




Mössbauer spectra of iron (III) sulfide particles

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Abstract Trivalent iron sulfide (Fe_2S_3) particles were synthesized using a modified polyol method. These particles exhibited a needle-like shape (diameter = 10–50 nm, length = 350–1000 nm) and generated a clear XRD pattern. Mössbauer spectra of the product showed a paramagnetic doublet at room temperature and distributed hyperfine magnetic splitting at low temperature. The Curie temperature of this material was determined to be approximately 60 K. The data suggest that the Fe_2S_3 had a structure similar to that of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) with a lattice constant of $a = 10.6 \text{ \AA}$. The XRD pattern calculated from this structure was in agreement with the experimental pattern and the calculated hyperfine magnetic field was also equivalent to that observed in the experimental Mössbauer spectrum.

Keywords Iron (III) sulfide · Nanoparticle · X-ray diffraction · Mössbauer · Curie temperature

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2017), Saint-Petersburg, Russia, 3-8 September 2017*
Edited by Valentin Semenov

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1 Introduction

The iron sulfides FeS, FeS₂ and Fe₃S₄ are readily available and their structures and properties have been investigated in detail. In contrast, there have been few reports concerning iron (III) sulfide (Fe₂S₃) and the structure of this compound is not yet well understood. The significance of Fe₂S₃ as a catalyst for coal liquefaction has attracted considerable attention [1, 2]. The synthesis of Fe₂S₃ was reported by Boehm, who also provided the X-ray diffraction (XRD) pattern and Mössbauer spectrum of this sulfide [3]. Yamaguchi also published an XRD pattern obtained from Fe₂S₃ nanoparticles, which was similar to that of γ -Al₂O₃ [4–6], but not the Mössbauer spectrum. The sulfur K-edge X-ray absorption spectrum of Fe₂S₃ has been acquired as a means of elucidating the bonding nature of the S²⁻ ions [7]. The Mössbauer spectra of Fe₂S₃ at 78 and 4.2 K were reported by Stiller [8]. These spectra showed a paramagnetic doublet at 78 K and magnetic splitting at 4.2 K. The XRD pattern of the sample was not published because the sample was found to be amorphous. A metastable hexagonal Fe₂S₃ phase has been discovered, but only within the crystal structure of pyrrhotine [9]. In addition, Lyubutin fabricated nanoparticles consisting of a mixture of Fe₃S₄ and Fe₂S₃ [10]. Despite these prior studies, to the best of our knowledge, the Mössbauer spectrum and XRD pattern of neat Fe₂S₃ having a well-defined lattice structure has not yet been reported.

Our own group has previously produced Fe₂S₃ particles using by a polyol method [11, 12], although this material was found to contain amorphous Fe₂S₃ and FeS phases as impurities, such that it was difficult to determine the Fe₂S₃ lattice structure. In the present study, we succeeded in obtaining pure Fe₂S₃ particles by modifying the previous synthetic method, and the structure of the resulting material was studied using transmission electron microscopy (TEM), XRD and Mössbauer spectroscopy.

2 Experimental

The procedure used to synthesize Fe₂S₃ particles employed in this study was almost the same as that described in our previous reports [11, 12], except for the addition of hexadecane as a surface protective agent. A mixture of 2 mmol ferrocene, 8 mmol 1,2-hexadecanediol, 4 mmol 1-octadecanethiol, 4 mmol hexadecane and 20 mL oleylamine was stirred for 1 h in an Ar atmosphere. The mixture was subsequently refluxed for 2 h at 320 °C under an Ar flow and then cooled to 0 °C and held at that temperature for 30 min. The resulting precipitated particles were washed four times with ethanol and hexane and then separated by centrifugation. The particles were dispersed in a small amount of hexane and dried under an Ar flow, and then stored in an aluminized plastic bag under Ar.

The as-prepared particles consisted of a mixture of α -Fe and Fe₂S₃, and magnetic separation was employed to remove the α -Fe. To do so, the particles were dispersed in hexane in a sonication bath, after which a neodymium magnet was inserted into the dispersion and sonication was continued for 30 min. The neodymium magnet, together with the attached α -Fe particles, was removed from the solvent and the remaining Fe₂S₃ particles were obtained by filtration.

The product was characterized using XRD (Rigaku, RINT2500, Cu-K α), Mössbauer spectroscopy (Wissel, MDU1200, ⁵⁷Co/Rh), TEM (Hitachi, H-9500) and energy dispersive X-ray spectrometry (EDS; JEOL, JSM7001F). The XRD patterns were generated using the RIETAN [13] and VESTA [14] programs, and the hyperfine Fe₂S₃ magnetic fields were determined using the WIEN2k [15] software package.

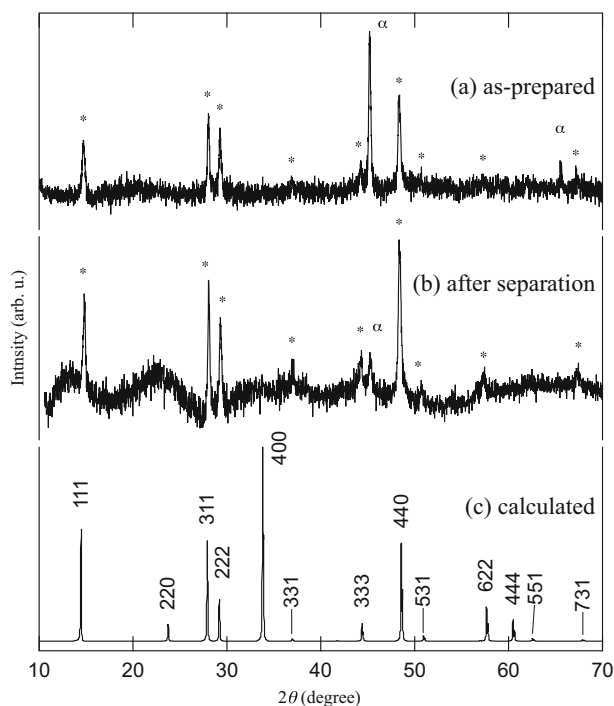


Fig. 1 XRD patterns of nanoparticles: **a** the as-prepared sample, which was a mixture of Fe_2S_3 (*) and α -Fe metal (α) nanoparticles, **b** the sample after removal of the α -Fe using a magnet, and **c** the XRD pattern calculated using the RIETAN program

3 Result and discussions

3.1 XRD patterns

The XRD pattern of the as-prepared sample prior to the magnetic separation of the α -Fe particles is shown in Fig. 1a. The peaks at $2\theta = 44.7^\circ$ and 65.0° were assigned to α -Fe, based on the literature [16]. The remainder of the XRD peaks were attributed to Fe_2S_3 , according to data obtained in our previous study [12]. Thus, the as-prepared sample was a mixture of α -Fe and Fe_2S_3 , and no other side products (Fe_3S_4 or Fe_{1-x}S) were obtained. In our prior work, the synthesis was performed without adding hexadecane (where 1-octadecanethiol acted as a surface protective agent) and a mixture of Fe_{1-x}S and Fe_2S_3 was obtained, such that the XRD patterns exhibited significant overlapping of peaks from the two iron sulfides. In the current synthesis, the hexadecane acted as a surface protective agent and so the transformation of metastable Fe_2S_3 to stable Fe_{1-x}S was inhibited. In this method, the polyol is reduced to generate an Fe^0 precursor in the solution and iron sulfide is subsequently obtained due to the presence of a sulfate source. If the Fe^0 particle surfaces are not protected sufficiently, the product will be a stable divalent iron sulfide species (Fe_{1-x}S). In contrast, overprotection of the surface of the Fe^0 precursor gives only α -Fe particles. It was therefore crucial to select the appropriate concentrations of the sulfur source and the surface protective reagent. The Fe_2S_3 particles obtained from the synthesis were estimated to be 30.3 nm

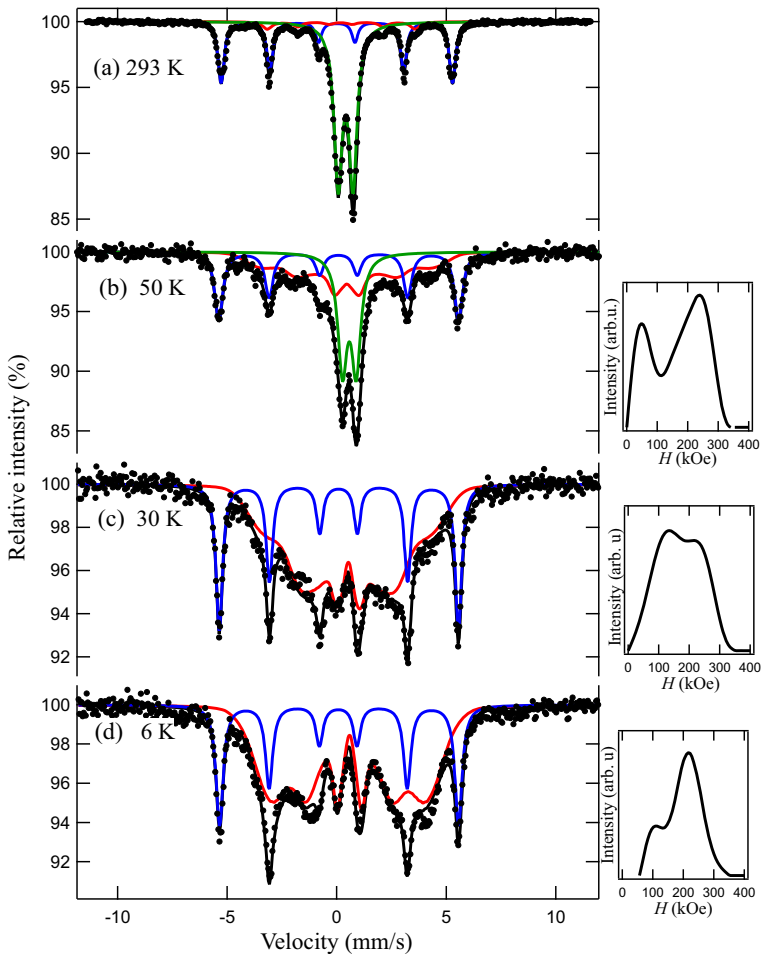


Fig. 2 Mössbauer spectra of the as-prepared sample, which was a mixture of Fe_2S_3 and $\alpha\text{-Fe}$ nanoparticles. The distributions of the hyperfine magnetic fields are shown to the right of the corresponding Mössbauer spectra

in size using Scherrer's equation [17] in conjunction with the peak width at $2\theta = 48.8^\circ$ and assuming that the particles were spherical. It was found that Fe_2S_3 particles were stable for about three months if they were kept in an Ar atmosphere below 0°C .

The magnetic properties of Fe_2S_3 particles were not known prior to this work, although it was anticipated that this compound would be ferrimagnetic (similar to maghemite) and that the magnetization of Fe_2S_3 would be weaker than that of metallic $\alpha\text{-Fe}$. As noted, ferromagnetic $\alpha\text{-Fe}$ particles could be removed from the mixture using a neodymium magnet, although this decreased the yield of pure Fe_2S_3 . The XRD pattern of the specimen following the application of the neodymium magnet is shown in Fig. 1b. Although this pattern demonstrates the presence of a trace amount of $\alpha\text{-Fe}$, the concentration of $\alpha\text{-Fe}$ was obviously decreased, demonstrating that it was possible to magnetically remove the $\alpha\text{-Fe}$ particles.

Table 1 Mössbauer parameters of the spectra shown in Fig. 2

Temperature	Species	$\delta / \text{mm s}^{-1}$	$\Delta E_q / \text{mm s}^{-1}$	$\Gamma / \text{mm s}^{-1}$	H / kOe	Area intensity
(a) 293 K	α -Fe	0.00 (0)	0.00 (1)	0.38(6)	327(0)	36%
	sextet	0.19(3)	0.03(6)	0.50(2)	209(2)	6%
	doublet	0.40(0)	0.68(0)	0.45(0)		58%
(b) 50 K	α -Fe	0.08 (1)	0.01 (1)	0.44(1)	339(1)	32%
	DHFM	0.46(3)	-0.01(5)		167*	38%
	doublet	0.57(1)	0.63(1)	0.50(2)		30%
(c) 30 K	α -Fe	0.09 (1)	0.01 (1)	0.36(1)	338(1)	29%
	DHFM	0.51(1)	-0.04(1)		170*	71%
(d) 6 K	α -Fe	0.09 (1)	0.04 (1)	0.39(1)	338(1)	28%
	DHFM	0.56(1)	-0.04(1)		205*	72%

“DHFM” denotes the component of the distributed hyperfine magnetic fields

The values marked with “*” in the H column represent the average H values of the DHFM

3.2 Mössbauer spectra

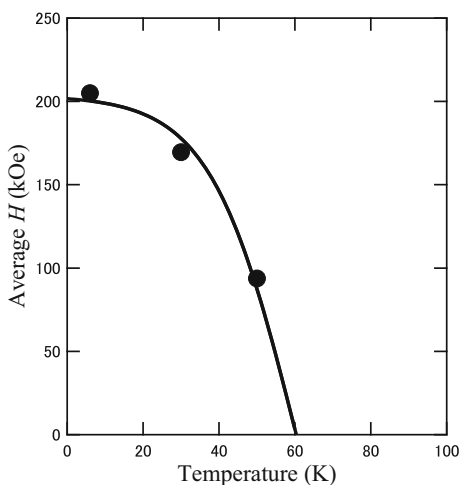
Mössbauer spectra of the as-prepared sample prior to magnetic separation were acquired between 298 and 6 K (Fig. 2). The spectrum obtained at 293 K was fitted to give a combination of a paramagnetic doublet ($\delta = 0.40 \text{ mm/s}$, $\Delta E_q = 0.68 \text{ mm/s}$) and two sets of sextets. One of the sextets was attributed to α -Fe and the other, which exhibited very minimal intensity (6%), was assigned to cementite (Fe_3C) particles based on the Mössbauer parameters, even though Fe_3C was not observed in the XRD patterns (Fig. 1). This compound is believed to have been produced by a reaction with the organic solvent during the polyol synthesis [18].

The Mössbauer spectrum acquired at 6 K (Fig. 2d) shows a combination of an α -Fe sextet and a magnetic component with broad absorption. This broad absorption was fitted by assuming distributed hyperfine magnetic field (DHMF) splitting. The lattice defects decreased the hyperfine magnetic fields H , which appeared as the DHMF. The resulting distribution is shown to the right of the spectrum and has an average H value, H_{av} , of 205 kOe. This component was assigned to Fe_2S_3 because the isomer shift (δ) of 0.56 mm/s was in agreement with the value expected for trivalent Fe. Although the Fe_2S_3 particles were large enough to generate sharp XRD patterns, they still contained a significant number of defects, as shown by the DHMF data.

The Mössbauer spectrum acquired at 30 K (Fig. 2c) was also fitted to give a combination of an α -Fe sextet and a DHMF resulting from Fe_2S_3 particles, with a smaller H_{av} value of 170 kOe. The spectrum obtained at 50 K (Fig. 2b) shows a paramagnetic doublet as well as the α -Fe sextet and the DHMF. At this temperature, the smaller Fe_2S_3 particles and/or those Fe atoms surrounded by a larger number of defects evidently became paramagnetic, while the larger particles and/or those Fe atoms surrounded by a smaller number of defects still produced a magnetic field.

The Mössbauer parameters are summarized in Table 1. In each spectrum, the α -Fe peaks accounted for approximately 30% of the total area. The $\text{Fe}_2\text{S}_3 H_{av}$ values, including both the DHMF and the doublet, are plotted in Fig. 3, in which the data are fitted with a Brillouin function.

Fig. 3 The temperature dependence of the average H value of Fe_2S_3 nanoparticles



This plot demonstrates that the Curie temperature of the Fe_2S_3 was approximately 60 K. Because the Fe_2S_3 particles had a size distribution, the blocking temperatures of the particles would be expected to differ, depending on size. It has been reported that smaller α - FeOOH particles exhibit a lower Néel temperature [19]. Therefore, in the case of the Fe_2S_3 spectrum at 50 K (Fig. 2b), smaller Fe_2S_3 particles or Fe atoms surrounded by numerous defects (representing 44% of the total Fe_2S_3) and having a blocking temperature below 50 K generated the doublet, while the larger Fe_2S_3 particles (the remaining 56%) with a higher blocking temperature simultaneously generated the DHMF.

Mössbauer spectra of the magnetically-separated sample were acquired at 298, 50 and 6 K (Fig. 4). These spectra are quite weak, with lower signal-to-noise values, because the amount of Fe_2S_3 in the sample was reduced, while the α -Fe sextet is completely absent. These results are in agreement with the data shown in Fig. 2. The associated Mössbauer parameters are summarized in Table 2. The spectra obtained from this material at 298 and 50 K contained a paramagnetic doublet, while that acquired at 6 K consisted of magnetic components showing a DHMF with an H_{av} of 221 kOe. The peak shape of the DHMF was very similar to that reported previously for amorphous Fe_2S_3 [8].

3.3 TEM images

Typical TEM images of the Fe_2S_3 are presented in Fig. 5, demonstrating a mixture of small spherical particles (believed to be α -Fe) and needle-like particles, along with the absence of disk-shaped Fe_{1-x}S particles [4]. The needle-shaped particles (diameter = 10–50 nm, length = 350–1000 nm) were not observed in our previous studies regarding iron sulfide particles, and thus are evidently the Fe_2S_3 . In our prior work, the Fe_2S_3 particles were too small to show this unique morphology. High-resolution analyzes of the needle-like Fe_2S_3 particles found the d spacing to be 0.31 nm. Thus, it is evident that that the Fe_2S_3 particles synthesized in this study were not amorphous but rather had a well-defined lattice structure and so generated an XRD pattern. EDS was employed to estimate the stoichiometry of the needle-shaped particles and the Fe/S ratio was found to be 2/2.9, as expected for Fe_2S_3 .

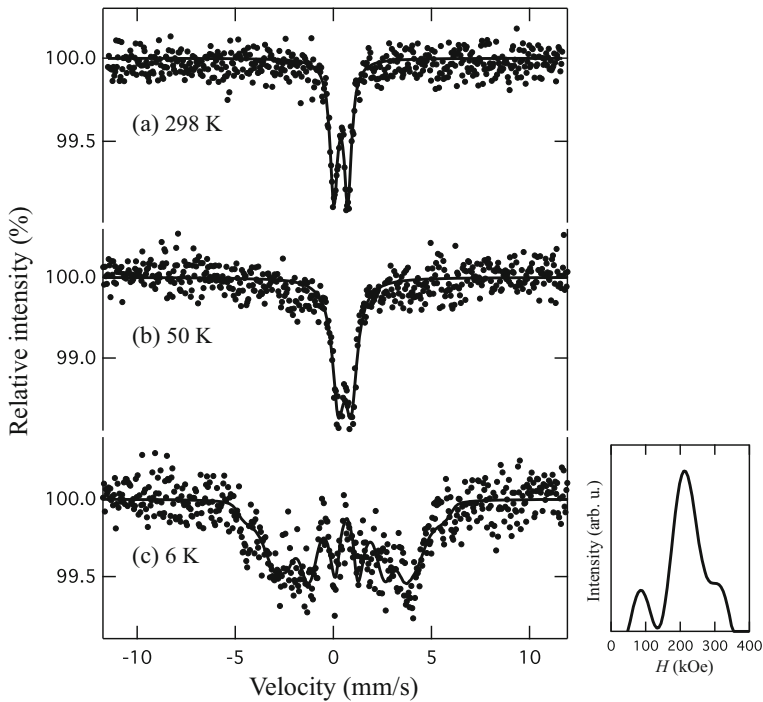


Fig. 4 Mössbauer spectra of the Fe₂S₃ nanoparticles after removal of α-Fe metal particles

Table 2 Mössbauer parameters of the spectra shown in Fig. 4

Temperature	Component	$\delta / \text{mm s}^{-1}$	$\Delta E_q / \text{mm s}^{-1}$	$\Gamma / \text{mm s}^{-1}$	H / kOe
(a) 293 K	doublet	0.37 (1)	0.71 (1)	0.46(2)	
(b) 50 K	doublet	0.57 (1)	0.66 (2)	0.73(4)	
(c) 6 K	DHFM	0.61 (3)	-0.11 (4)		221*

“DHFM” denotes the component of the distributed hyperfine magnetic fields

The values marked with “*” in the H column represent the average H values of the DHFM

3.4 Theoretical calculations using the RIETAN and WIEN2k programs

The XRD pattern of Fe₂S₃ has been previously reported [4, 6] and a maghemite γ -Fe₂O₃ structure, Fe^{III}(□_{1/3}, Fe^{III}_{5/3})S₄, with a lattice constant, a , of 9.87 Å has been proposed. However, the XRD pattern obtained in this study was different. We therefore performed calculations to predict the structure of Fe₂S₃ required to fit our experimental XRD pattern using the RIETAN [13] and VESTA [14] programs. A structure analogous to that of spinel maghemite (γ -Fe₂O₃) was employed as a starting point, but with a larger a value of 10.6 Å (Fig. 6). The XRD pattern calculated using the RIETAN program coincided reasonably well with the observed pattern in Fig. 1, although the calculated (400) peak at $2\theta = 33.4^\circ$ was less intense in the actual XRD pattern. It is known that the XRD peak intensity will vary

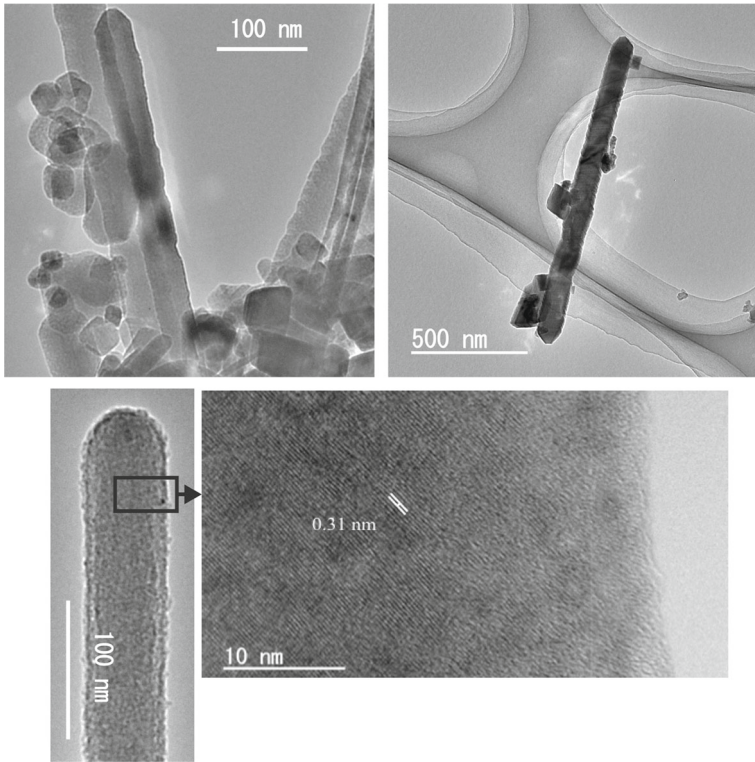


Fig. 5 TEM images of Fe_2S_3 nanoparticles

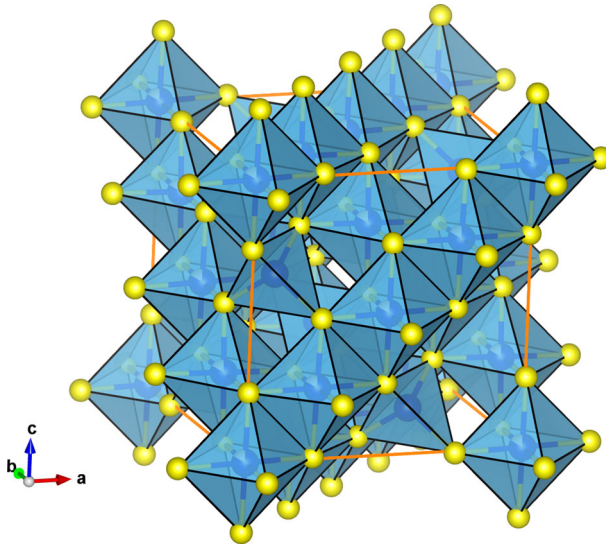


Fig. 6 Proposed structure of Fe_2S_3

with changes in the particle morphology [20]. This difference in the intensities is therefore attributed to the anisotropy of the needle-like particles. That is, the (400) face disappeared as the crystal grew in the longitudinal direction. Furthermore, the peak at $2\theta = 28.8^\circ$ corresponding to the (222) surface along the side of the particles, had a d value of 0.31 nm, in agreement with the high-resolution TEM image (Fig. 5).

Assuming that the calculated structure described above was correct (Fig. 6), density functional calculations were performed to estimate the hyperfine magnetic fields of the Fe atoms in the Fe_2S_3 using the WIEN2k program [15]. The H values of Fe atoms in the Oh and Td positions were determined to be 237 and 216 kOe, respectively. This result is in reasonably good agreement with the DHMF values obtained from the Mössbauer spectrum of Fe_2S_3 at 6 K.

4 Conclusion

Metastable Fe_2S_3 particles were successfully prepared by a modified polyol method. The synthesized sample consisted of metallic α -Fe and Fe_2S_3 particles but the α -Fe was readily separated simply by using a magnet. The Fe_2S_3 particles had a needle-like shape 10–50 nm in diameter and 350–1000 nm in length. The XRD pattern of this Fe_2S_3 was obtained and the compound was found to have a similar structure to that of maghemite. Mössbauer spectra of the Fe_2S_3 particles showed a DHMF with an H_{av} value of 221 kOe and a Curie temperature of approximately 60 K.

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