



Revista Facultad de Ingeniería Universidad de Antioquia

ISSN: 0120-6230

revista.ingenieria@udea.edu.co

Universidad de Antioquia
Colombia

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Revista Facultad de Ingeniería Universidad de Antioquia, núm. 49, septiembre, 2009, pp. 185-191
Universidad de Antioquia
Medellín, Colombia

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Magnetic structure of synthetic akaganeite: A review of Mössbauer data

Estructura magnética de la akaganeita sintética: Revisión de resultados Mössbauer

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(Recibido el 8 de octubre de 2008. Aceptado el 26 de mayo de 2009)

Abstract

The refinement of the Mössbauer spectra, i.e. the assignation of the correct number of spectral components and their physical origin, has been a long controversy in the case of akaganeite. Most interpretations are based upon the earlier reported tetragonal structure, and very few upon the recently reported monoclinic structure. On the other hand, the magnetic structure has been proposed to be collinear antiferromagnetic, speromagnetic or asperomagnetic. In this paper we critically revise some of the works that have been done to date and outline future experimental and theoretical studies required to gain a better understanding of the magnetic structure of akaganeite.

----- *Keywords:* Akaganeite, Mössbauer spectrum, magnetic structure.

Resumen

El refinamiento del espectro Mössbauer, i.e. la asignación del número correcto de componentes espectrales y su origen físico, ha sido por mucho tiempo un tema controversial en el caso de la akaganeita. La mayoría de las interpretaciones están basadas en la estructura tetragonal reportada anteriormente, y muy pocas en la recientemente reportada estructura monoclinica. Por otro lado, la estructura magnética se ha propuesto como

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colineal antiferromagnética, esferomagnética ó asferomagnética. En esta reseña revisamos críticamente algunos de los trabajos que se han hecho hasta la fecha y se esbozan futuros estudios experimentales y teóricos necesarios para conocer mejor la estructura magnética de la akaganeita.

----- **Palabras clave:** Akaganeita, espectro Mössbauer, estructura magnética.

Introduction

Akaganeite, β -FeOOH, from the Akagane mine in Japan is an iron oxyhydroxide commonly found in chloride rich environments [1-14]. It has recently been the subject of numerous investigations specially related with its role in the understanding of weathering process in steels [3, 11] and meteorites [12, 14]. In the former case, its presence has been related to high corrosion rates, whereas in the later, it might act as a catalyst promoting the breakdown of the meteorites. 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, particularly the number of components needed to properly fit the Mössbauer spectra (MS) and their physical origin in both the paramagnetic and the magnetic states. In this paper, we review some studies of structural and magnetic properties of akaganeite, in order to point out several unsolved questions that require to be studied.

Crystallographic structure

The crystal structure is similar to that of hollandite, which consist of double chains of edge linked Fe(O, OH) octahedral that share corners to form a framework containing large tunnels with square cross sections. The Cl ions reside in the tunnels, and their negative charges can be offset by additional H ions (see figure 1). Depending on composition, the phases with hollandite structure can have tetragonal or monoclinic structure. Mackay [15] assumed that β -FeOOH is tetragonal with space group $I4/m$, whereas recently, Post and Buchwald [13, 14] proposed a monoclinic

structure with space group $I2/m$. We have noticed that previous Mössbauer investigations were all interpreted in terms of the tetragonal structure, but only recently the monoclinic one has been considered.

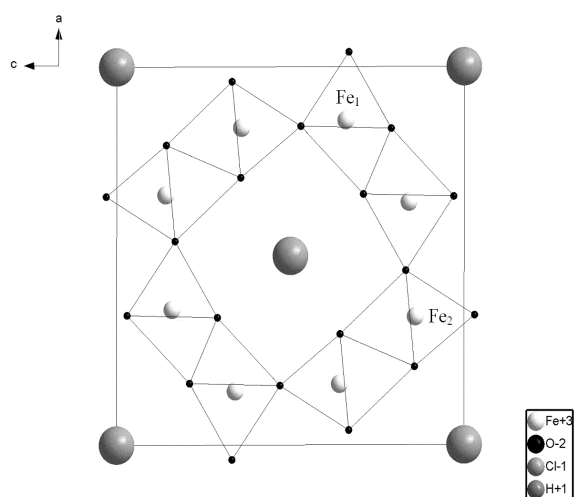


Figure 1 Projection of the akaganeite structure in the ac plane

Room temperature Mössbauer spectrum

As is shown in figure 2, a typical 300 K Mössbauer spectrum of synthetic akaganeite consists of a quadrupolar doublet with broadened lines. This spectrum has been well fitted using either two or three doublets but with poor agreement about their physical origin. Indeed, let us now briefly review some of the different interpretations given to the origin of the two doublets, which are based upon the tetragonal structure. Murad [16] 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 [17].

Chambaere et al. [17-19] attributed the lower and the higher quadrupole splitting component to the ferric ions located in $\text{FeO}_3(\text{OH})_3$ and $\text{FeO}_2(\text{OH})_4$ octahedral units, respectively. However, recent investigations have suggested that only $\text{FeO}_3(\text{OH})_3$ coordination is present in akaganeite [11, 13, 14].

According to studies of by Chambaere et al. [17-19] and Murad [2, 16] the two quadrupolar components are generally accepted as the most adequate way of fitting the room temperature Mössbauer spectrum. But it is important to emphasize that such a “mathematical” description is not supported by any physical origin of these two components.

Rézel and Génin [20] have proposed that the room temperature spectrum must be fitted with three quadrupolar doublets, where the intensity of two of them is always in the 2:1 ratio. These two doublets differ by the relative orientation of the principal axis of the electric field gradient with respect to the fourfold axis of symmetry. They argue that the replacement of Cl ions by OH ions in the structure is an important factor for 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.

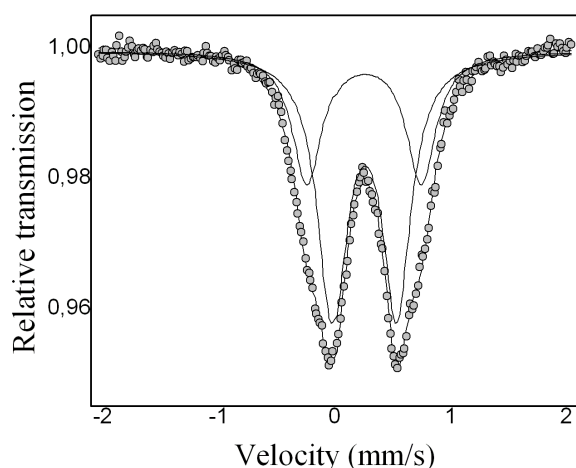


Figure 2 Typical room temperature Mössbauer spectrum of synthetic akaganeite

All the previously mentioned interpretations have considered the tetragonal unit cell of akaganeite. Now let us review the interpretations based on the monoclinic structure. Post and Buchwald [13] have suggested that the two doublet components are consistent with the two non-equivalent iron sites, Fe_1 and Fe_2 , 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 much Fe_1 sites as there are Fe_2 sites per unit cell. If it is assumed that the Debye-Waller factor for both sites is similar as 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. Barrero et al. [8, 21, 27, 28] have recently proposed that one component originates from those irons located close to the chloride sites, while the other component is attributed to iron atoms located close to the chloride vacancy sites. Consequently, theoretical calculations of the magnitude and direction of the principal axis of the electric field gradient (EFG) for each iron site should be done in order to elucidate the relationship between the different iron sites and the EFG directions.

Low temperature Mössbauer spectra

Figure 3 shows the 4.2 K MS of akaganeite, which can be adequately described by introducing three, four or a distribution of sextets. Most of the authors reviewed here agree that three sextets are required to properly fit the spectra. The investigations based on the tetragonal structure, concur in the opinion that the presence of Cl ions within the channels originates non-equivalent iron sites in the structure. According to Murad [2, 16] the three magnetic components do 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 [18]: two sextets are attributed to the $\text{FeO}_3(\text{OH})_3$ and $\text{FeO}_2(\text{OH})_4$ octahedral units in agreement with paramagnetic while

the third one is a contribution with fluctuating magnetization, the intensity of which vanishes down to zero at 0 K. On the other hand, Rézel and Génin [20] 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 chlorides. According to Oh et al. [22] the low temperature 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 chloride 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 reported by Stahl et al. [11]. For these authors, the components are related with the two crystallographic sites required by the monoclinic space group subjected to a disorder due to the chloride disorder. But the assumption of chloride subjected to a disorder clearly contradicts the results by Post and et al. [13, 14] and Weckler and Lutz [23] who propose an ordering scheme with every third chloride site vacant in a particular tunnel. Recently, Barrero et al. [21] have proposed a four sextet fitting model based upon both the monoclinic structure and the chloride content. It is important to mention that several fits with four sextets with either some or no constraints on the values of the hyperfine parameters are possible. However, they reported that among them, the one for which the centre shift, the quadrupole shift, the line widths as well as the areas of components are constrained to be equal, gives the more reasonable results. They have proposed that two of the components are ascribed Fe_1 and Fe_2 sites close to the chloride ions, respectively, while the other two components are attributed to the Fe_1 and Fe_2 sites close to the chloride vacancies, respectively. Clearly, more investigations are required especially to study the temperature dependence of the hyperfine parameters, and to derive important magnetic information.

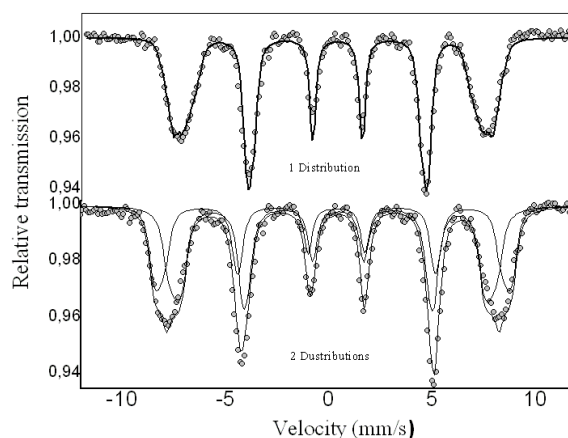


Figure 3 Typical 4.2 K Mössbauer spectrum of synthetic akaganeite. The spectrum can be adequately fit with 3 (upper part), 4 (middle) or a distribution (lower) of sextets

In field Mössbauer spectra

In relation to the magnetic structure we notice that collinear antiferromagnetic, speromagnetic and asperomagnetic behaviors have been proposed in the case of akaganeite: consequently further studies are thus needed to clearly solve this item. At this stage, it seems important to emphasize that very few techniques are able to give unambiguously evidence for such non collinear magnetic structures: among them, in-field ^{57}Fe Mössbauer spectrometry is well adapted in the case of Fe containing crystalline and amorphous systems see as examples review of J.M. Greneche [29] and J. Chappert [30]. Let us briefly describe the existing models. In-field Mössbauer spectrum of akaganeite is very complex, and consist of a superposition of subspectra corresponding to different orientations of the particles in the powder absorber (see Figure 4). One first observes that the lines are broader than those of the zero-field spectrum, and that the intensity of the intermediate lines is consistent with Fe magnetic moments oriented rather perpendicular to the external field, i.e. the presence of antiferromagnetic interactions. The relative line intensities of a magnetically split spectrum with negligible electric quadrupole

interaction are given by $3: (4\sin^2q/(1+\cos^2q)) : 1$; where q is the angle between the incident γ -ray and the effective field, B_{eff} which is obtained by the vector addition of the applied field, B_{app} , and the hyperfine field, B . We will review experiments for which B_{app} is directed parallel to the γ -ray direction, so called longitudinal geometry. The line shapes of the Mössbauer spectrum in applied field, clearly show that the second and fifth lines are neither completely perpendicular, because the line intensities are not equal to 4, nor completely parallel, because they are far from being zero. However they are closer to 4, suggesting rather perpendicular orientation to the external field, i.e. antiferromagnetic interactions.

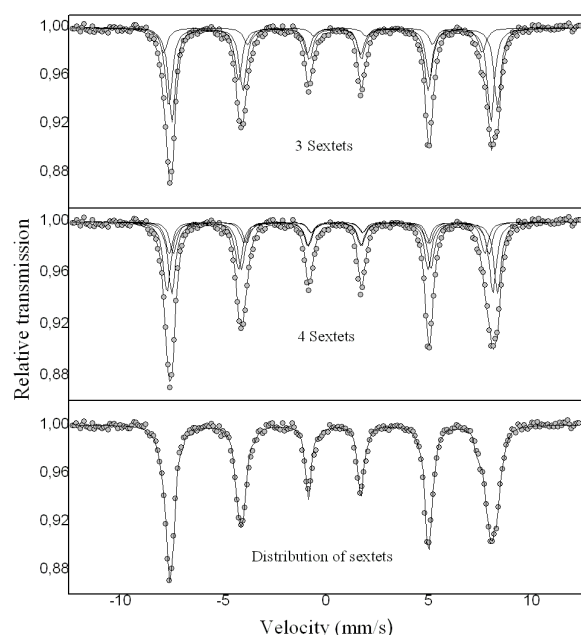


Figure 4 Mössbauer spectrum of synthetic akaganeite at 10 K in the presence of and external field of 6 T applied parallel to the direction of the gamma rays. The spectrum can be adequately fit with one distribution of sextets (upper part) or two distributions (lower) of sextets

Pollard et al. [24] have fitted the spectrum with three sextets of Voigt line shapes, and they assumed strong antiferromagnetic exchange and reasonably large anisotropy field. On

the other hand, De Grave et al. [25] have fit these spectra with two sextets, and assume also antiferromagnetic interactions. Coey [26] suggested speromagnetism instead of antiferromagnetism in iron oxyhydroxides, including akaganeite. Coey has pointed out that by assuming a normal antiferromagnetism in iron oxides, an anisotropy value of two orders of magnitude larger than the experimental values is obtained. Thus, the interpretation of the applied field Mossbauer spectra in terms of the speromagnetic model is preferred. Barrero et al. [21] suggested 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 none of both, but perhaps it is characterized by some degree of disorder, which can be induced by the Cl ions. And second, they have obtained an angular distribution of about 100° and not a 360° angular distribution, as required by the speromagnetism. Further work is necessary to be done in this sense. Perhaps neutron diffraction studies complemented with magnetization curves at different temperatures on well characterized samples should be required to fully understand the magnetic structure.

Conclusions

This review reports on a great number of studies devoted to the analysis of the Mössbauer spectra of akaganeite, and allows to conclude that very few of them supports a physical description, because of the controversies found in the crystallographic and magnetic structures. Indeed, most of the published Mössbauer works assumed the tetragonal structure and few of them the monoclinic one, whereas most of them use a collinear antiferromagnetic structure, rather than a speromagnetic or asperomagnetic behaviour. Akaganeite remains a very important iron oxyhydroxide, with many technological applications, commonly found in different

natural environments and it is also a by-product of technical processes, like the corrosion of iron and steels. To gain deeper understanding of the role that akaganeite can play into these areas; the requirement of fully knowledge of the crystallographic and magnetic structures is a task that it is still waiting to be done.

Acknowledgements

The financial support given by COLCIENCIAS (Centro de Excelencia de Nuevos Materiales) under contract CENM-COLCIENCIAS RC-043-2005), CODI for project: IN1248CE and sustainability program for Solid State Group 2007-2008. Universidad de Antioquia, are greatly acknowledged.

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