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Study of Al-substituted hematites, prepared from thermal treatment of lepidocrocite

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Abstract A study of the characteristics of the Morin transition in aluminous hematites, α-$(Fe_{1-x}Al_x)_2O_3$, produced from thermally transformed lepidocrocites, is reported. Six compositions with Al contents between 0.2 and 10 at% have been considered. It is argued that these samples present the advantage that they contain smaller amounts of hydroxyl and water as compared to hematites obtained by other preparation methods. The samples were characterised by a variety of conventional techniques, including thermal analyses, X-ray diffraction, FTIR, TEM/EDX, BET surface-area measurements and diffuse reflectance spectroscopy. All results indicate that the Al is structurally incorporated in the hematite lattices. Transmission Mössbauer spectra were recorded at various temperatures between 80 K and room temperature in order to precisely determine the Morin-transition region and the spin structure in both the low-temperature antiferromagnetic and weakly ferromagnetic states. It was found that the Morin-transition temperatures are markedly higher as compared to similar hematites made from aluminous goethites and that a transition phenomenon persists to an Al substitution of up to at least 10 at%. This different behaviour is ascribed to lower concentrations of structural hydroxyl groups in these lepidocrocite-based hematites.

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Introduction

The well-known oxide hematite (α-Fe_2O_3) has been investigated by a countless number of researchers since the early days of the past century, using a variety of relevant physical techniques. It has the same crystal structure as corundum (Al_2O_3) and can be looked upon as either rhombohedral or hexagonal. The space group is $R\bar{3}c$ or D^6_{3d}, respectively. Despite intensive research, some of its features are still not fully resolved. One of these properties concerns the Morin transition (MT), a temperature (and external magnetic field)-driven transition, characterised by a change in magnetic structure from weakly ferromagnetic (WF) at high temperatures, with the spins lying in the basal plane (111) (rhombohedral unit cell) and slightly canted from the antiparallel alignment, to pure antiferromagnetic (AF) at low temperatures, with the spins parallel to the [111] direction. For pure, well-crystalline hematite this transition takes place at a transition temperature $T \approx 265$ K and was given a phenomenological explanation by Artman et al. (1965). For a recent overview of the various macroscopic magnetic properties of hematite, the reader is referred to the booklet written by Morrish (1994).

Briefly, theory predicts the MT to occur at the temperature T_{M}, where the critical field, necessary to align the spins along [111], becomes zero. At this temperature, the relevant relation between the various anisotropy fields can be written as Eq. (1):

$$H_{K1} = (H_D^2 - 2H_E H_{K2})/2H_E \ , \tag{1}$$

where H_{K1} describes the field associated with the first-order crystallographic anisotropy constant K_1 for the rhombohedral lattice, given by $H_{K1} = K_1$

$(\cos^2\theta + \sin^2\theta)$ and θ is the angle between the direction of the magnetic field and the [111]-axis. Similarly, the second-order crystallographic anisotropy is described by the field $H_{K2} = K_2(\cos^4\theta + \sin^4\theta)$ with K_2 a second-order anisotropy constant. This second-order anisotropy was first added on empirical bases to account for some fitting errors occurring in magnetic measurements (Morrish 1994). H_D is the mean field associated with the Dzyaloshinsky antisymmetric exchange interaction (Dzyaloshinsky 1958) and H_E the exchange mean field. In first approximation, i.e. neglecting H_{K2}, the MT occurs where K_1 changes sign. Since H_{K1} is the result of two opposing contributions with different temperature dependencies, namely the magnetic dipolar anisotropy (favouring spin orientation in the basal plane) and single-ion anisotropy (resulting from spin-orbit coupling and favouring alignment along [111]), the MT takes place at the temperature where these two anisotropy terms cancel each other out.

Substituting a diamagnetic element for Fe alters the anisotropy terms, in particular the dipolar one (Besser et al. 1967), and the exchange energy, hence affecting T_M. Several other factors, however, are interacting and/or competing, such as associated impurities, structural water and hydroxyl groups, defects, strain etc. All these features have significant effects upon the MT, commonly concomitant with those resulting from substitutions. Some authors have even claimed to observe that at low temperatures the WF phase is restored after the hematite has been irradiated with neutrons (Bakkaloglu et al. 1992; Zhetbaev et al. 1992). Originally, changes in the unit cell caused by the presence of substituting cations were assumed to be isotropic. However, a recent paper of Dang et al. (1998) emphasised the aspect of non-isotropic changes in the unit cell, and their effects on the occurrence of an MT, after thermal annealing of the hematite powder. In summary, the large variety of influencing elements explains the large variety of T_M reported in the literature (de Bakker et al. 1991).

In this paper, aluminium-substituted hematites, prepared by thermal decomposition of aluminous lepidocrocites, will be considered. In an evaluation of literature data, de Bakker et al. (1991) have indicated that non-substituted lepidocrocite-based hematites exhibit T_M that are among the highest ever reported. The present study is an extension of a previous one on aluminous hematites obtained from goethites, hereafter referred to as HGO samples (De Grave et al. 1988a, b). From the point of view of purity, the circumstances under which the transformation from goethite to hematite takes place are known to be problematic, since the process develops at cracks and pores, growing from the outside to the inside of the α-FeOOH grains (Wells et al. 1989). This means that a high amount of water molecules and hydroxyls are likely to be incorporated in the hematite structure (formation of protohematite), which, in turn, will influence T_M. Heating of this protohematite to 475–500 K would not completely eliminate this water. According to Wolska (1981), hematite can retain up to 3% of structural hydroxyl and water, even being resistant to heating near 1000 K. The release of water from the latter, so-called hydrohematite, is believed to be slow and not characterised by any specific transformation temperature. On top of the reduction of the mean crystallographic grain size, aluminium incorporation in the hematite structure favours the substitution of O^{2-} by OH^- and associated cation vacancies (Wolska 1981). Thus it is obvious that it is not straightforward to separate the effects of structural water, aluminium substitution and crystallographic parameters. For this reason, hematite powders were prepared by firing lepidocrocites (γ-FeOOH), a method presenting the advantage that the amount of structural water is limited, since a first dehydration step (characterised by the transformation temperature of γ-FeOOH into γ-Fe_2O_3, hereafter called LMT) is well separated in temperature from the structural transformation from maghemite to hematite (characterised by the transformation temperature of γ-Fe_2O_3 into α-Fe_2O_3, hereafter called MHT).

Experimental methods

A series of six lepidocrocite samples was prepared following the wet synthesis described by Schwertmann and Wolska (1990). Mixtures of suitable amounts of 0.1 M $FeCl_2$ and $Al(NO_3)_3$ solutions were oxidised during 3 h with CO_2-free synthetic air while being thoroughly agitated and kept at constant pH = 8 (with NH_3 and an NH_3/NH_4Cl buffer). Aluminium-for-iron substitution was aimed at 0.2, 1, 2, 5, 7 and 10 at% respectively. Previous results of De Grave et al. (1996a) confirmed that lepidocrocites synthesised in this way have the aluminium structurally incorporated. The following identification labels are used for the samples: LEX (for the lepidocrocite powders) and HLEX (HLE = hematite from lepidocrocite) for the corresponding hematites with X the at% Al. When appropriate to express the Al concentration on a scale between 0 and 1, x is used. The temperatures of the successive thermal transformations of γ-$Fe_{1-x}Al_xOOH$ at atmospheric pressure were followed with DTA–TGA (differential thermal analysis) and DSC (differential scanning calorimetry), both at a scan rate of 5 K min^{-1} in the temperature range of 293–923 K. Based on the results of the thermal analyses, all samples were annealed at a maximum temperature of 925 K for 24 h. The hematites obtained were characterised using various standard techniques: BET-specific surface-area determination by N_2 adsorption, TEM/EDX, XRD, FTIR and diffuse reflectance spectroscopy.

Powder XRD patterns were obtained with a Phillips PW diffractometer using FeK_α radiation (wavelengths: $\mathrm{FeK}_{\alpha1} = 0.193597$ nm; $\mathrm{FeK}_{\alpha2} = 0.193991$ nm; mean value: $\mathrm{FeK}_\alpha = 0.193728$ nm). The patterns, recorded in steps of 0.02° (2θ), were computer-analysed with the GUFI 5.0 program (Dinnebier and Eysel 1990). From the broadening of the diffraction lines the mean coherence length in a direction perpendicular to an [hkl] plane, MCL_{hkl}, was derived using the well-known Scherrer approximation with $K = 0.9$ (Klug and Alexander 1974). These MCL values are a quantitative measure for the degree of crystallinity, provided that any substituents present in the lattice do not have a substantial effect on the unit-cell parameters. This is the case for Al-for-Fe substitution in hematite. Global and local EDX measurements in TEM on dispersed clusters of particles were performed for Al and Fe using a metallurgical and biological thin-film correction method, to obtain a qualitative measure for the distribution of aluminium between and inside clusters. The IR spectra were measured on a MIDAC FTIR spectrometer. Samples for these studies were dispersed in dry KBr pellets, about 1 mg in 300 mg KBr. The spectral manipulations of baseline adjustment, smoothing and normalisation were performed using the software package GRAMS (Galactic Industries Corporation, New Hampshire, USA). Band component analyses in the range between 400 and 600 cm^{-1} were carried out with Gaussian line profiles. It is known that FTIR spectra allow differentiation between the incorporation of foreign cations, e.g. Al, and the presence of OH^- in α-Fe_2O_3, which is based on the observation that hydroxyl and Al shift the absorption bands in opposite directions with respect to those for pure bulk hematite, and on the appearance of additional bands in the spectra (Wolska and Szajda 1988).

Reflectance measurements on the HLEX series were determined with a Varian Cary 1E spectrophotometer equipped with a diffuse reflectance attachment. To prevent orientation and saturation effects, the measurements were carried out on mixtures of 3 wt% HLE–97 wt% $BaSO_4$. The reflectance (R) values were taken at intervals of 0.5 nm in the range 380–710 nm. The second-derivative curves of the Kubelka-Munk remission function, $[(1-R)^2/2R]$, were obtained according to a method described by Scheinost et al. (1998). Minima in these curves quantify the positions of the absorption bands due to Fe^{3+} ligand-field transitions and transitions due to magnetically coupled Fe^{3+} in adjacent sites (Sherman and Waite 1985) and hence may be affected by the presence of substituting cations.

Mössbauer spectroscopy was applied to examine the spin structures and to determine T_M intervals, making use of a temperature-controlled cold-finger cryostat, cooled with liquid nitrogen. To prepare absorbers with a reasonably uniform thickness of ~10 mg Fe cm^{-2}, the hematite powders were dispersed in sugar and the mixtures subsequently sealed in a brass holder. A ^{57}Co source in a Rh matrix was mounted and kept at room temperature (RT). Spectra were accumulated in 1024 channels on a time-mode spectrometer with constant-acceleration drive and triangular reference signal. Off-resonance count rates were typically at least 10^6 counts per channel. The spectrometer was regularly calibrated with a standard α-Fe_2O_3 absorber. The velocity increment per channel was ~0.045 mm s^{-1}.

For substitutions of up to 7 at% Al, Mössbauer spectra (MS) were taken between 80 and 293 K in steps of 30 K outside the region of the MT and in steps of 5 K where the transition gradually evolves. For higher Al contents, for which the MT is more smeared-out, a step of 10 K was taken. Fitting symmetrical, Lorentzian-shaped sextets using house-made software analyses of the MS was performed. Isomer shifts δ, quoted hereafter with respect to α-Fe at RT, quadrupole shifts $2\varepsilon_Q$ and hyperfine fields H_{hf} were adjustable parameters, as well as line widths Γ and $\Delta\Gamma$, and intensities.

Results

As referred to in the Introduction, the observed T_M is strongly dependent on the origin and preparation of the oxide. Therefore, the samples will be characterised in a thorough manner before T_M will be considered from the point of view of Mössbauer spectroscopy.

Sample characterisation

Measurement data can be summarised in the following figures and tables. All numerical data are available on request. Figure 1 reproduces some selected DSC curves of the parent LEX.

The hematite lattice parameters a and c of the (rhombohedral) unit cell, and some MCL_{hkl} values are listed in Table 1.

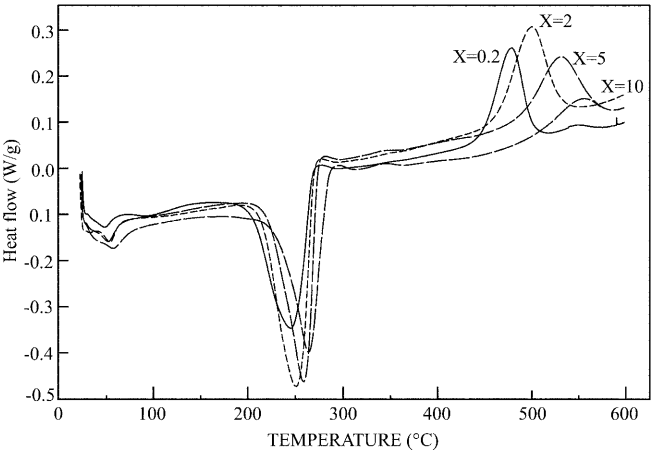

Fig. 1 DSC scans of Al-substituted lepidocrocite (LEX series)

The positions of the five relevant Gaussian profiles fitted to the experimental FTIR spectra (range 400–600 cm^{-1}) of the HLEX are given in Fig. 2.

Another important aspect related to the Al substitution and its influence upon T_M is the degree of porosity of the oxide. Commonly, the specific surface area S_{HLE} (in m^2g^{-1}) as determined by BET quantifies this feature. For HLEX, a linear relationship between S_{HLE} and the aluminium content x (between 0.002 and 0.1) was found:

$$S_{HLE} = 10 + 200x \ (r^2 = 0.98) \tag{2}$$

Not only the surface changes with Al, but also the morphology (Fig. 3).

The results of the diffuse optical reflection measurements on our materials are reproduced in Fig. 4.

Mössbauer spectroscopic characterisation and determination of MT

The relevant hyperfine parameters of the hematite powders are listed in Table 2 and (multiple) regression analysis of H_{hf} as a function of x and of $1/MCL_{104}$ (in nm^{-1}) leads to the following Eq. (3):

Table 1 MCL_{hkl} values calculated from Sherrer's formula (K = 0,9) for the HLE series (Å) and unit-cell parameters a and c (Å) of the corresponding rhombohedral unit cells. The unit-cell parameters are calculated from the spectra with a zero-correction method using the program UnitCel, Holland and Redfern (1995)

HLE X=	MCL_{hkl}			a	c
	hkl = 012	104	110		
0.2	1845	1539	1552	5.0343	13.7378
1	1711	1742	1645	5.034	13.7469
2	910	807	1050	5.0299	13.7402
5	886	800	861	5.0287	13.7276
7	816	698	849	5.0233	13.7026
10	514	502	545	5.0251	13.7278

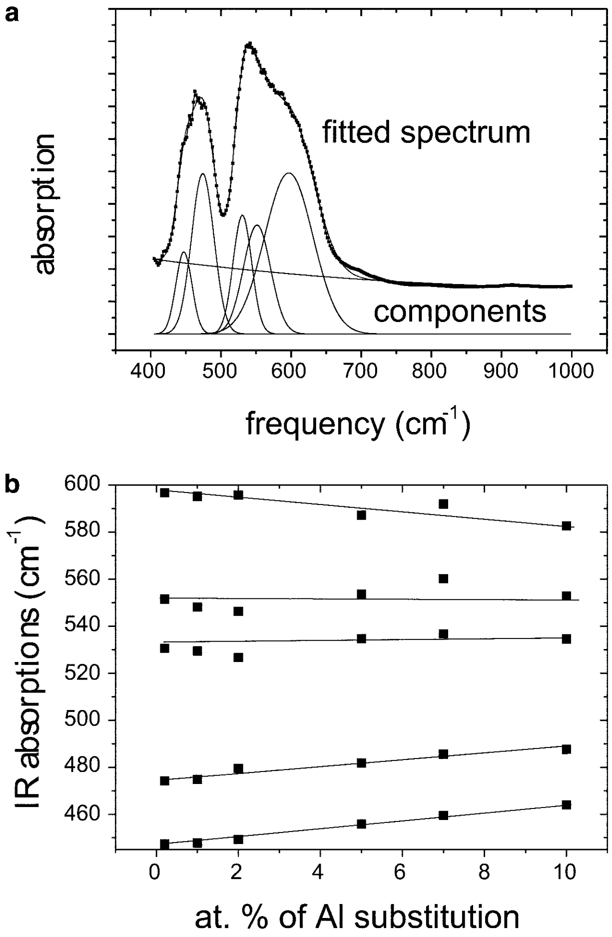

Fig. 2a, **b** FTIR data on the HLEX series. **a** Fitting of HLE0.2. **b** Evolution of the peak positions as function of Al substitution

$$H_{hf} = 517 - 66x - 13.3/\mathrm{MCL}_{104} \; (r^2 = 0.98, n = 6) \quad (3)$$

Extrapolation to $x = 0$ yields the value of 517 kOe which is typical of pure well-crystallised hematite.

Table 2 also contains the T_M values for the different samples and Fig. 5 depicts the variations of T_M as a function of the Al substitution x and of the unit-cell parameters a and c.

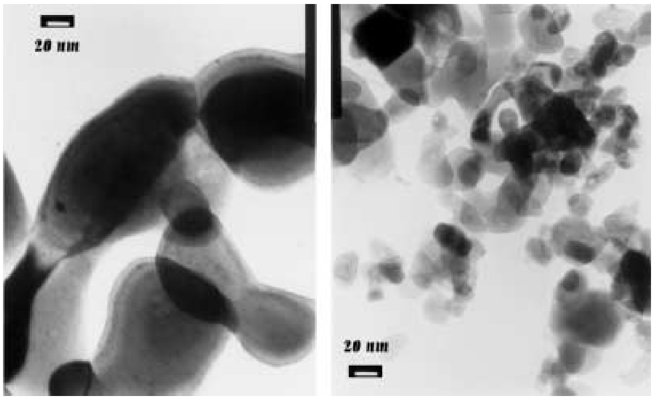

Fig. 3 TEM micrographs of HLE1 (*left*) and HLE10 (*right*), showing an aluminium-induced morphological change from acicular to small, rounded and disc-like particles with rising Al content

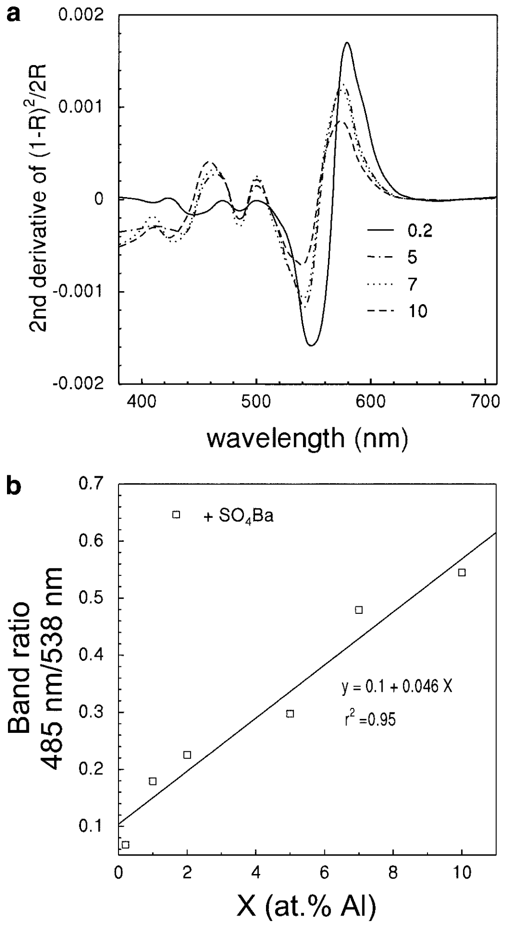

Fig. 4a, **b** Optical reflectance analysis of the HLEX hematites. **a** Second derivative of $(1-R^2)/2R$ for selected X. **b** Ratio between two band amplitudes in function of Al

Discussion

Sample characterisation

During the thermal transformation processes of LEX, there is an overall weight loss between RT and 650 °C of 11 wt%, slightly increasing to 14 wt% for higher Al concentrations. However, taking into account the uncertainties of the method, the amounts of water and structural OH$^-$ groups released from the powders may as well be considered to remain constant. Weight loss is completed just after the formation of γ-$(\mathrm{Fe}_{1-x}\mathrm{Al}_x)_2\mathrm{O}_3$ after which the weight remains constant. This finding explains why the transformations result in hematite particles with a low H_2O content. In first approximation both LMT and MHT rise by ~1% per at% Al and they are also broadened by the substitution (Fig. 1), which is in line with expectations reported in the literature (Cornell and Schwertmann 1996). A correlation between

Table 2 Parameters derived from Mössbauer analysis of the HLE series (*I* and *II* are explained in the text). An error of 1 K on T_M, 0.5 kOe on H_{hf}, 0.01 mm s^{-1} on δ and $2\varepsilon_Q$ and at least 2% on the relative area fractions is taken into consideration

HLE X=	T_M (I) (K)	T_M (II) (K)	H_{hf},RT, kOe	$H_{hf,AF}$ 80 K, kOe	$H_{hf,WF}$ 80 K, kOe	δ (α-Fe) 80 K, mm s^{-1}	$2\varepsilon_{Q,AF}$ 80 K, mm s^{-1}	$2\varepsilon_{Q,WF}$ 80 K, mm s^{-1}	% AF 80 K
0.2	241	241	516.2	540		0.48	0.38		100
1	229	229	514.2	539		0.47	0.38		100
2	223	223	513.3	539		0.48	0.40		100
5	205	197	511.2	538	534	0.47	0.35	−0.01	73
7	195	190	509.7	537	533	0.47	0.39	−0.02	80
10	197	123	506.7	537	529	0.47	0.33	−0.14	53

excess water in the parent lepidocrocite powders and the MHT temperature as reported for pure lepidocrocites by de Bakker et al. (1991) could, however, not be confirmed in the present study. For all these reasons, it is believed that Al is indeed substituting Fe in HLEX and that the Al-for-Fe substitution is the most dominant factor determining the shifts of the LMT/MHT temperatures. This suggestion is further supported by a study of Vajpei et al. (1987), who found that microporosity of the samples, morphology and particle profiles (rather than the grain size) are the more important parameters that govern both the LMT and MHT.

The XRD data (Table 1) indicate single-phase hematite structures for all compositions, with some line-broadening that increases with the Al concentration. Obviously, there are straightforward correlations between these structural parameters on the one hand, and the Al content on the other. Compared to the study of Stanjek and Schwertmann (1992) about the influence of aluminium substitution on the structural parameters of hematite, our values for *a* and *c* are higher than the corresponding values for the oxide which the latter authors used as high-temperature material. However, caution should be taken to interpret this solely in function of proton and OH^- uptake since a large number of parameters interplay, including the preparation method of the hematite. This is reflected by the low r^2 values in the fitted relationships between the degree of substitution for Fe and the cell parameters.

As for the FTIR measurements (Fig. 2), the frequencies of two absorption bands attributable to Fe–O lattice vibrations (Wolska and Szajda 1988; Wolska 1988) are clearly correlated with the Al content. Their values, 447 and 474 cm^{-1} for the non-substituted sample, both shift to higher (more corundum-like) wave numbers. The 597-cm^{-1} band evolves to lower values as the Al content increases. This band is reportedly due to OH^- groups (Wolska and Szajda 1988). Compared to the IR spectra reproduced by these authors, the intensity of that peak for the present hematites remains limited and comparable to spectra of low water-containing samples. The positions of our bands at 530 and 550 cm^{-1} have no clear relation with the Al content and they probably both result from the interplay between Al and changes in the particle geometry (going from ellipsoidal to rounded discs). Vempati et al. (1990) observed similar absorption frequencies (reportedly resulting from vibrations parallel to the *ab* plane), depending on the preparation route and/or the resulting particle shape. Serna et al. (1987) considered the effect of Al substitution on IR spectra, based on the work of Barrón et al. (1984). In that case, hematites were hydrothermally synthesised from ferrihydrites. Only two peaks were observed between 400 and 600 cm^{-1} (Eu 450–482 and Au 535–565), with the first (lower) absorption band rising in relative intensity and the second one becoming smaller as the crystallographic *c*-axis, normal to the disc-like particles, became smaller in function of the Al substitution. Since our frequency of 550 cm^{-1} lowers in relative intensity with a higher Al content, and since the TEM photographs show a more disc-like morphology at higher Al concentration (Fig. 3), the behaviour of the frequencies at 550 and 530 cm^{-1} is in line with this explanation.

The order of magnitude of S_{HLE} (Eq. 2) shows that macroporosity for these samples is similar to that for HGO hematites (De Grave et al. 1982), although the LEX have much higher surface values. Therefore, strong effects of porosity on T_M are not to be expected.

For the present hematite preparation route, Schwertmann and Wolska (1990) have performed a chemical analysis showing the aluminium to be structurally incorporated in the lepidocrocite. The EDX results on Al for the derived HLEX hematites indicate that for samples with up to 5% Al substitution, the oxides also contained the aimed at% Al, with a limited concentration distribution between grains of about ~1%. This remains the case for the mean concentrations of HLE7 and HLE10, but larger inhomogeneities (2 to 3%) are measured, with some of the smaller particles in HLE10 containing up to 15 at% Al. No Al_20_3 grains could be identified for any of the Al concentrations.

The second derivatives of the optical reflectance re-emission functions (Fig. 4a) of HLEX clearly exhibit three minima, namely one in the interval 445–420 nm, one around 485 nm and a dominant signal with a minimum in the range 548–539 nm, each of them corresponding to specific electronic transitions. It is interesting at this point to compare the results obtained for the Al hematites with those recently obtained for hematites in which structural incorporation of phos-

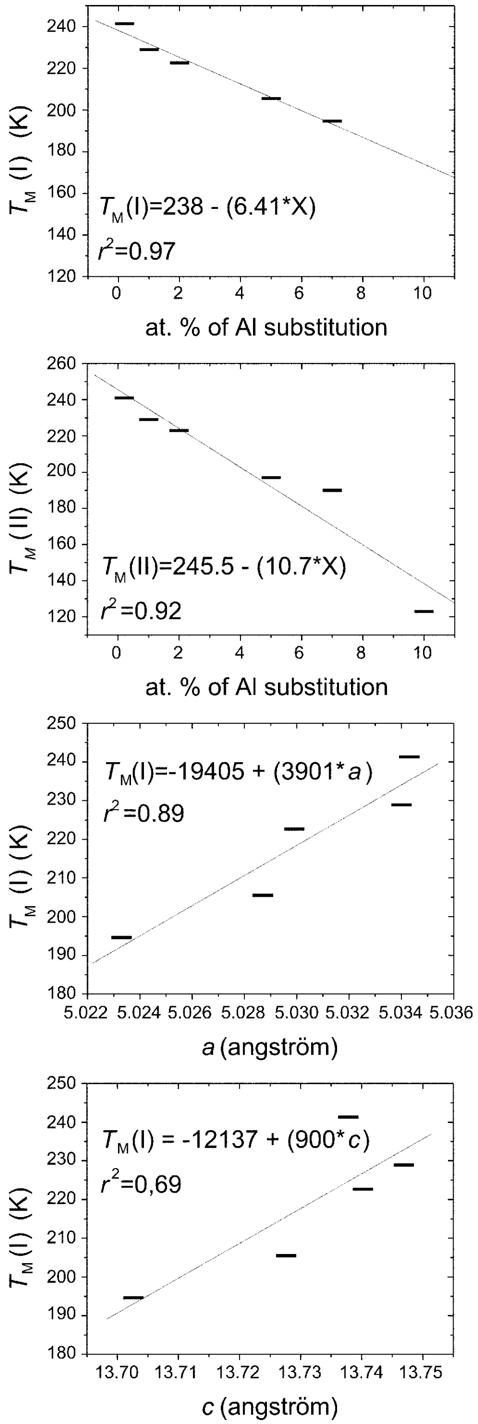

Fig. 5 $T_{\mathrm{M\ HLE}}$ in function of Al substitution and unit-cell parameters *a* and *c* (rhombohedral unit cell). *I* and *II* are explained in the text

phorus was claimed (Gálvez et al. 1999). The authors attributed the 485-nm peak (in their case 488 nm) to a goethite-like behaviour caused by both superficial or structurally incorporated OH^- groups and occluded P atoms. Goethite-like behaviour means in this context: the $2(^6A_1) \rightarrow 2(^4T_1)(^4G)$ pair excitations of Fe^{3+}, typical for goethite, and which also occur in the hematite notwithstanding the proven absence of the latter oxyhydroxide (XRD, MS). The 445–420-nm absorption was related to the electronic transition $^6A_1 \rightarrow {}^4E^4A_1(^4G)$ in hematite and the third peak (548–539 nm) was suggested to be due to Fe^{3+}–Fe^{3+} pair excitations of the type $2(^6A_1) \rightarrow 2(^4T_1)$ (Sherman and Waite 1985). An important result of this P-hematite study is confirmed for the HLE hematites: the increase in the relative intensity ratio of two bands (485–548 nm) with increasing Al-for-Fe substitution (Fig. 4b). A straight line can approximate its correlation with x. This ratio is important in the study of substitution in iron oxides because it is a ratio between a band whose presence is believed to be reflecting substitution-related effects (485–500 nm) and a band normally occurring in hematite (548–539 nm). It is also interesting to note that the regression coefficients of Fig. 4b (HLEX) are considerably smaller than those for P-hematites ($Y = 0.39 + 0.13\,y$ with y the ratio P/Fe in %). From this observation it can be derived once again that only a limited amount of OH^- is captured in HLEX, while in the second material the uptake of OH^- is believed to mount concurrently with the substitution of P-for-Fe. Possibly, grain growth and sintering phenomena also play some role in the determination of the regression coefficients.

There are also some other significant differences in the reflectance behaviour of HLEX and the P-containing samples. Gálvez et al. (1999) found the positions of all the absorption bands to be independent upon the P/Fe ratio. The HLEX (Fig. 4a) show a significant correlation between Al and the positions of both the lowest-wavelength absorption band (minima between 446 and 423 nm) and the highest-wavelength one (minima between 548 and 539 nm). This suggests the covalence of Fe–O to be influenced by the Al substitution. The shift of the electron pair transition at 548 nm to lower wavelength when Al increases is in line with the results given by Kosmas et al. (1986) for Al-hematites and more recently by Scheinost et al. (1999) for Al-goethites. Thus, Al substitution affects the magnetic coupling of neighbouring Fe^{3+} centres, which is responsible for this absorption band. This can only be the case if Al is indeed structurally incorporated in the oxide. As in the P study, the position of the 485-nm absorption seems to remain unaffected by the Al content; but from the point of view of relative intensities, this goethite-like absorption band was much more intense in the P-hematite series than for our present HLE hematites. Bringing all these findings together, it is suggested that the differences in the optical absorptions of Al- and P-hematites are due to a combination of the following elements: (1) the very low hydroxyl incorporation in HLEX, which is not the case for the P-hematites; (2) a different structural positioning of Al in the sense that less interstitial incorporation is likely to be present in the Al-hematites than in the P-hematites; (3) the smaller substitution range in the phosphorus hematite study (0–3 at% P).

Concluding the sample characterisation, one can state that a non-microporous and low OH^--containing oxide is obtained, with the aimed Al concentration incorporated in the structure, but still showing a correlation between the aluminium substitution and morphology. In this way, already one parameter interfering in the MT is omitted.

Mössbauer spectroscopic characterisation and determination of MT

The MS (Table 2) of the HLEX are very similar to those of the HGO hematites (De Grave et al. 1988b). Single sextets are observed at temperatures above T_M with hyperfine parameters characteristic for the WF spin state, and with line widths slightly increasing with the Al content.

The degree of reduction of H_{hf} with the aluminium concentration (~0.7 kOe per at% Al, Eq. 3) is in agreement with the value found for well-crystallised Al-hematites, made from (Fe, Al) oxinates, which were recently studied by G.M. da Costa et al. (submitted, 2001), and smaller than for hematites prepared from a goethite precursor for which the corresponding regression coefficient is ~0.8 (Murad and Johnston 1987). The physical reason for the decrease in the hyperfine field with Al is ascribed to an increase in the number of Fe^{3+}–O^{2-}–Al^{3+} links and hence a decrease in the average supertransferred hyperfine fields (De Grave et al. 1982).

Also the effect of MCL_{hkl} (Eq. 3) upon the RT hyperfine field is smaller for the HLE samples than for the hematites referred to by Murad and Johnston (1987), who reported a value of 32 for the regression coefficient. The presence of larger amounts of structural OH^-, and probably associated cation vacancies in these latter hematites, are likely to be the reason for this higher value. The dependence of the magnitude of H_{hf} upon the particle size and upon the crystallinity in general is believed to be due to a multitude of different effects of which collective magnetic excitations, interparticle interactions and surface effects are the most important (Mørup 1987).

At low temperatures, the spectra consist of either a single sextet for $x \leq 0.02$, typical for the AF spin state, or of a superposition of AF and WF sextets for higher $x \geq 0.05$, the contribution of the latter at a given temperature increasing with increasing Al content. Some relevant Mössbauer parameters are collected in Table 2. It should be noted that for those spectra exhibiting two sextets, the centre shifts were forced to be equal. The general behaviour of these parameters is similar to that observed for the HGO hematites, except for the fact that for all x up to ~0.08 the AF and WF states coexist down to low temperatures (12 K). A detailed study and explanation of this coexistence and of the spin orientations of the respective states for the HGO series have been reported by De Grave et al. (1988b).

Following previous work from this laboratory, the definition of the MT temperature called (I), T_M (I), is based on the adjusted area fractions of the two subspectra corresponding to the two spin states. The value of T_M (I) is taken as the temperature where the AF contribution is reduced to half its value found from the 80-K spectrum. This latter value can be assumed to be the saturation value, since only insignificant changes will occur on further cooling down from 80 to 4 K. An alternative definition (hereafter called II) of T_M could be to take the transition temperature at the point where 50% of the spectral area fraction is in the WF state. Values are collected in Table 2. From the present measurements, no preference can be expressed and, in order to remain consistent with the previous work, we will continue to use definition I.

The key question to be answered in view of the MT theories as summarised in the Introduction is whether the present results can give any indication as to the order of importance of each structural parameter with respect to T_M. The best linear correlations (Fig. 5) for T_M (I) are found with the substitution degree x ($r^2 = 0.97$), with both x and 1/MCL ($r^2 = 0.98$) and with the unit-cell parameter a ($r^2 = 0.89$). The cell parameter c hardly varies along the HLE series and therefore does not seem to be a prevailing factor as far as the variation of the T_M is concerned. Moreover, as demonstrated by Yamamoto (1968), a change in a has a ten times stronger influence on the dipolar magnetic field than a change in c.

According to Dang et al. (1998), the existence of a MT of pure hematites is determined by the precise values of a and c – which, in turn, are functions of the amounts of OH^- and H_2O incorporated in the structure – rather than by particle size, as is commonly assumed. This vision is not completely transposable to the situation in our aluminium-substituted hematites. The HLE series is situated in what the authors call the hydrohematite region. This assessment is based on the finding that the weight loss on heating at 600 °C for 24 h does not significantly depend on the Al content, whereas it is expected that the hydrophilic nature of Al^{3+} would strongly favour the incorporation of OH^- and create a defect structure. It is therefore believed that changes in T_M (I) must be caused by other factors in addition to the presence of vacancies and structural water. On the other hand, the Al content by itself cannot be the only factor determining T_M (I) since extrapolation (Fig. 5) to $x = 0$ (using the unit-cell parameters $a = 0.5036$ nm and $c = 1.374$ nm for pure bulk hematite) yields a value of ~240 K, which is about 20 K below the value to be expected for well-crystallised non-substituted hematite. Therefore, both grain size and Al-for-Fe substitution are likely to determine the transition temperature to an equal extent. Since a smaller grain size means a larger surface-to-bulk ratio, surface anisotropy may become a relevant parameter. Theoretical considerations of Chow and Keffer (1974) attributed the role of the surface to softening of surface magnons, thus nucleating the WF state in surface regions with strong negative anisotropy fields. These regions then gradually expand inside the crystal (=actual MT) with increasing temperature.

Some authors even reported that in the top surface layers of single-crystal hematite the MT is shifted to higher values with respect to the bulk as a result of surface anisotropy (Nikolov et al. 1988). In the present authors' opinions, no clear-cut evidence for such behaviour was presented.

For the present HLE samples, two more or less strong indications were found that the role of the surface and shape is relevant: (1) the T_M values correlate well with the observed specific surface areas, and (2) ILEEMS (integral low energy electron Mössbauer spectroscopy) measurements, currently in progress, which have a depth sensitivity of only ~5 nm (De Grave et al. 1996b), are revealing that the MT does not to occur from 2% Al onwards, an effect which is so strong compared to the situation in bulk that it cannot merely be explained by a surface enrichment with Al.

The sample HLE10 behaves somewhat differently as compared to the other samples. Its transition temperature T_M (I) of 197 K is not in line with the values of the other HLE samples and the variation with T of the WF quadrupole shift, $2\varepsilon_{Q,WF}$, is unusual in view of the observed variations for the other compositions. This is illustrated in Fig. 6b, where the $2\varepsilon_{Q,WF}(T)$ curves for HLE7 and HLE10 are reproduced. The curves for the other HLE samples are all similar to that of HLE7 in the sense that their saturation values ($T = 80$ K) are between zero and -0.05 mm s^{-1} and that they pass through the point of around -0.14 mm s^{-1} at $T \approx T_M$ (I), to finally reach a constant value of ~-0.20 mm s^{-1} after the MT is completed. In contrast, for HLE10 at 80 K, the WF phase has $2\varepsilon_{Q,WF} = -0.14$ mm s^{-1}, a value which remains constant up to $T \approx T_M$ (I). On further increase of the temperature, $2\varepsilon_{Q,WF}$ decreases very slowly to -0.21 mm s^{-1}, in the sense that there appears to be no real "transition region". The same "smearing-out effect" is also obvious in the temperature variation of the WF spectral area fraction (data not shown).

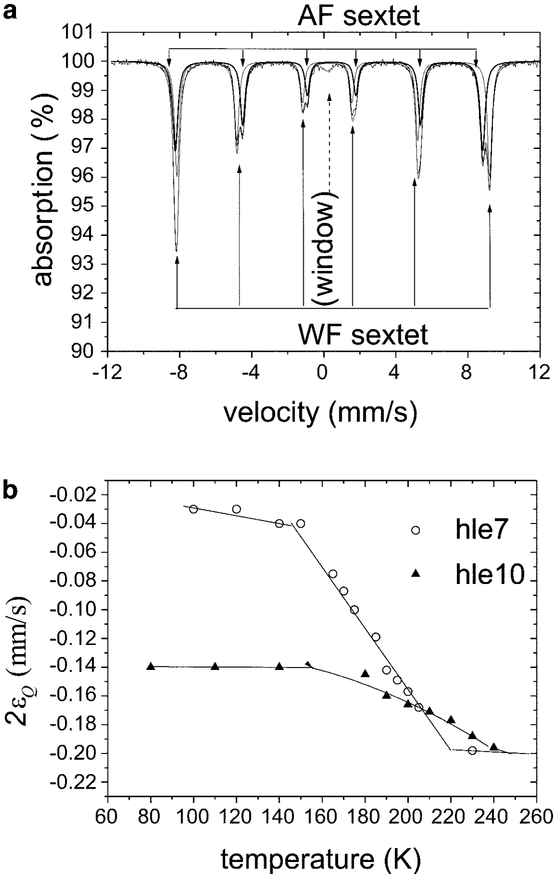

Fig. 6a, b Fitted 80 K Mössbauer spectrum of HLE10 **a** and comparison between the temperature evolution of the fitted WF quadrupole shift for HLE10 and HLE7 **b**

Since the MS (see Fig. 6a for an example) consist of two well-resolved, undistributed sextets with relatively narrow line widths (~0.31 mm s^{-1} for the outer lines at 80 K) and since no traces of a third component could be detected at any temperature, it is unlikely that the high T_M (I) and low $2\varepsilon_{Q,WF}$ (80 K) for HLE10 would be the result of the sample being composed of a mixture of grains with a broad range of Al substitutions, say between $x = 0.0$ and $x = 0.2$. Furthermore, since the WF and AF sextets are well resolved, the difference of 0.1 mm s^{-1} between the low-temperature quadrupole shifts of HLE7 and 10 cannot be due to a fitting anomaly.

De Grave et al. (1983) pictured the MT in Al hematites as a process in which the orientations of the spins of the coexisting AF and WF states at saturation temperatures, both being canted away from their respective axes, gradually change as the temperature rises and finally end up by lying in the (111) plane as in non-substituted α-Fe_2O_3 at RT. The present results for the HLE samples with $x \leq 0.07$ are consistent with this picture. For HLE10, the saturation value of $2\varepsilon_{Q,WF}$ (-0.14 mm s^{-1}) corresponds to spins that are close to being aligned in the basal plane. Furthermore, the 80-K values of $2\varepsilon_Q$ for both AF and WF are in line with those of the other HLE samples while being in the middle of the transition region. Therefore, it can be proposed that for high Al-for-Fe substitutions the MT proceeds with temperature as a continuous reorientation of the highly canted AF spins towards the WF state. A further possible difference between the hematites with low and high Al-for-Fe substitutions could be that for the former ones the WF and AF states do not form physically separated regions in the material and that a thermal equilibrium is established between the two states throughout the grains, as suggested by De Grave et al. (1983) and later by Dang et al. (1998), while for higher concentrations WF and AF fractions are two separate, non-interacting regions, one growing at the expense of the other as suggested by Kvardakov et al. (1991) to be the case for single-crystal hematites. This suggestion is supported by the finding that even at low temperatures the WF spins are not significantly rotated away from the (111) planes, in contrast to the situation for the low substitutions, and indicating that there is probably no interaction between the two states for HLE10.

Obviously, additional research is required to clarify the distinct behaviour of hematites possessing low and high Al-for-Fe substitutions. To this extent, the MT is currently being examined for bulk Al-substituted samples, prepared from firing (Fe, Al) oxinates (da Costa et al. submitted 2001). These hematites exhibit particle sizes which do not significantly depend upon the Al substitution, and their water uptake is presumed to be limited due to the fact that the precursor oxinate products are non-polar organic complexes. The results of this investigation will be presented in a forthcoming paper.

Conclusions

In an attempt to separate the effects of Al-for-Fe substitution on the one hand, and structural and morphological effects and the presence of water and hydroxyl groups (associated with cation deficiencies) on the other, the Morin transition was carefully determined for hematites produced by thermal transformation of aluminous lepidocrocites. Due to the nature of the involved chemical transformation process, hematite powders are obtained which contain far less water, even for high Al-for-Fe substitutions, than the corresponding materials obtained from aluminous goethite precursors. Further separation between the effects of unit-cell dimensions, grain size and Al substitution has remained, however, not feasible. Nevertheless, a few interesting conclusions could be drawn from the characterisation of the Morin transition for the investigated samples. Firstly, notwithstanding the lower hydroxyl uptake in the structure, T_M extrapolated to 0 at% Al substitution remains about 20 K lower than for pure bulk hematite. Secondly, contrary to the case for goethite-based hematite, a 10% Al-substituted sample still undergoes a Morin-like transition, although following a supposedly different mechanism than for the low-substituted hematites, in the sense that a more gradual transition from AF to WF spin states is observed, rather than a real "transition region".

The effect of structural water upon T_M is one factor that has been isolated. Comparison between a 6% Al-containing goethite-based hematite, HGO6, with particle size comparable to that of the corresponding HLEX (De Grave et al. 1988b), shows a Morin transition temperature which is about 20 K lower than the corresponding HLEX (X = 5 or 7) and this difference is even more pronounced for higher Al substitutions. Since ($T_{M,HLE5}$-$T_{M,\text{ pure single crystal hemat.}}$) ≈ 58 K, the effect of hydroxyl on T_M is about one third of the effect due to Al substitution. This is indeed a basic effect related to hydroxyl, since annealing of the HGO6 sample to 950 °C brings the Morin transition temperature to the same value as for the as-prepared HLE7 and HLE5. As the measurements of De Grave et al. (1988b) proved that this annealing did not substantially changed the bulk Al concentration of the goethite-based hematite particles, it is believed that Al depletion cannot be the explanation for the rising of T_M with annealing temperature.

For lower Al substitutions (between 0 and 5 at%), $T_{M,HGO}$ is closer to $T_{M,HLE}$ but, in the first case, the hydroxyl causes the correlation between T_M and Al to be very diffuse, while for the HLEX material a consistent linear relationship between these two quantities is obvious.

The fact that $T_{M,HGO}$ exhibits a significant influence from dehydration is expected in view of the nature of the transformation processes (Mathieu and Rousset 1993). Roughly speaking, dehydration of goethite is such that concurrent with the movement of dislocations to transform the structure, water needs to diffuse through channels, creating voids in the inner structure, thus facilitating structural trapping of H_2O. The structure of lepidocrocite (space group $Cmc2_1$) is such that perpendicular to [111] two layers of (Fe^{3+}, O^{2-}) are alternating with two layers of OH^- so that water is driven out before the first grain of hematite is formed by taking away one full OH layer together with the hydrogens of the adjacent OH layer. The latter is accompanied by a compaction of the (Fe^{3+}, O^{2-}) layers along [111] over a distance a/2 (=0.154 nm). This is a much easier procedure than what happens for goethite and resulting in a more dry material. Therefore, it is important to focus equal emphasis on the preparation route of the hematite materials and on the actual determination of T_M if one wants to compare these data.

At this stage, a next step to be considered is the separation of the effects of crystallinity parameters and aluminium substitution. For this purpose, the preparation method suggested by G.M. da Costa et al. (submitted, 2001) has been explored: hematites were prepared by firing an organic coprecipitate of iron and aluminium oxidants. The short and violent reaction of the organic compounds is believed to inhibit the influence of Al upon the grain size. The produced materials are currently being examined in all details and the results will be reported in a forthcoming paper. The preliminary conclusion of this study so far is that the combination of particle morphology and a reducing of the grain size by a factor of ~10 might lower T_M by approximately 20 K.

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