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New analysis of the Mössbauer spectra of akaganeite

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Abstract

The Mössbauer spectra of akaganeite have always been interpreted considering both the tetragonal structure and the chlorine content. However, very recently it has been suggested that the crystallographic structure is not tetragonal but monoclinic, thus another interpretation for the Mössbauer spectra is required. For this purpose, we have prepared and characterized by several techniques synthetic akaganeite. Our results suggest that the two crystallographic sites required by the monoclinic symmetry are not distinguishable in the paramagnetic state as previously assumed, but they are only discernible in the low temperature magnetic region. At room temperature the spectrum is fitted with two doublets whose origin is related to the chlorine content, i.e. one Fe site assigned to Fe³⁺ ions located close to chloride ions and the other Fe site to those located close to chloride vacancy sites. The low temperature spectra can be adequately fitted with four sextets, whose hyperfine parameters must be subjected to some constraints. The origin of these components is related to the two different crystallographic sites and to the chlorine content. In-field Mössbauer spectrometry at low temperature suggests that the magnetic structure behaves as a system which consists of two asperimagnetic-like structures antiferromagnetically coupled, and not as a collinear antiferromagnet as usually assumed.

1. Introduction

Akaganeite, β -FeOOH, is an iron oxyhydroxide, commonly found in chloride rich environments, which has recently been the subject of numerous investigations, particularly

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related to its role in the understanding of weathering process in steels and meteorites [1–15]. An essential requirement to achieve this goal is to have a deep understanding of the physical, crystallographic and chemical properties of akaganeite. However, in spite of the great number of investigations, these subjects are still matter of controversy. One point that needs to be solved is if akaganeite can be stable without chloride ions in the tunnels. Most investigations support the idea that the presence of Cl ions is of critical importance for the akaganeite formation and stabilization [8–10]. However, other studies have suggested that in exceptional circumstances, like weathering of some meteorites, akaganeite may form with OH⁻ alone, instead of Cl⁻, occupying the tunnels [7]. Rézel and Génin [16] have suggested that Cl ions can be substituted by OH ions without losing stability. Another point of controversy is its space group. X-ray diffraction studies by Mackay [17] and Murad [18] points to the tetragonal *I4/m* symmetry. However, the first crystal structure refinement by Post and Buchwald [8] showed that the monoclinic *I2/m* symmetry produced better fit to the observed x-ray powder diffraction data than the tetragonal one. Additionally, recent synchrotron x-ray and neutron diffraction investigations on both natural and synthetic samples supported this finding [9, 10]. In this way, it seems that the monoclinic should be the space group of choice. Contradicting this result, earlier detailed infrared (IR) spectroscopic studies by Weckler and Lutz [19] suggested that the *I4/m* symmetry is more reliable than the *I2/m* one, because the latter implies that more translational modes of vibration are IR active than the observed ones.

Another point that has also been very controversial is the number of components and their physical origin for the Mössbauer spectra (MS) in both the paramagnetic and the magnetic states. Room temperature MS have been fitted with either two or three doublets. Let us now briefly review some of the different interpretations given to the origin of these two doublets. More models are discussed in the introduction part of the paper by Chambaere *et al* [20]. Murad [18] proposed that the two doublet components arise because of the increasing distortion of mid-wall to channel near iron sites. This interpretation has been based upon a superstructure concept, which was lately rejected by other authors [20]. Chambaere *et al* [20, 21] attributed the lower quadrupole splitting component to the iron site with O₃(OH)₃ coordination and the higher quadrupole splitting doublet to the iron site with O₂(OH)₄ coordination. However, recent investigations have suggested that only O₃(OH)₃ coordination is presented in akaganeite [8–10]. All the previously mentioned interpretations have considered the tetragonal unit cell of akaganeite. Post and Buchwald [8] have suggested that the two quadrupolar components are consistent with the two non-equivalent iron sites, Fe₁ and Fe₂, required by the monoclinic structure. However, there is a problem with this interpretation, because the number of iron ions per unit cell is equal to four for both crystallographic sites, i.e. there are as many Fe₁ sites as there are Fe₂ sites per unit cell. If it is assumed that the Debye–Waller factor for both sites is similar to what it should be, then it is expected that the area ratio of both sites should be approximately equal to one, and not to about $35/65 = 0.53$ as normally observed. Thus another interpretation is required.

Rézel and Génin [16] have proposed that the room temperature spectrum must be fitted with three instead of two doublets, and they argue that the replacement of Cl ions by OH ions in the structure is an important factor to the presence of different iron sites. However, the replacement of Cl ions for OH ions needs further experimental support and is still a matter of controversy. It is noticed that since the works by Chambaere *et al* [20–22] and Murad [13, 18] the two doublet components are generally accepted as the most adequate way of fitting the room temperature Mössbauer spectrum; however, as noticed there is poor agreement about the physical origin of these components.

Now in relation to the magnetic region, most works agree that three sextets are required to adequately fit the spectra. Most investigations based on the tetragonal structure agree in

that the presence of Cl ions in the channels are the cause of the non-equivalent iron sites in the structure. According to Murad [18] the three components arise because of the increasing distortion of mid-wall to channel near iron sites. A different interpretation was put forward by Chambaere and De Grave [22], for whom two sextets are attributed to the Fe–O₃(OH)₃ and to the Fe–O₂(OH)₄ octahedra and the third one is a contribution with fluctuating magnetization, whose intensity at absolute 0 K approaches zero. On the other hand, Rézel and Génin [16] proposed that two of the three components originate from the iron atoms which have chloride ions as first nearest neighbours, whereas the third component is due to iron atoms far from the chlorines. According to Oh *et al* [23] the 77 K spectrum should be fitted with a distribution of hyperfine fields originating from the several magnetically non-equivalent iron sites. This way of fitting does not allow quantitative information on the crystallographic parameters and chlorine content to be directly retrieved. To the best of our knowledge, the only work that has tried to interpret the Mössbauer spectra with three components in terms of the monoclinic structure is that given by Stahl *et al* [9]. For these authors, the components are related to the two crystallographic sites required by the monoclinic space group subjected to a disorder due to the chlorine disorder. However, this work assumes that chlorine is subjected to a disorder, which clearly contradicts the results by Post and co-workers [10] and Weckler and Lutz [15], who propose an ordering scheme with every third chloride site vacant in a particular tunnel.

It is evident that there is poor agreement in the methodology of analysis of the Mössbauer spectra of akaganeite. The purpose of the present study is restricted to an interpretation of the Mössbauer spectra both in the paramagnetic and magnetic states based upon the monoclinic structure and the chlorine content.

2. Experimental details

An akaganeite sample was prepared by thermal hydrolysis of 0.1 M FeCl₃ solution at 70 °C for 48 h according to the procedure as described by Cornell and Schwertmann [24]. The powdered samples obtained are pure as the x-ray diffraction (XRD) analysis shows (see below), i.e. only akaganeite peaks were present, but of course the amount of both chlorine and water present to stabilize the structure remains difficult to estimate accurately. The XRD pattern was obtained using a D500 Siemens diffractometer equipped with Cu K α radiation; data were collected in the 15°–120° 2 θ range with a 0.02° step and a counting time of 10 s per point. The XRD pattern was analysed using a program called MAUD, which combines the Rietveld method and a Fourier transform analysis, well adapted, especially in the presence of broadened Bragg peaks [25]: this program allows us thus to derive crystalline cell parameters and average crystallite size as well as microstrains. The structural model used was that reported by Post and Buchwald [8]. The scale factor, sample displacement, unit cells, five-order polynomial background, chlorine occupancy, and average crystallite size were refined [26]. The average crystallite size and the texture were assumed to be isotropic and arbitrary respectively in the present study. The Mössbauer spectra were collected in a time-mode spectrometer working in the transmission geometry using a constant acceleration drive with triangular reference signal. RT (300 K), 77 and 4.2 K experiments were performed using a bath cryostat while the in-field spectrum was registered in a superconducting cryomagnetic system where the powdered sample is located in an external field parallel to the γ -beam. Calibrations were achieved from a standard α -iron foil at 300 K. The spectra were analysed using a program called MOSFIT, which is based on non-linear least squares fitting procedures assuming Lorentzian Mössbauer lines while the isomer shift value is quoted relative to that of α -Fe at 300 K.

The infrared measurements were made in a Hewlett Packard instrument with a LiTaO₃ detector and without the use of KBr for making the pellets; the sample was poured directly in

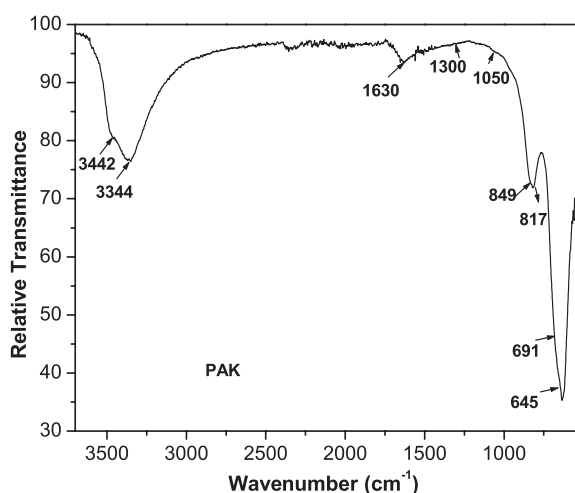


Figure 1. Infrared spectrum of the pure akaganeite.

the equipment over a diamond surface pressing with a pressure gauge. Transmittance spectra were taken in the wavenumber range from 4000 to 500 cm^{-1} . Thermogravimetric (TGA) experiments were performed using a Universal V2.5H TA Instruments Module with samples of about 15 mg under a constant flow of synthetic dry air in the temperature range 20–700 $^{\circ}\text{C}$. The heating rate was 10 $^{\circ}\text{C min}^{-1}$. BET analysis with N_2 was performed in an ASAP 2010 V4.00 D.

The high resolution transmission electron microscopy (HRTEM) and electron diffraction (ED) studies were performed on a 200 kV side entry JEOL 2010 transmission electron microscope (tilt $\pm 30^{\circ}$). A small amount of powder was suspended in alcohol then dispersed using an ultrasonic bath. One droplet of the suspension was deposited on a holey amorphous carbon film, supported by a copper grid. The grid was inserted in the microscope after drying. The particles, which were well dispersed on the grid, were unstable and decomposed under an intense electron beam. Consequently it was difficult to adjust the diffraction patterns and to get HRTEM images.

3. Results and discussion

Figure 1 shows the IR spectrum of the synthesized sample. All bands can be assigned only to akaganeite phase, demonstrating the purity of the sample [19, 27]. The OH- and H_2O -stretching region is characterized by two intense bands. The main band is located near 3334 cm^{-1} with a weaker band near 3442 cm^{-1} . The H_2O -bending band is considerably weaker than the OH- and H_2O -stretching bands and is located at an average wavenumber of 1630 cm^{-1} . The spectrum showed a band at 849 cm^{-1} that has been alternatively assigned to interactions of H_2O molecules with the tunnels or to O–H \cdots O bending vibrations, and a shoulder at 817 cm^{-1} . Two modes of librations, O–H \cdots Cl at 691 and 645 cm^{-1} , are assigned to the two hydrogen bonds [19].

The TGA curve is shown in figure 2. The first derivative of the weight with respect to the temperature suggests the existence of at least two different regimes of weight loss. The first one, which ends at about 80 $^{\circ}\text{C}$, is mainly assigned to the departure of surface adsorbed water (% H_2O) [9, 21, 28]. The second and most important region of weight loss, which ends at about 490 $^{\circ}\text{C}$, is associated with the departure of structural hydroxyl and chloride ions. The TGA curve in this region is not as abrupt as for other curves reported in the literature [9, 28]. In fact, the first derivative shows three peaks located at about 245, 334 and 490 $^{\circ}\text{C}$. Above this last

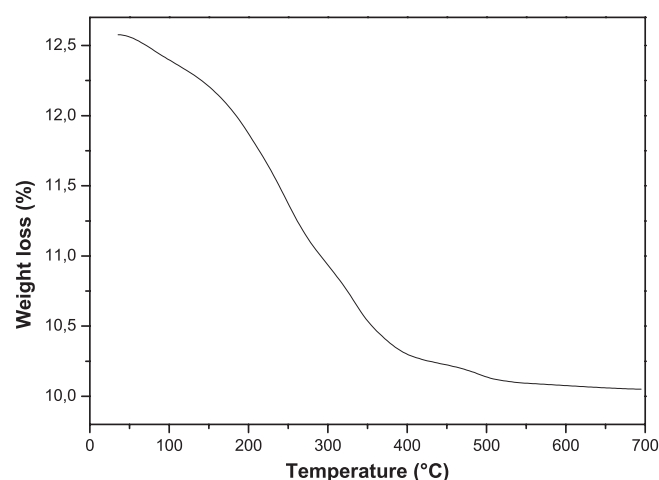


Figure 2. Thermogravimetric curve of akaganeite.

temperature the weight remains rather constant and it is associated with haematite formation. The shape of this curve could be thus related to the different degree of crystallinity and chlorine content of our sample. The overall weight loss is reflected in the following equation:



The akaganeite formula on the left part of (1) considers explicitly the crystallographic data reported by Stahl *et al* [9] and by Post *et al* [8, 10]. The unit cell contains 2×4 octahedrally surrounded Fe atoms, 4×2 O atoms and 4×2 OH atoms. The square brackets represent the chlorides in the tunnels: there are three of these sites, but only two (or less than two) are occupied, whereas the third one is vacant. Two charge compensating protons and the absorbed water content per cell are also included in the formula. It is found that (1) predicts a weight loss of about 19%, which is in good agreement with the observed TGA weight loss estimated at about 20%. The small difference could be related to some degree of non-stoichiometry in the akaganeite. The adsorbed surface water accounts for just 1% of the weight loss in the sample.

A BET surface area value of $25 \text{ m}^2 \text{ g}^{-1}$ was obtained, which is very close to the value reported by Schwertmann and Cornell [24].

Figure 3 shows the XRD pattern of the powdered sample. The x-ray pattern is adjusted by introducing only a single phase, akaganeite (PDF: 80-1770) [29]. The pattern was adequately adjusted with the $I2/m$ monoclinic space group, giving the unit cell values of $a = 10.5422(6) \text{ \AA}$, $b = 3.0349(1) \text{ \AA}$, $c = 10.5259(6) \text{ \AA}$ and $\beta = 90.1133(5)^\circ$ [26]. The chloride site occupancy was estimated at about 0.6.

TEM images (figure 4) have revealed that the crystallites were very homogeneous both in size and shape. Most of the particles looked like needles, about 250 nm in length and 50 nm in width, but a few crystalline grains had the shape of crosses or six-arm stars. A characteristic 30° angle was observed between the branches of both crosses and stars. The size of the branches was very similar in all crystals. The contrast of the images was changing with the defocalization. So either the channel structure or the atomic structure was evidenced. The particle presented a regular contrast with an alternation of dark and white fringes (period about 20 Å). The particles show very fine lines without defects. The intersections of the branches of the crystal were well defined.

The selected area electron diffraction (SAED) study was recorded from a few crystallites (see figure 5). All the spots could be indexed using the monoclinic cell according to previous x-ray diffraction results. The reflection condition $h + k + l = 2n$ leads to an I- - extinction

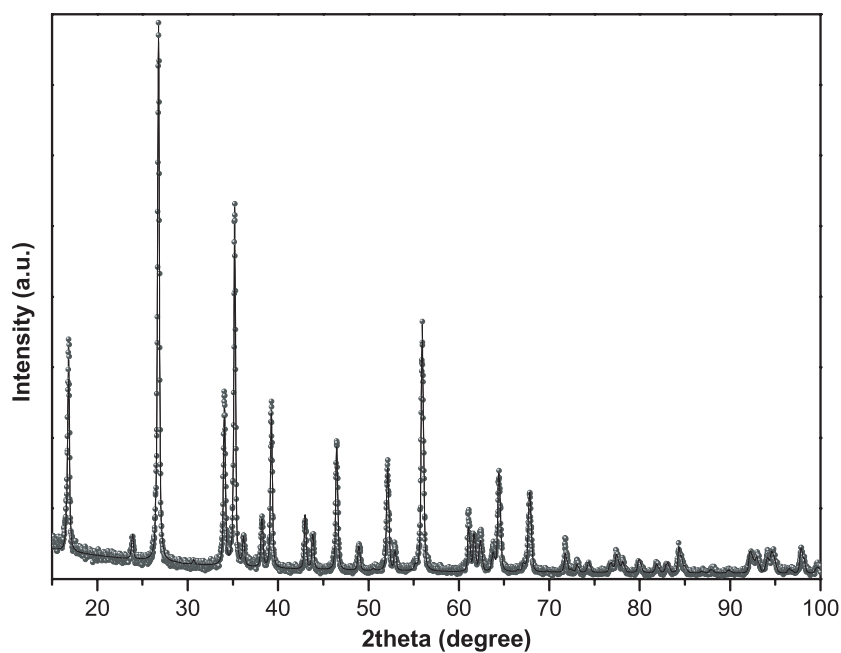


Figure 3. X-ray diffraction pattern of pure akaganeite. The circles represent the experimental data and the solid line represents the fit using the Rietveld method as explained in the text.

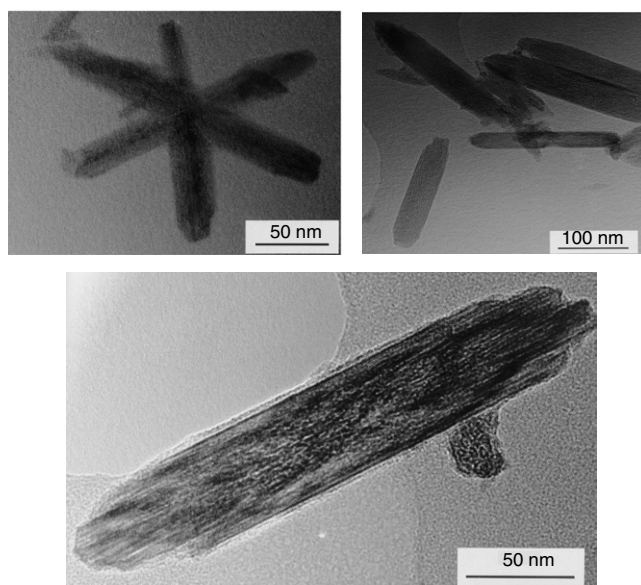


Figure 4. Transmission electron micrographs (TEM).

symbol, consistent with space group $I2/m(N^{\circ}12)$. The spots are slightly streaked rather along a^* and c^* directions: this might suggest either some disorder along the a and c axes or the presence of crystalline domains preferentially oriented along the same b axis.

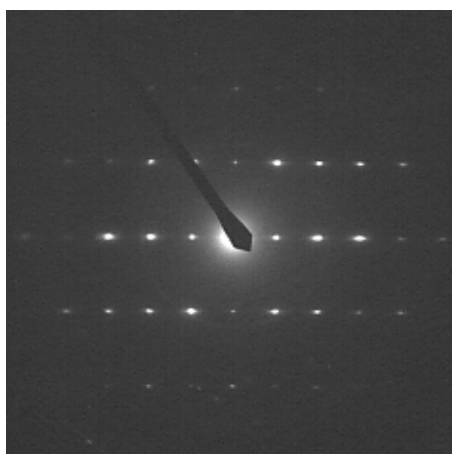


Figure 5. Electron diffraction pattern of akaganeite.

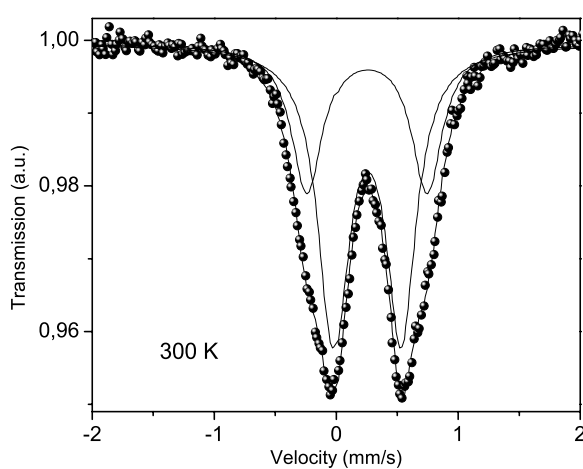


Figure 6. 300 K Mössbauer spectrum of akaganeite. The spheres represent the experimental data, whereas the solid lines show the total fit as well as the subspectral components.

Figure 6 shows the 300 K Mössbauer spectrum (MS) of akaganeite. The quadrupolar structure is described with two quadrupolar components whose hyperfine parameters are reported in table 1. These data are in good agreement with those reported in the literature [1, 13, 18, 20, 21]. However, the origin of these two sites is interpreted in another way. It is possible to see that the area of component D1 with the lowest quadrupole splitting value is of about 65%. This value is very close to the chloride site occupancy of about $2/3 = 0.67$ (or 67%). One is thus tempted to propose that component D1 originates from those irons located close to the chloride sites, while component D2 is attributed to iron atoms located close to the chloride vacancy sites, which accounts for 35% (very close to the value of about $1/3 = 0.33$, for the chloride vacancy site occupancy). It is finally important to emphasize that the area value of component D1 (with the lowest quadrupole splitting) obtained from the room temperature MS is directly related with the chloride site occupancy. According to Post *et al* [10], the Cl ions fill two-thirds of the channel sites in an ordered way with every third channel site vacant. It is also important to recall that the charge balance of the Cl ions is achieved with extra H ions, which are located at 0.190 nm from the nearest O atom and 0.175 nm from the Cl anion. These extra H ions do influence the quadrupole splitting values. Theoretical calculations are required to confirm our suggestions.

Table 1. Hyperfine parameters obtained from the fit of the 300, 77, 4.2 and 10 K with 6 T Mössbauer spectra. Estimated errors are about $\pm 0.01 \text{ mm s}^{-1}$ for the centre shift, δ , line broadening, Γ , quadrupole splitting, Δ , and quadrupole shift, 2ϵ , about $\pm 0.1 \text{ T}$ for the magnetic hyperfine field, B_{hf} , and about $\pm 5\%$ for the area, A . Centre shifts are given relative to α -Fe at room temperature.

T (K)	Components	δ (mm s^{-1})	Γ (mm s^{-1})	Δ or 2ϵ (mm s^{-1})	B_{hf} (T)	Area (%)
300	D1	0.36	0.15	0.54	—	65
	D2	0.36	0.15	0.97	—	35
77	S1	0.45	0.18	-0.12	47.7	32
	S2	0.45	0.18	-0.12	46.3	32
	S3	0.42	0.20	-0.41	45.9	18
	S4	0.42	0.20	-0.41	43.6	18
4.2	S1	0.45	0.21	-0.12	49.5	35
	S2	0.45	0.21	-0.12	48.1	35
	S3	0.42	0.20	-0.39	47.9	15
	S4	0.42	0.20	-0.39	46.7	15
10 K	S1–S2 parallel	0.41	0.25	-0.23	53.0	23
	S1–S2 antiparallel	0.41	0.25	-0.23	46.8	23
6 T	S1–S2 perpendicular	0.41	0.25	-0.23	49.6	23
	S3–S4 parallel	0.41	0.19	-0.21	51.1	11
	S3–S4 antiparallel	0.41	0.19	-0.21	44.1	11
	S3–S4 perpendicular	0.41	0.19	-0.21	48.5	11

Figure 7 shows the 77 K MS of akaganeite, which can be adequately adjusted by introducing either three or four sextets. However, the four sextet fitting model is consistent with the monoclinic structure as well as the chlorine content as is shown below. It is important to mention that several fits with four sextets with either some or no constraints in the values of the hyperfine parameters are possible [26]. However, we have found that among them, the one for which the centre shift, the quadrupole shift, and the line widths as well as the areas for components S1 and S2 and also for components S3 and S4 are constrained to be equal gives the more reasonable results. The derived parameters for this kind of fit are listed in table 1. Several interesting things can be observed. Firstly, the sum of the area values for components S1 and S2 gives 64%, which is very close to the value of 65% for the area of component D1 found in the 300 K MS. Consequently, the sum of the areas for S3 and S4 is very close to that of the D2 component. Moreover, the magnitudes of the quadrupole shifts for S1 and S2 components are lower than the corresponding ones for S3 and S4 components. On the other hand, the magnitude of the quadrupole splitting is lower for the D1 component than for the D2 component. Thus, taking into consideration the area and the quadrupole interaction values, we can assume that S1 and S2 have a similar origin as D1, i.e. come from those iron atoms located close to the chloride sites, and that S3 and S4 are similar to D2, i.e. come from those iron atoms located close to the chloride vacancy sites. This analysis explains why the 300 K MS is fitted with two components while the 77 K MS is fitted with four components: it is because of the constraints imposed on the centre shifts and on the quadrupole splittings to be equal for every two pairs of components that they cannot be distinguished at 300 K where only doublets are observed. To the best of our knowledge, this is the first time that a four sextet model has been proposed to fit the Mössbauer spectrum of akaganeite in the magnetic region.

Figure 8 shows the 4.2 K MS of akaganeite, which again can be reasonably fitted with either three or four sextets. But a model based on a distribution of hyperfine fields also describes

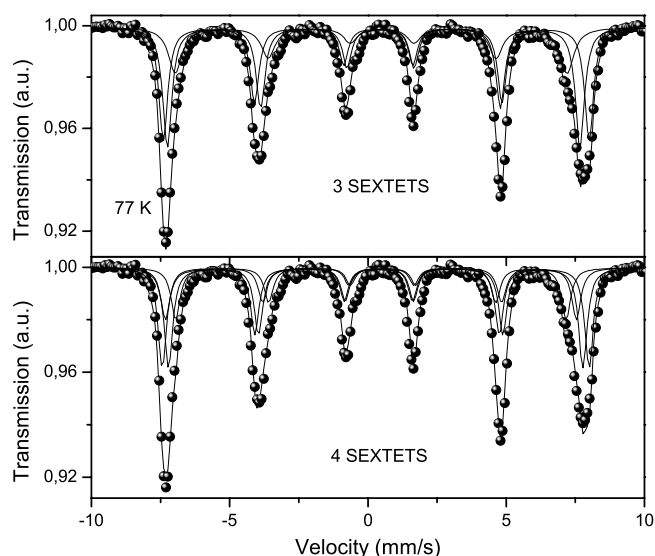


Figure 7. Comparison of the three sextet and four sextet models used to fit the 77 K Mössbauer spectrum of akaganeite. The spheres represent the experimental data, whereas the solid lines show the total fit as well as the subspectral components.

very well the experimental data (data not shown). The derived hyperfine parameters for the four sextets fit subjected to the same constraints as mentioned above are reported in table 1. Again, the sum of the areas for S1 and S2 components at 4.2 K is very similar to that obtained at 77 K, and to the area of the D1 component at 300 K. Moreover, the quadrupole shifts for S1 and S2 at 4.2 K are very similar to those at 77 K, as well those of S3 and S4 for both temperatures. Chambaere *et al* [20] have found that the quadrupole splitting above the Néel temperature is only weakly dependent with temperature, as usually expected in the case of Fe^{3+} . Similar results have also been reported for synthetic goethites above and below the Néel temperature [30, 31].

We will concentrate now upon the origin of these four components. Post and Buchwald [8] have explained that the monoclinic cell requires two symmetrically different iron sites, named Fe_1 and Fe_2 (see figure 1 of that paper). On the other hand, the Cl sites in the channels are clearly represented in figure 5 by Post *et al* [10]. One can see that there are Fe_1 and Fe_2 ions located closer to the chloride ions and other Fe_1 and Fe_2 ions located closer to the vacant chloride sites. Because both Cl^- and OH^- are located in channels, their presence should affect the hyperfine field at Fe sites. It is usually established that the octahedra close to the Cl ions should be more distorted than the octahedra close the vacancies. However, the crystallographic data suggest that this distortion is very similar for both octahedral sites. Next, Post *et al* [10] found that Fe–(O, OH) distances range from 0.194 to 0.211 nm and from 0.198 to 0.213 nm for Fe_1 , and Fe_2 site, respectively. Among the Fe–O distances, the Fe– O_1 and Fe– O_3 are the longest ones, and O_1 and O_3 are the OH^- sites. On the other hand, the Fe–O–Fe bond angles range from about 106° to 132° . The lowest angles are for Fe– O_1 –Fe, whereas the largest ones are for Fe– O_2 –Fe or for Fe– O_4 –Fe. Now, the magnetic superexchange interactions between Fe ions on adjacent sites depend on Fe–(O, OH) bond lengths and specially on bond angles, in such a way that both shorter lengths and higher angles imply stronger magnetic interactions. Taking into consideration these facts, we propose that the larger magnetic fields are for Fe_1 sites (components S1 and S3), whereas the lower magnetic fields are for the Fe_2 sites (components

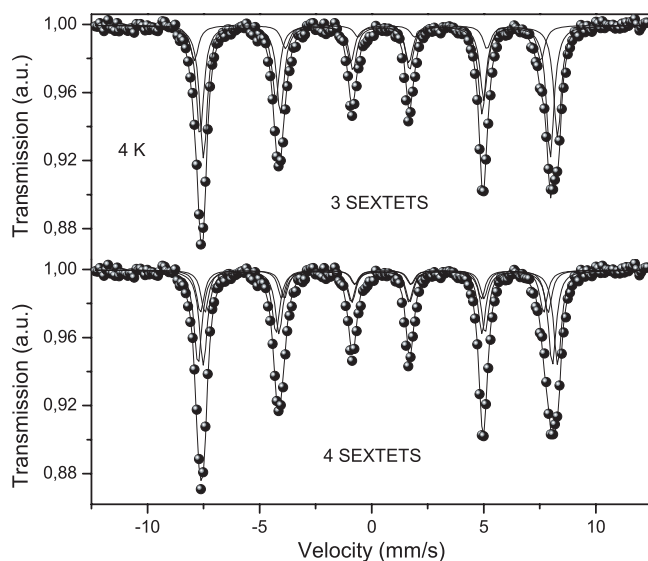


Figure 8. Comparison of the three sextet and four sextet models used to fit the 4.2 K Mössbauer spectrum of akaganeite. The spheres represent the experimental data, whereas the solid lines show the total fit as well as the subspectral components.

S2 and S4). Thus, S1 and S2 components are ascribed Fe_1 and Fe_2 sites close to the chloride ions, respectively, while S3 and S4 components are attributed to the Fe_1 and Fe_2 sites close to the chloride vacancies, respectively.

At this point it is worth mentioning that Yamamoto *et al* [32] have shown that Fe^{3+} ions located at the surface layers of about 0.1 nm thickness are involved in magnetic order and that their hyperfine fields decrease with increasing temperature faster than those attributed to the bulk. It could also occur that surface sites do not strictly relate to the monoclinic structure, which pertains more to a crystalline system but of course may explain the presence of four iron sites. The surface sites do give rise to different magnetic behaviours. To investigate possible surface contributions to the Mössbauer spectrum of akaganeite, we have calculated the shell to core volume ratio, $\Delta V/V$, for different values of the shell thickness, x , taking into account the needle-like morphologies as observed by TEM (see figure 4). If the particles are assumed to have a cylindrical shape of height, h , and radius, r , then $\Delta V/V$ is given by

$$\frac{\Delta V}{V} = 1 - \frac{(r-x)^2(h-2x)}{r^2h}. \quad (2)$$

The shell to core volume ratio, $\Delta V/V$, is plotted for two different values of h and r in figure 9. It is observed that only about 0.01 of $\Delta V/V$ is obtained for $x = 0.1$ nm. Consequently, $\Delta V/V$ should be nearly equal to one of the area values obtained from the fit in the magnetic region (see table 1). However, none of the spectral areas approach 1%. Thus, the influence of the surface effects cannot be clearly evidenced in the MS of akaganeite.

Figure 10 compares the low temperature in-field (6 T) and zero-field Mössbauer spectra of akaganeite: one first observes that (i) the lines are broader than those of the zero-field spectrum, and (ii) the intensity of the intermediate lines is consistent with Fe magnetic moments rather perpendicular to the external field, i.e. the presence of antiferromagnetic interactions. Consequently, the first fitting model consists of a distribution of effective fields which is found to be broader than that of hyperfine fields, as shown in figure 11, and suggesting thus

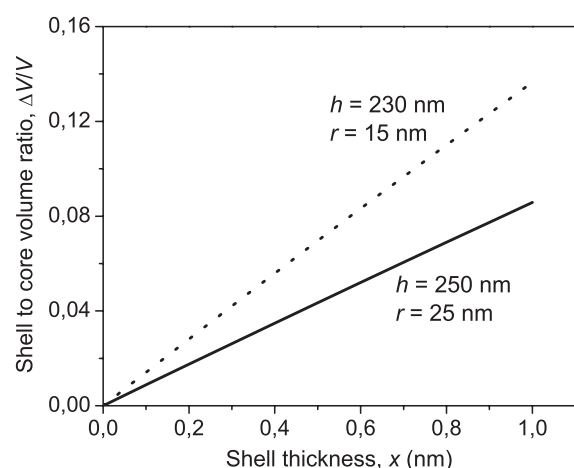


Figure 9. Shell to core volume ratio, $\Delta V/V$, as a function of the shell thickness, x , for two different values of height, h , and ratio, r .

a distribution of canting angles. As a first approximation, according to previous results, one can consider four components which are split into three components, one accounting for the perpendicular orientation (90°) of the hyperfine field to the external field, another one with antiparallel orientation (180°) and the last one with parallel orientation (0°). Such a procedure has been satisfactorily applied in the case of goethites [31, 33]. Thus, 12 sextets (four components multiplied by three split components) are required to fit the spectrum, but the large overlap of the different components prevents a quantitative model from being refined. In order to avoid this overlapping and to reduce the number of components, we can couple the respective S1 and S2 components as well as the respective S3 and S4 components for each orientation. This means that the effective field for each coupled component should be the average of the expected original hyperfine fields. The other parameters, i.e. δ , Γ , and 2ϵ , are restricted to be the same for each one of the three components of S1 and S2 and also for the other three components of S3 and S4. Let us explain in detail one example: according to table 1, the hyperfine field value B for S1 (S2) at 4.2 K is 49.5 T (48.1 T), thus the effective field parallel to the external field should have a value of 49.5 T + 6 T = 55.5 T (54.1 T), giving rise to an average hyperfine field equal to 54.8 T. From the derived parameters listed in table 1, it is also possible to see that a value of 53.0 T is obtained instead of the expected value of 54.8 T. This difference of 1.8 T is much less than the magnitude of the applied external field, suggesting that there is no strict parallel alignment, thus it can be concluded that the moments are canted, due to some topological frustration of antiferromagnetic interactions. Such observation well agrees with the line area ratio, which differs from 3:0:1 for components S1–S2 parallel and S1–S2 antiparallel as expected for parallel alignment between the direction of gamma rays and effective hyperfine fields. These results allow us to propose a first fitting model resulting from two non-collinear magnetic sublattices not perfectly antiparallel: the two asperimagnetic-like sublattices coupled antiferromagnetically well describe the in-field hyperfine structure, as shown in figures 12 and 11 (bottom), respectively. Interestingly, the sum of areas for S1–S2 parallel, S1–S2 antiparallel, and S1–S2 perpendicular gives about 69%, which is very close to those values obtained at other temperatures, and all the other parameters are reasonable and consistent with the methodology of analysis.

Our view is rather consistent with that published by Coey [34], who suggested speromagnetism instead of antiferromagnetism in iron oxyhydroxides. First, the experimental line shapes of the applied field Mossbauer spectra of akaganeite and goethite are very

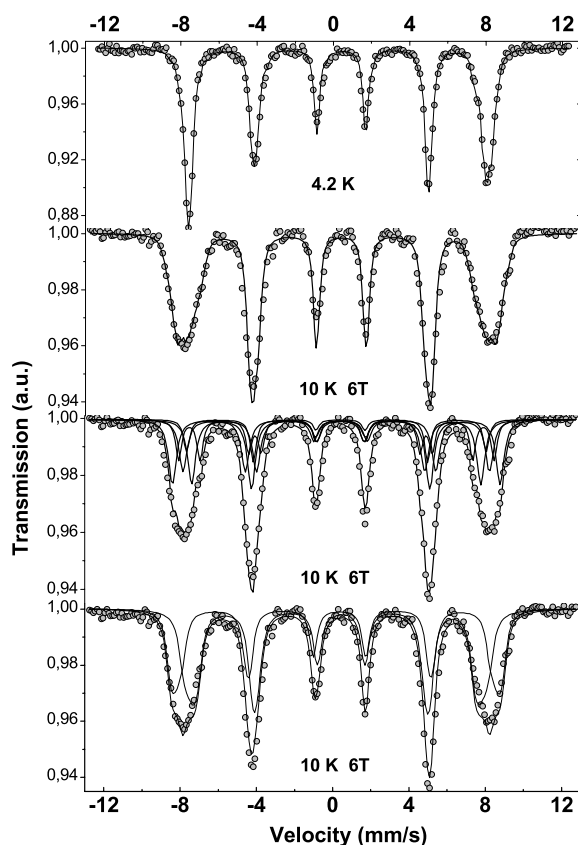


Figure 10. Zero field Mössbauer spectrum of akaganeite obtained at 4.2 K (top) compared to the 6 T field Mössbauer spectrum recorded at 10 K described by three different models as discussed in the text; from top to bottom, using a distribution of effective fields, six discrete components and two asperimagnetic structures antiferromagnetically coupled.

similar [35]. Second, Coey [34] reported that the experimental uniaxial anisotropy values, K_1 , of goethite ($0.01 \times 10^5 \text{ J m}^{-3}$) and akaganeite ($0.03 \times 10^5 \text{ J m}^{-3}$) are very similar too. However, by assuming a normal antiferromagnetism in goethite, a K_1 value of $3 \times 10^5 \text{ J m}^{-3}$ has been reported [36], which is clearly two orders of magnitude larger than the experimental values reported by Coey. Thus, the interpretation of the applied field Mossbauer spectra in terms of the speromagnetic model is preferred. Now, we suggest asperomagnetism instead of speromagnetism in akaganeite for the following reasons. First, it is important to mention that speromagnetism requires that the magnetic materials are either amorphous or highly disordered with the presence of antiferromagnetic interactions, or with the presence of strong local anisotropy. However, akaganeite is neither, but perhaps it is characterized by some degree of disorder, which can be induced by the Cl ions. Second, if the applied field B_{app} , were perfectly aligned to B_{hf} , then the magnitude of the difference between the effective field, B_{eff} , and B_{hf} should be equal to 6 T, i.e. the magnitude of B_{app} . However, the difference is lower, thus it is possible to say that the spins are somewhat canted due to the presence of the applied field. It is possible to calculate, from the effective field distribution and the distributed angles, the hyperfine field distribution without a field. This is a difficult task because there can exist several distributions, and it is probable that for each field, which is distributed, there

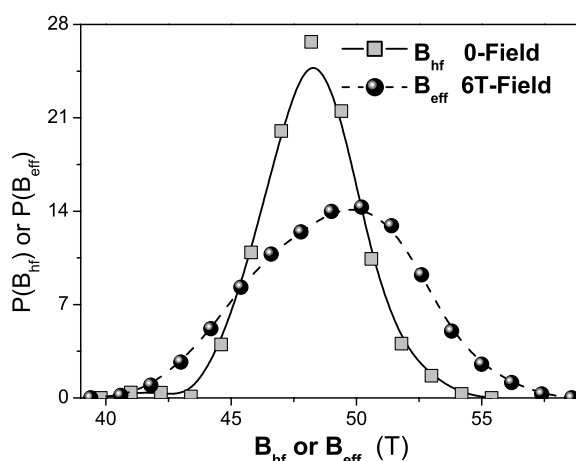


Figure 11. Effective and hyperfine field distribution obtained from the 6 T Mössbauer spectrum at 10 K and the zero-field Mössbauer spectrum at 4.2 K, respectively.

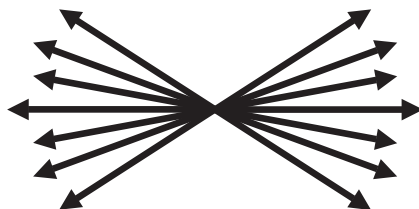


Figure 12. Schematic representation of the distribution of Fe magnetic moments giving evidence for a distribution of hyperfine fields and of canting angles.

exists an angular distribution too. However, it is possible to deduce from figure 11 that we have an angular distribution of about 100° (from -50° to $+50^\circ$) and there are two antiparallel sublattices as shown in figure 12. Clearly there is not a 360° angular distribution, as required by the ferromagnetism.

4. Conclusions

We propose a new analysis of the Mössbauer spectra of akaganeite at all temperatures and in the presence of an external field. This approach is strictly based upon the recently reported monoclinic crystallographic structure and the chlorine content. The previous confusing observation that two components were required to fit the 300 K MS but three components were necessary for the low temperature MS is solved here. Our methodology of analysis is very consistent at all temperatures: instead of assuming that two components are necessary to fit some spectra, while another number of components is required at lower temperatures, we can always think about the necessity of four components at all temperatures. Two of them are not discernible at 300 K (i.e. above the Néel temperature) because in our approach both the isomer shifts and the quadrupole interactions for the two pairs of components (i.e. for S1 and S2 sites on the one hand, and for S3 and S4 sites on the other hand) are restricted to be the same at all temperatures. Thus, Mössbauer spectrometry suggests the presence of four non-equivalent iron sites, arising from Fe_1^{3+} and Fe_2^{3+} located close to the Cl ions and Fe_1^{3+} and Fe_2^{3+} located near

the vacant chloride sites. Because the disorder implies different local atomic neighbouring, the magnetic structure behaves as a system which consists of two asperimagnetic-like structures antiferromagnetically coupled.

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