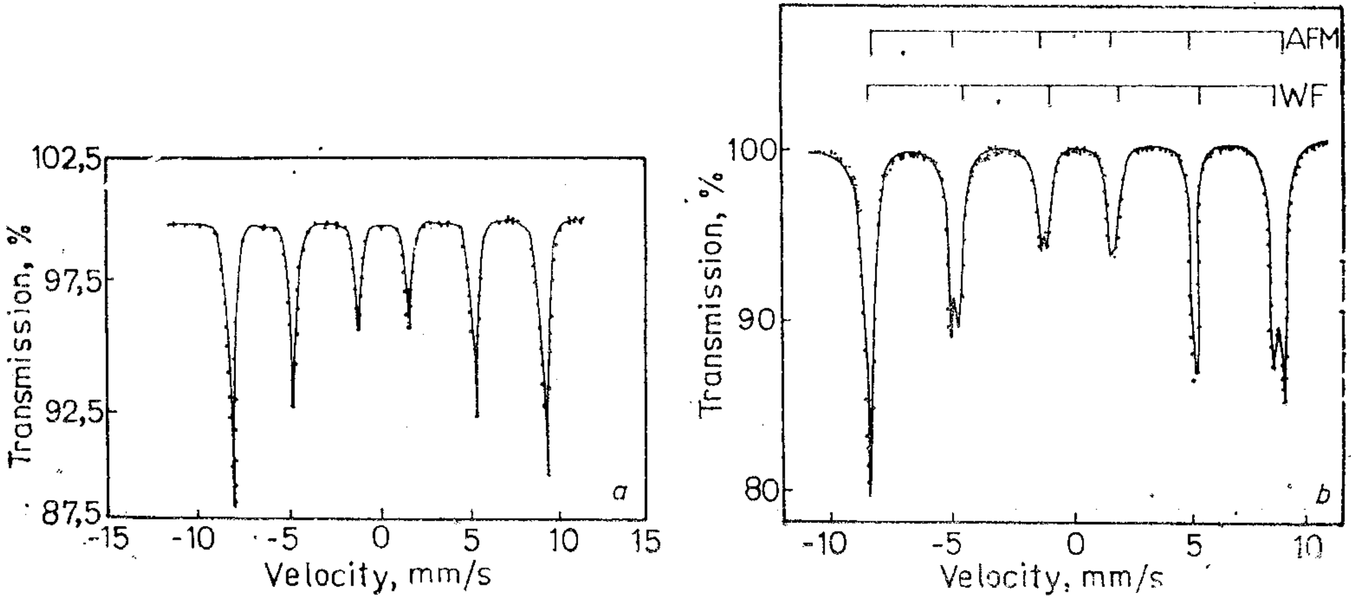


Fig. 10. Mössbauer spectra of Al-hematites at 4,2 K for *a* — pure hematite (Fysh, Clark, 1982b) and *b* — 4,3 mol.% Al_s (Murad, 1988)

Фиг. 10. Мьосбауерови спектри на Al-хематити при 4,2 K за *a* — чист хематит (Fysh, Clark, 1982b) and *b* — 4.3 mol.% Al_s (Murad, 1988)

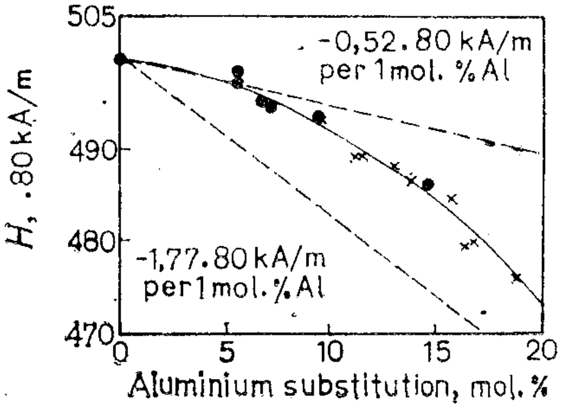


Fig. 11. Magnetic hyperfine field vs. aluminium substitution of the goethites at 77 K (Fysh, Clark, 1982a)

Фиг. 11. Зависимост на магнитното свръхфино поле от съдържанието на алуминия в гьотитите при 77 K (Fysh, Clark, 1982a)

cell and d-spacing compared to pure phases (Thiel, 1963; Jonas, Solymar, 1970; Schulze, 1982). Therefore, XRD may be successfully used for this purpose. But with the samples having less than 10 mol.% Al_s such XRD lines can hardly be used as they get masked by the lines of other minerals. Mössbauer spectroscopy, however, can be used both above and below 10 mol.% Al_s and hence has greater efficiency than XRD in such studies.

Fitting of the relaxed spectra

Two models are primarily used for the fitting of relaxed spectra. Mørup et al. (1976) and Govaert et al. (1976) have used the models of Van der Kraan (1973) in which the distribution of hyperfine field is parametrized to fit the spectra.

A stochastic model devised by Blume and Tjon (1968) is more used. This model however has some limitations. To derive the equations for the fit all photons emitted by a nucleus in time of excitaton *t* are counted.

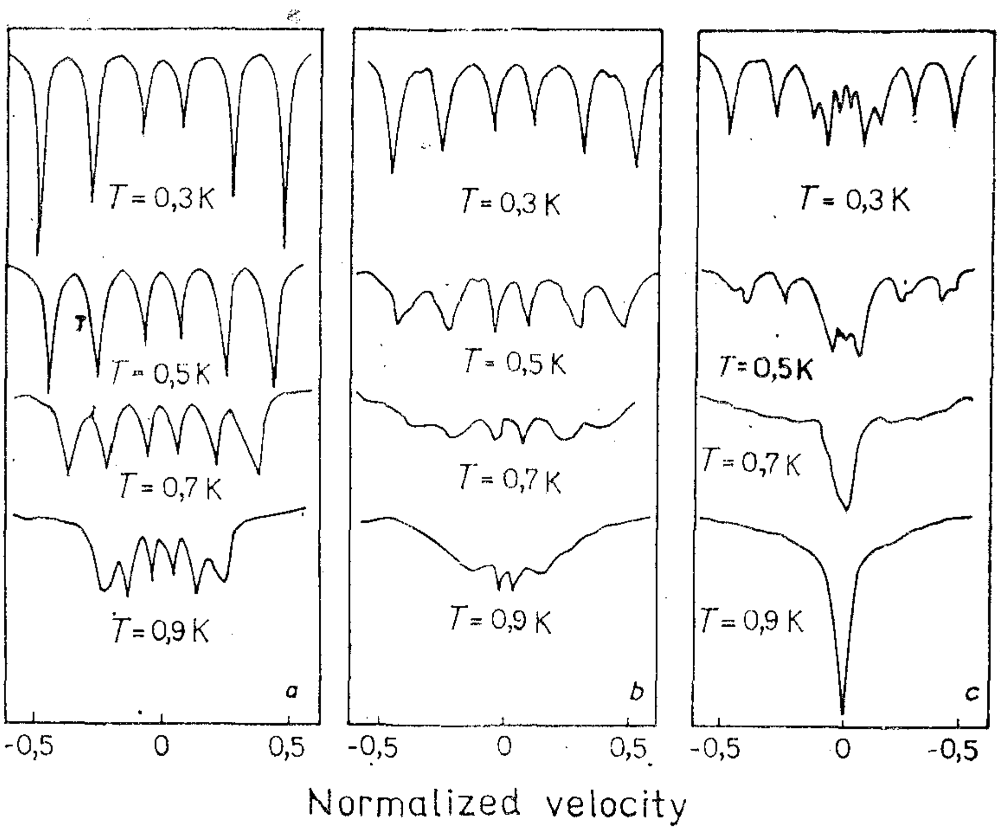


Fig. 12. Mössbauer spectra predicted for materials with: a — x=0,1, b —x =0,5 and c — x=0,9 at several different temperatures (Coey, Sawatzky, 1971b)

Фиг. 12. Предсказани мьосбауерови спектри за материали с: a — x=0,1, b — x=0,5 и c—x=0,9 и за няколко различни температури (Coey, Sawatzky, 1971b)

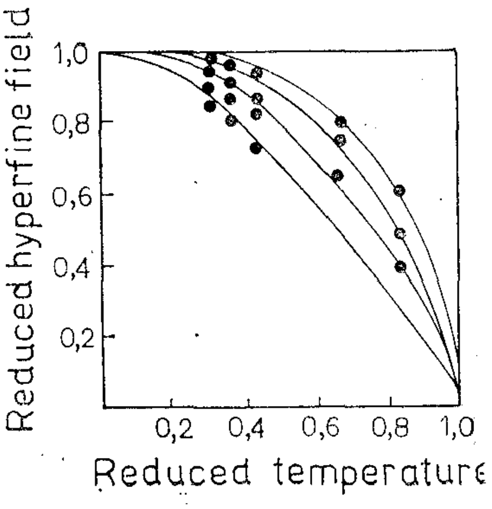


Fig. 13. Measured hyperfine field (dots) for ^{57}Fe in different environments in (Zn$_{0,34}$Mn$_{0,66}$) Fe$_2$O$_4$. The solid lines are the prediction of the equations of reduced field determination (Coey, Sawatzky, 1971b)

Фиг. 13. Измерени стойности на свръхфиното поле (точки) за ^{57}Fe в различно обкръжение в (Zn$_{0,34}$Mn$_{0,66}$) Fe$_2$O$_4$. Плътните линии са предсказаните зависимости по уравненията за определяне на редуцирано поле (Coey, Sawatzky, 1971b)

Only a poor fit at room temperature was observed using this model (Golden et al., 1979). Unless the particle size and magnetic dilution are considered in the model, qualitative approach to the fitting of spectra becomes a difficult one. For this reason, the spectra fitted at 300 K are either of completely magnetically ordered phase or of the completely relaxed highly aluminous phase.

Particle size effect and magnetic dilution caused by Al^{3+} are the two main factors of the relaxation of the Mössbauer spectra. As stated earlier, relaxation effect decreases with temperature. Samples with different particle sizes but containing same aluminium gave identical spectra at 77 K (Fysh, Clark, 1982a). Therefore, at that temperature the influence of particle size on hyperfine splitting may be neglected at 77 K. The relaxed shape at that temperature is due to decreasing T_N with increasing Al-substitution and in goethite this effect is shown in Fig. 11. The upper broken line and the solid line indicate the relation of the hyperfine field with aluminium substitution at 4,2 K and 77 K respectively. The lower broken line exhibits the results of Golden et al. (1979). This figure shows clearly that hyperfine field values are the same for both 4,2 K and 77 K up to 4 mol.% Al_s. But beyond 7 mol. % Al_s the hyperfine value at 77 K decreases sharply in contrast to the value at 4,2 K.

Prediction of the Mössbauer spectra in a substituted system

The Mössbauer spectra can be predicted on the basis of molecular orbital theory as suggested by Coey and Sawatzky (1971b) (Fig. 12) which is in conformity with the experimental observations (Fig. 13) made at different temperatures except the temperature below magnetic ordering temperature and at higher percentages of substitution. The molecular orbital theory is applicable where two ions of different magnetism occur in the same crystallographic site. Therefore it may be useful for the prediction of Mössbauer spectra in aluminium substituted iron oxides and hydroxides. In the molecular orbital theory superexchange of iron with its neighbouring cations is considered as the dominant interaction affecting the hyperfine field. Therefore for the complex spectra of a substituted system hyperfine field will depend on the number and type of neighbouring cation (Coey, Sawatzky, 1971b).

Hyperfine field

The hyperfine field reduction due to the substitution of Fe^{3+} by Al^{3+} is shown in Figs 11 and 14 at different temperatures (Fysh, Clark, 1982a). At room temperature pure goethite exhibits antiferromagnetic six line spectrum. But the samples with more than 12 mol.% Al_s show paramagnetic doublet since this amount of aluminium can lower the T_N of goethite (393 K) to 295 K (Fleish et al., 1980). The paramagnetic doublet at temperatures above T_N has $\delta Fe=0{,}36$ mm/s and $\Delta E_Q=0{,}52$ mm/s which is characteristic of Fe^{3+} in octahedral coordination.

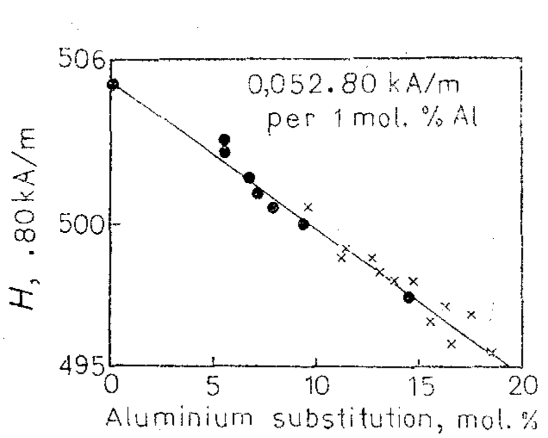


Fig. 14. Variation of hyperfine field with Al-substitution in goethites at 4,2K (Fysh, Clark, 1982a)

Фиг. 14. Изменение на свръхфиното поле в зависимост от съдържанието на Al в гьотити при 4,2 K (Fysh, Clark, 1982a)

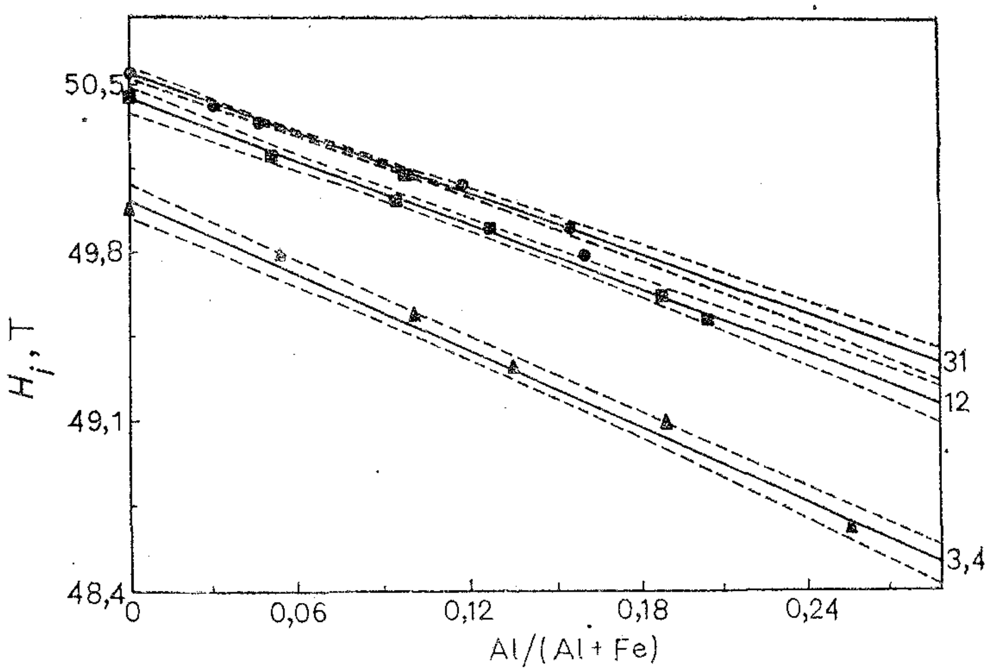


Fig. 15. Effect of Al-substitution on the magnetic hyperfine field of goethite at 4,2 K (Murad, 1988)
Фиг. 15. Влияние на съдържанието на Al върху магнитното свръхфино поле на гьотита при 4,2 K (Murad, 1988)

At varying temperatures Al-goethites show a linear relationship of magnetic hyperfine field with mole percentage of aluminium substitution. The regression equations of this relationship as studied by different workers are shown in Appendix A. The most recent study in this line has been made by Murad (1988) in which the regression equation (Fig. 15) is

$H_i(T) = 50{,}65(4) - 4{,}2(3)\ \mathrm{Al_s} - 8{,}7(7)/\mathrm{MCD}_{111},\quad n = 19,\quad r = 0{,}984,$

Table 1

Isomer shift (δ), quadrupole splitting (2 ε), magnetic hyperfine field (H_{hf}) and line width of outer absorption lines (r) for $(\mathrm{Fe}_{1-C}\mathrm{Al}_C)_2\mathrm{O}_3$ samples at 77,3 K (De Grave et al., 1982b)

C	δ, mm/s,	2ε, mm/s	H_{hf}, 80kA/m	r, mm/s
0,000	0,239(3)	0,387(6)	538,9(2)	0,41(1)
0,034	0,245(5)	0,334(9)	537,4(3)	0,49(2)
0,040	0,243(4)	0,375(8)	537,8(3)	0,49(1)
0,041	0,240(4)	0,355(8)	537,5(3)	0,56(2)
0,077	0,236(2)	—0,146(4)	530,0(2)	0,44(1)
0,081	0,234(4)	—0,180(8)	527,1(3)	0,51(2)
0,117	0,238(4)	—0,198(9)	526,8(3)	0,43(2)
0,171	0,234(3)	—0,197(6)	525,2(3)	0,48(1)
0,183	0,240(4)	—0,221(8)	524,2(3)	0,47(2)
0,189	0,236(3)	—0,212(7)	524,6(3)	0,49(2)
0,237	0,228(5)	—0,22(1)	524,2(5)	0,47(2)
0,279	0,234(6)	—0,22(1)	520,1(4)	0,53(2)
0,282	0,229(4)	—0,206(7)	519,5(3)	0,44(2)
0,324	0,227(5)	—0,20(1)	519,3(4)	0,60(2)

Numbers within parentheses represent the errors on last digit.

Table 2

Mössbauer data for Al-substituted hematite at room temperature (Murad, Schwertmann, 1986)

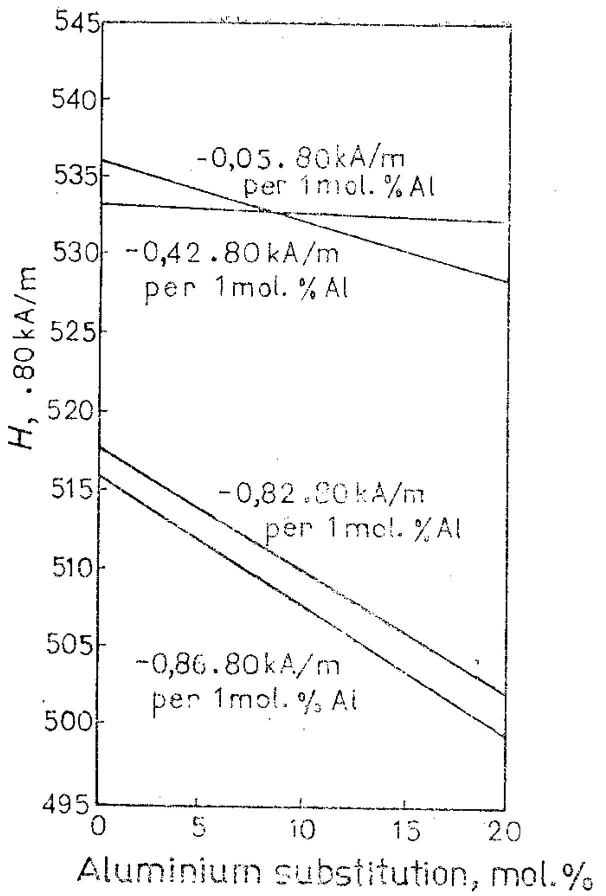
Chemical/XRD data		Mössbauer data				
Al/(Al + Fe)	MCD$_c$	WID$_1$	WID$_2$	WID$_3$	ΔE_Q	H_i
0,000	bulk	0,269	0,273	0,258	−0,187	51,77
0,018	bulk	0,285	0,276	0,267	−0,197	51,60
0,043	bulk	0,302	0,283	0,265	−0,201	51,48
0,049	bulk	0,314	0,296	0,267	−0,200	51,38
0,053	bulk	0,326	0,306	0,262	−0,203	51,33
0,072	bulk	0,341	0,315	0,264	−0,205	51,20
0,095	bulk	0,374	0,326	0,273	−0,214	50,94
0,098	bulk	0,369	0,325	0,278	−0,209	51,00
0,000	40	0,359	0,347	0,319	−0,204	51,02
0,008	53	0,359	0,342	0,288	−0,205	50,97
0,018	77	0,354	0,326	0,277	−0,204	50,96
0,043	55	0,377	0,347	0,288	−0,205	50,95
0,053	67	0,434	0,387	0,294	−0,207	50,65
0,072	51	0,483	0,427	0,330	−0,200	50,33
0,095	27	0,570	0,500	0,353	−0,203	49,92

MCD$_c$ are mean crystal diameters parallel to [001] as determined by XRD, bulk indicates no appreciable line broadening, WID$_1$ is half width of lines 1 and 6, WID$_2$ is half width of lines 2 and 5, WID$_3$ is half width of lines 3 and 4. ΔE_Q is quadrupole splitting, and H_i is magnetic hyperfine fielp.

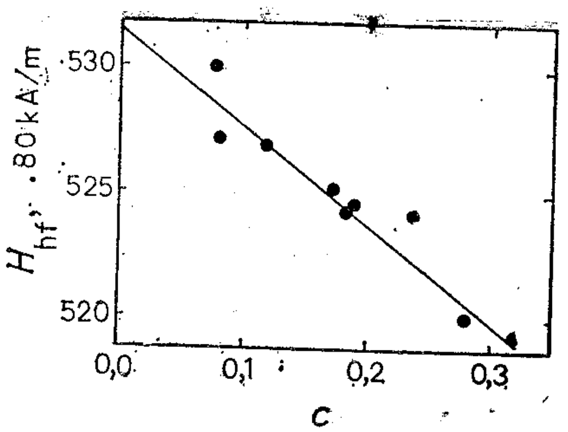
where MCD (calculated from the half widths of XRD line) from [111] line is more preferable than MCD$_{110}$ since it has components in all directions and also the multiple coefficinet factor is higher (r^2=0,969) for MCD$_{111}$ compared to MCD$_{110}$ (r^2=0,937). For well crystallized samples (MCD>100 nm), influence of crystallinity on hyperfine field may be neglected but it becomes significant with decrease in crystallinity (Murad, Schwertmann, 1983). The particle size of ~21 nm gives the same hyperfine field (4,2.80 kA/m at 4,2 K) as that due to 10 mol.% Al$_s$.

In hematite the magnetic hyperfine field is also influenced by mol.% Al$_s$. Tables 1 and 2 represent such relations. The gradual decrease of hyperfine field with increasing Al-substitution is shown in Figs 5*a*, 16, 17 and 18. The regression equations of different workers are shown in Appendix B. Considering the effects of both Al-substitution and crystallinity on the hyperfine field Murad (1988) has shown the regression equation (Fig. 19) at room temperature as $H_i(T)$=51,72(6) —7,6(10) Al$_s$−32(3)/MCD$_{001}$: n=15, r=0,974.

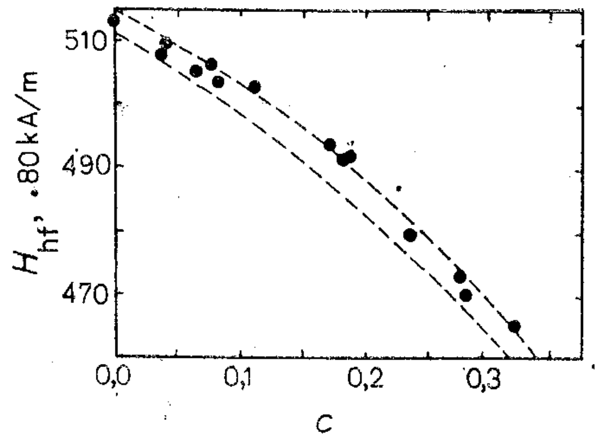
Commentary. From the above discussion it becomes evident that the hyperfine fields of goethite and hematite decrease linearly with increasing Al-substitution. The question now arises as to how the Al-substitution reduces the magnetic hyperfine field. Hyperfine field of iron hydroxides and oxides is produced mainly due to: interaction of *s*-electrons with 3*d*-electrons of Fe^{3+} and interaction of *s*-electrons of Fe^{3+} with the electrons of next neighbour Fe^{3+} which is also referred to as superexchange phenomenon (Murad, 1984). In this case, the electron transfer takes place via the ligands as Fe–O–Fe. In aluminous phases many aluminium (diamagnetic) atoms act as neighbouring atoms of Fe^{3+} resulting in the reduction of supertransfer of electrons and hence causes the magnetic dilution. The reduction of hyperfine field with the Al-substitution is therefore primarily due to reduction in supertransfer exchange (Sa-



Фиг. 16



Фиг. 17



Фиг. 18

Fig. 16. Variation of hyperfine field with Al-substitution in hematites. The upper two lines are at 4,2 K, and the lower two are at 300 K (modified from Fysh, Clark, 1982b)
Фиг. 16. Изменение на свръхфиното поле в зависимост от съдържанието на Al в хематити. Горните две линии са при 4,2 K, а долните две — при 300 K (с изменения по Fysh, Clark, 1982b)

Fig. 17. Magnetic hyperfine fields at 77,3 K vs. composition C for α-$(Fe_{1-C}Al_C)_2O_3$ in the weakly ferromagnetic state (De Grave et al., 1982b)
Фиг. 17. Зависимост на магнитното свръхфино поле при 77,3 K от състава C за α-$(Fe_{1-C}Al_C)_2O_3$ в слабо феромагнитно състояние (De Grave et al., 1982b)

Fig. 18. Magnetic hyperfine fields at room temperature vs. composition C for α-$(Fe_{1-C}Al_C)_2O_3$ (De Grave et al., 1982b)
Фиг. 18. Зависимост на магнитното свръхфино поле при стайна температура от състава C за α-$(Fe_{1-C}Al_C)_2O_3$ (De Grave et al., 1982b)

watzky et al., 1969; Coey, Sawatzky, 1971a). XRD study and incongruent dissolution of aluminous goethite in HCl (Schwertmann, 1984) indicate that Fe^{3+} and Al^{3+} are distributed in distorted octahedral sites. Some Fe^{3+} may have more of Al^{3+} and fewer Fe^{3+} as neighbours than the average thereby producing a cluster of several unit cells. This type of local inhomogeneity causes the lowering of magnetic ordering temperature and consequently the lowering of the magnetic hyperfine field.

Reduction in hyperfine field is also due to small particle size effect (Van der Kraan, Van Loeff, 1966; Tamamoto, 1968; Golden et al., 1979; Murad, 1982a). Particle size effect on hyperfine field resembles qualitatively those of Al-substitution (Golden et al., 1979) and is solely due to relaxation phenomena (Fysh, Clark, 1982a). Supermagnetic (encompassing superparamagnetic, superantiferromagnetic, etc.) relaxation dec

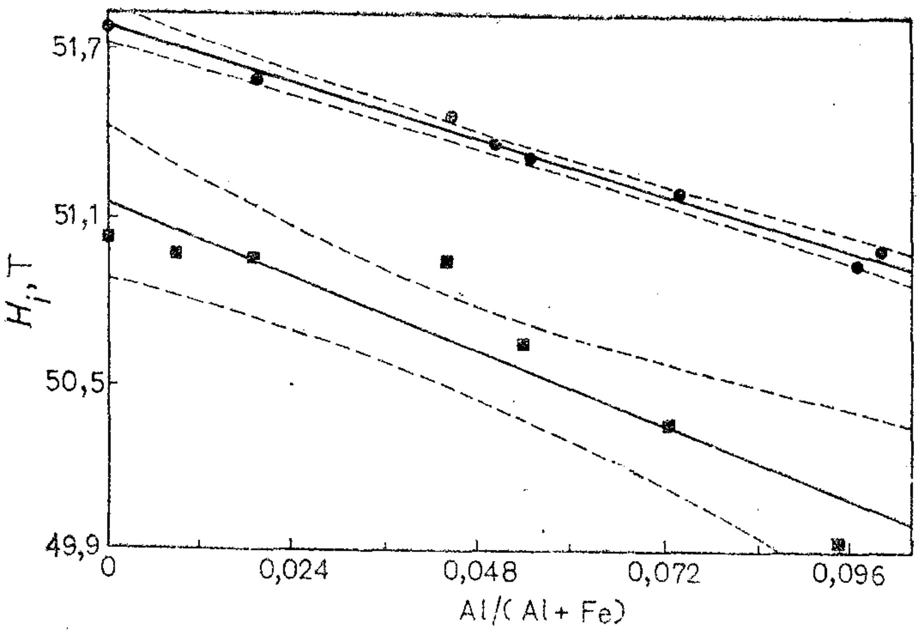


Fig. 19. Effect of Al-substitution on the magnetic hyperfine field of hematite at room temperature. Squares: samples formed at 70°C; and circles: samples formed at 1000°C (Murad, 1988)
Фиг. 19. Влияние на съдържанието на Al върху магнитното свръхфино поле на хематита при стайна температура. Квадратчета: проби, образувани при 70° C; и кръгчета: проби, образувани при 1000°C (Murad, 1988)

reases with temperature and this effect is observed down to 4,2 K. With decrease in particle size many Fe^{3+} ions come near to the surface and the supertransfer lacks the next nearest neighbour interaction and the hyperfine field is reduced (Schroeer, 1970).

The particle size increases with increase in aluminium content (as in goethite, Fysh, Clark, 1982a). Thus the effect of aluminium substitution can only be predicted from the hyperfine field reduction when the effect of particle size (crystallinity) is known.

Isomer shift

Studies on the isomer shifts at different temperatures could prove no remarkable affectation by Al-substitution in goethite and hematite. The isomer shift at 77 K for natural goethite is ~0,49—0,48 mm/s while the room temperature Mössbauer spectra of aluminous hematite with 0—20 mol.% Al_s shows a constant isomer shift value of 0,36±0,01 mm/s (Fysh, Clark, 1982b). In some cases, however, a very slight decrease of isomer shift has been reported (Table 1) with increasing Al-substitution (De Grave et al., 1982b).

Recoil free fraction

The recoil free fraction of the 14,4 keV gamma ray changes with the substitution of Fe^{3+} by Al^{3+} in oxide and hydroxide phases of iron. Fysh and Clark (1982a, b) found that the recoil free fraction (*f*) increases with increasing Al-substitution from about 0,69 for pure hematite to 0,82 for 14 mol.% Al_s stu-

Table 3

Aluminium content and recoil-free fraction, f, for substituted goethites at 4,2 K (Fysh, Clark, 1982a)

Al, mol. %	f
0,0	0,69±0,02
6,7	0,70±0,02
14,6	0,84±0,02
18,7	0,89±0,02

Table 4

Calculated Mössbauer fractions at 80 K and 300 K, relative to the calculated value for commercial bulk hematite (De Grave et al., 1985)

Al substitution (mol. %)	Relative Mössbauer fraction	
	T=80 K	T=300 K
0,0	1,000	1,006
1,5	1,004	1,022
2,9	1,008	1,029
4,0	1,022	1,075
4,8	1,004	1,015
6,5	1,005	1,015
7,7	1,000	1,002

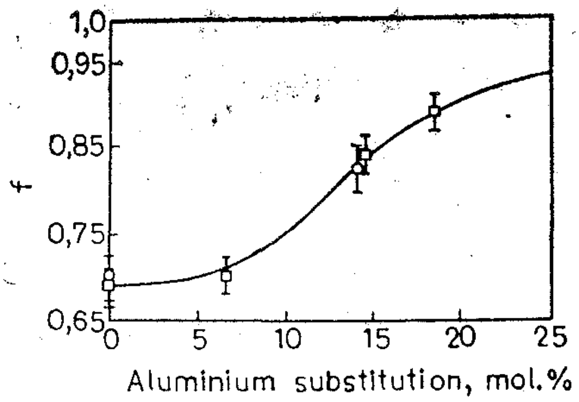


Fig. 20

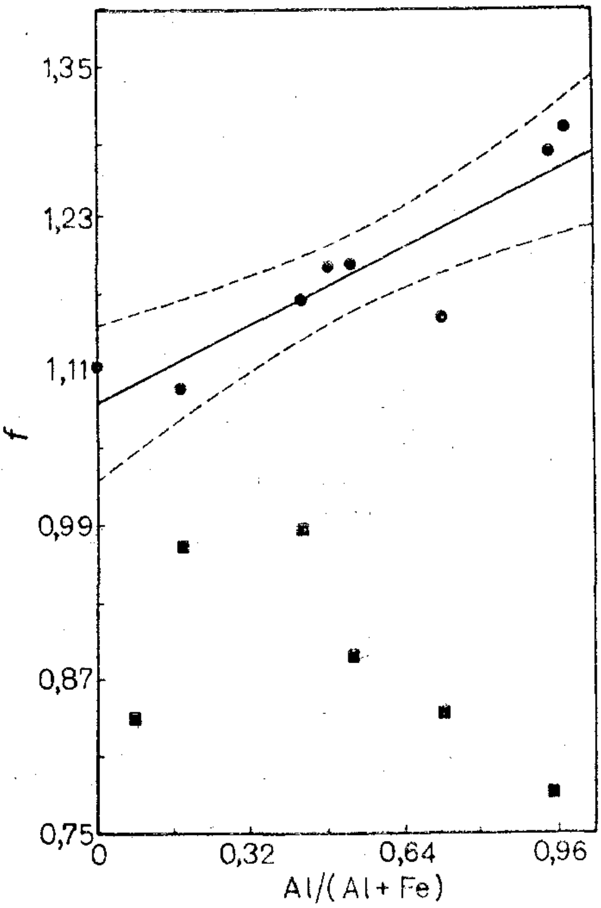


Fig. 21

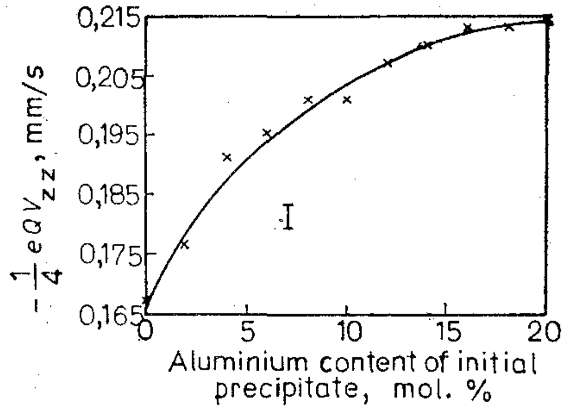


Fig. 22

Fig. 20. Measured recoil free fraction for Al-goethites (□) and Al-hematites (○) at 4,2 K (Fysh, Clark, 1982b)

Фиг. 20. Измерени стойности на нееластичното разсейване за алуминий-съдържащи гьотити (□) и хематити (○) при 4,2 K (Fysh, Clark, 1982b)

Fig. 21. Recoil free fractions vs. Al-substitution. Areas under hematite sextets relative to those under Fe sextets are recalculated to equal Fe densities. Circles: 1000° C hematites; and squares: 70° C hematites (Murad, 1985)

Фиг. 21. Зависимост на нееластичното разсейване от съдържанието на алуминия. Площите под хематитовите секстети са преизчислени към равни плътности на Fe по отношение на площите под Fe секстети. Кръгчета:хематити при 1000°C; и квадратчета: хематити при 70° C (Murad, 1985)

Fig. 22. Variation of quadrupole splitting with Al-substitution at room temperature (Fysh, Clark, 1982b)

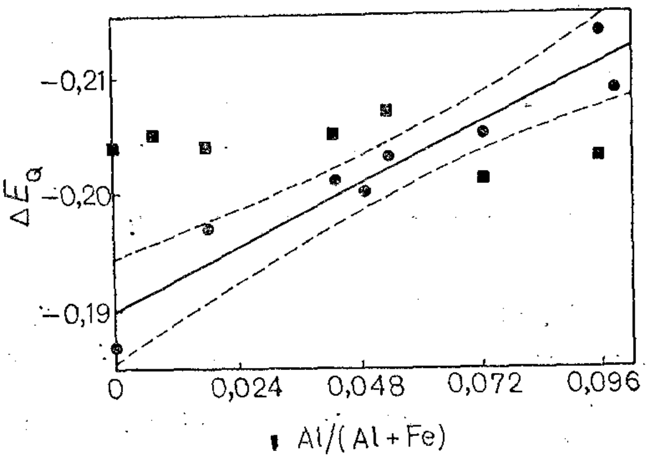
Фиг. 22. Зависимост на квадруполното разцепване от съдържанието на алуминия при стайна температура (Fysh, Clark, 1982b) died at 4,2 K (Fig. 20). The relationship of f fraction with mol.% Al_s is presented in Table 3. Increase in f results from increase in Al_s-substitution as well as particle size; both also bring about increase in line width (De Grave et al., 1985). The calculated Mössbauer fractions relative to the f-value (obtained from commercial bulk hematite) show a maximum at about 4 mol.% Al_s (Table 4) decreasing on either side of this mole content. This, however, contradicts with the results of Fysh and Clark (1982b) giving a gradual increase of f with Al-content (Fig. 20).

The variation in gamma ray absorption is caused by changes in the recoil free fraction, the saturation effects and by its deviation from Lorentzian line shape. Of these, the recoil free fraction dominates in determining the variation of gamma ray absorption. Murad (1985) has shown that in hematites (formed at 70° C with 27 to 40 nm crystalline diameter) the gamma ray absorption increases from that of Al-free hematite to a maximum near about 4 mol.% Al_s and then drops again, but in hematites (formed at 1000° C) the gamma ray absorption increases with Al-substitution (Fig. 21). It should be noted here that the crystallinity of the 70° C hematites is at an optimum between 3—5 mol.% Al_s and decreases for both higher and lower percentage of Al-substitution. Therefore the gamma ray absorption depends both on the crystallinity and Al-substitution. For aluminium substituted hematites of variable crystallinity Murad (1985) has related the gamma ray absorption with Al-substitution and crystallinity by a regression line (Fig. 22), the equation of which is

$$f(h)=1{,}09(3)+1{,}7(5)Al_s-14(1)/MCD_{001},\quad n=14,\quad r=0{,}954$$

where $f(h)$ is the ratio of the areas under the hematite sextets divided by those under the Fe sextets (recalculated to equal Fe concentrations).

Commentary. Thus, Murad (1985) and De Grave et al. (1985) are of the opinion that the gamma ray absorption initially increases up to 4 mol.% Al_s and then decreases with increasing Al-substitution. The ambi-



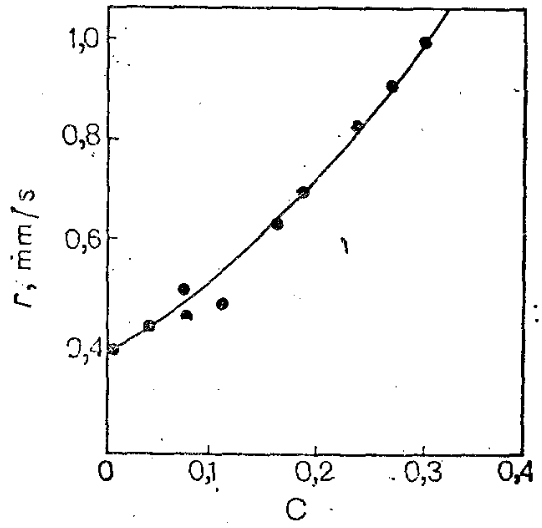


Fig. 23. Variation of quadrupole splitting of hematite as a function of Al-substitution. Squares: 70° C hematite. Cirlces 1000°C hematite (Murad, Schwertmann, 1986)
Фиг. 23. Зависимост на квадруполното разцепване при хематита от съдържанието на алуминия. Квадратчета: хематит при 70°C. Кръгчета: хематит при 1000°C (Murad, Schwertmann, 1986)

Fig. 24. Variation of line width of outer absorption vs. C for α-$(Fe_{1-C}Al_C)_2O_3$ samples (De Grave et al., 1982b)
Фиг. 24. Зависимост на ширината на линиите на външната абсорбция от C за проби от α-$(Fe_{1-C}Al_C)_2O_3$ (De Grave et al., 1982b)

guous results in part of Murad's (1985) experiment only reflect the absence of influence of crystallinity. The discrepancy in the results of Fysh and Clark (1982a, b) is perhaps due to the fact that they have measured the recoil free fraction only for Al-free hematite and 14 mol. % Al_s (Fig. 20) and thus they have missed to observe the variations at intermediate Al-substitution.

Increase in f-values with the increase of mol.% Al_s may be explained as that Al-substitution causes the stiffening of the lattice and thus decreases the phonon modes. Stiffening may be caused by 1) the decrease in bond length with increasing Al-substitution since Al^{3+} (0,57 Å) has lower ionic radius as compared to Fe^{3+} (0,67 Å); 2) decrease in the average mass of the lattice with increasing Al-substitution.

However, Distanik (1968) interpreted theoretically that change in mass of non-Mössbauer nuclei in a multicomponent crystal have little effect on the observed f-fraction. Therefore, lattice contraction is the major cause for the increase of the f-fraction.

Influence of the particle size on the recoil free fraction is also considerable. Small particles are not capable to absorb the recoil of incident gamma ray and therefore for recoilles absorption a cooperative momentum transfer to numerous particles in the powder must be taking place (Van Wieringen, 1968).

Quadrupole splitting

In iron hydroxides and oxides quadrupole splitting value varies with temperature and percentages of Al-substitution. The magnitude of quadrupole splitting with Al-substitution varies differently at different temperature. Variation of quadrupole splitting with temperature in hematite has already been discussed. At temperatures greater than Morin transition the quadrupole splitting value of hematite is independent of aluminium substitution (Srivastava, Sharma, 1972). At room temperature this value increases with Al-substitution (Fig. 22). At liquid nitrogen temperature, however, the magnitude of the quadrupole splitting value gradually decreases with increasing Al-substitution up to 32 mol.% (De Grave et al., 1982b) (Table 1). A revised work of those workers (De Grave et al., 1988b) has shown that up to about 3 mol.% Al_s the quadrupole splitting value increases and decreases beyond that (Fig. 5b). Murad and Schwertmann (1986) have shown that the quadrupole splitting value varies systematically with Al_s but strangely no relation between quadrupole splitting and crystal size could be established (Table 2). A plot of quadrupole splitting value against Al-substitution at room temperature (Fig. 23) can be represented by the equations (in mm/s).

$$\Delta E_Q = -0{,}198 - 0{,}10\ (Al_s),\quad r = -0{,}574,$$
$$\Delta E_Q = -0{,}197 - 0{,}10\ (Al_s) - 0{,}07/MCD_{001},\quad r = 0{,}592.$$

Commentary. The variation of quadrupole splitting value with Al-substitution is due to: 1) when Al^{3+} enters into the iron lattice it changes the angle between the c-axis and the magnetic moment of Fe^{3+} leading to the change of quadrupole splitting. Even the slight change of the position of iron and oxygen caused by the Al-substitution changes the EFG value considerably (Artman et al., 1968); 2) The substitution of Fe^{3+} by Al^{3+} causes inhomogeneous lattice contraction due to smaller ionic radius of Al^{3+} than Fe^{3+} resulting in the variation of quadrupole splitting with Al-substi-

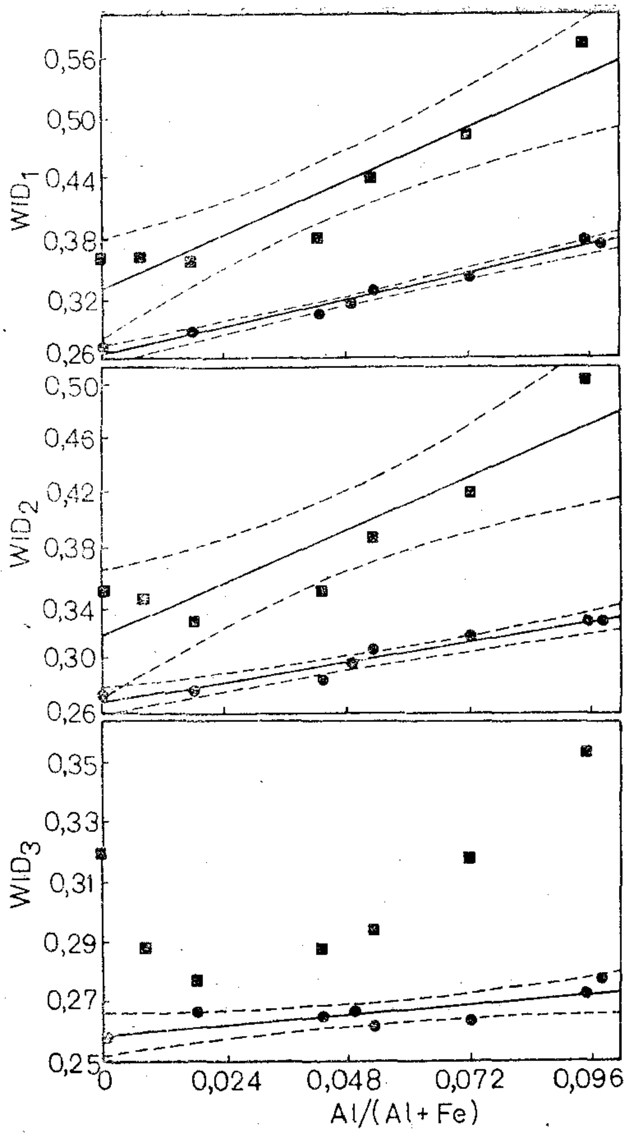


Fig. 25. Variation of widths of outer (WID_1), second and fifth (WID_2), and inner (WID_3) lines of hematites formed at 70°C (squares) and 1000°C (circles) as a function of Al-substitution at room temperature (Murad, Schwertmann, 1986)

Фиг. 25. Вариации на ширините на външната (WID_1), втората и петата (WID_2) и вътрешната (WID_3) линия при хематити, образувани при 70°C (квадратчета) и 1000°C (кръгчета) като функция от съдържанието на алуминия при стайна температура (Murad, Schwertmmann, 1986)

tution at room temperature. At 4,2 K the variation of quadrupole splitting with Al-substitution may be due to small relative changes in atomic position (Artman et al., 1968).

Mössbauer line widths

The Mössbauer line width increases with the increasing Al-substitution. De Grave et al. (1982b) have calculated the line widths of outer absorption lines of hematite and have shown that the line width increases with increasing Al-substitution (Table 1) (Fig. 24). Murad and Schwertmann (1986) have worked in detail about the variation of six lines of hematite at room temperature (Table 2). They have plotted the variation of WID_1 (half widths of lines *1* and *6*), WID_2 (half widths of lines *2* and *5*) and WID_3 (half widths of lines *3* and *4*) with Al-substitution (Fig. 25) and indicated that all the widths increase with increasing Al-substitution and decreasing crystal size. The regression equations of the plots are as follows (in mm/s):

$WID_1=0,265+1,08\ (Al_s)$, $r=0,991$ (for 1000°C hematite);
$WID_1=0,254+1,3\ (Al_s)+5,2/MCD_c$, $r=0,976$ (for 70°C hematite);
$WID_2=0,268+0,60\ (Al_s)$, $r=0,967$ (for 1000°C hematite);
$WID_2=0,256+0,8\ (Al_s)+4,3/MCD_c$, $r=0,976$ (for 70°C hematite);

$WID_3 = 0{,}259 + 0{,}14\ (Al_s)$, $r = 0{,}786$ (for 1000°C hematite);
$WID_3 = 0{,}255 + 0{,}19\ (Al_s) + 2{,}1/MCD_c$, $r = 0{,}966$ (for 70°C hematite).

Similar effects have been reported for goethite by Fysh and Clark (1982a) where the WID_1 and WID_2 are more broadened than the WID_3.

Commentary. Mössbauer line widths depend on sample thickness, source line width, minor instabilities in Mössbauer drives and most importantly on the percentage of Al-substitution in the absorber. From the Fig. 25 it is clear that the effects of Al-substitution and crystal size on Mössbauer line widths decrease from the outer to the inner lines. Since quadrupole splitting affects all lines to an equal extent therefore the variation of line widths is due to the distribution of hyperfine field which results from the variation of the environments of the next nearest neighbouring resonant atoms (Murad, Schwertmann, 1986).

Appendix. The equations on aluminium dependence in hyperfine field

A. Goethite

The equations showing the variation of hyperfine field with the Al-substitution in goethite at different temperatures (in. 80 kA/m) are as follows:

1. At 125 K for a series of medium crystalline samples, the equation (Murad, Schwertmann, 1983) is
(1) $H_i = 485{,}3 - 140Al_s$, $r^2 = 0{,}996$.

At this temperature the fitted curves deviate from the Lorentzian shape which may be due to incipient superparamagnetic relaxation and/or effect of mol.% A_s.

2. At 77 K, considering the surface area (S) of the particles Golden et al. (1979) have found that
(2) $H_i = 498 - 136\ Al_s - 0{,}11\ S$.

3. At 4,2 K the equation (Fysh, Clark, 1982a) is
(3) $H_i = 505 - 52\ Al_s$.

The samples with constant crystallinity with Al-substitution give the equation (Murad, Schwertmann, 1983)
(4) $H_i = 504{,}1 - 44Al_s$, $n = 7$, $r^2 = 0{,}994$.

But where crystallinity decreases with mol.% Al_s, the equation (Murad, Schwertmann, 1983) becomes
(5) $H_i = 500{,}0 - 52Al_s$, $n = 6$, $r^2 = 0{,}996$.

Considering the surface area (S) and the mean crystalline diameter (MCD) of the particles, the relations (Murad, Schwertmann, 1983) are
(6) $H_i = 505{,}4 - 33Al_s - 0{,}036S$, $n = 19$, $r^2 = 0{,}967$
(7) $H_i = 506{,}5 - 42Al_s - 87/MCD_{111}$, $n = 20$, $r^2 = 0{,}969$.

The similar relation of the effect of crystallinity has been also given by Murad (1988) as (in T)
(8) $H_i = 50,\ 65(4) - 4{,}2(3)Al_s - 8{,}7(7)/MCD_{111}$, $n = 19$, $r = 0{,}984$.

B. Hematite

In hematite the variations of hyperfine field with the Al-substitution at different temperatures, as studied by different workers, are as follows:

1. At room temperature up to 20 mol.% Al_s the hyperfine field decreases linearly with Al_s according to the equation (Jonas et al., 1980)

(9) $H_i=509-1,45\ \mathrm{Al_s}$.

Considering both the Al-substitution and crystallinity the relation (Murad, 1988) is (in T)

(10) $H_i=51,72(6)-7,6(10)\mathrm{Al_s}-32(3)/\mathrm{MCD}_{001}$, $n=15$, $r=0,974$.

2. At 300 K two types of hematite samples of different crystallinity give the relation (Fysh, Clark, 1982b) as (in .80 kA/m)

(11) $H_i=517,9-0,82\mathrm{Al_s}$

and

(12) $H_i=515,9-0,86\mathrm{Al_s}$.

But Murad and Schwertmann (1986) have given the following equations of two types of hematite samples formed at 70° C with sample crystallinity from 27 to 40 nm and at 1000° C of bulk crystallinity, respectively (in T):

(13) $H_i=51,72-7,6\mathrm{Al_s}-32/\mathrm{MCD}_0$, $r=0,971$,

(14) $H_i=51,78-8,2\mathrm{Al_s}$, $r=-0,993$.

3. At 4,2 K the equations (derived by the present authors from the data given by Fysh and Clark, (1982b) of two types of samples of different crystallinity are (in .80 kA/m)

(15) $H_i=533-0,05\mathrm{Al_s}$,

(16) $H_i=536-0,42\mathrm{Al_s}$.

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