The magnetic hyperfine field in tin-doped Fe$_3$O$_4$: variations during oxidation and subsequent phase transformations

The magnetic hyperfine field in tin-doped Fe_3O_4: variations during oxidation and subsequent phase transformations

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Abstract
Tin K-edge EXAFS recorded *in situ* at 498 K from tin-doped Fe_3O_4 show that
the octahedral coordination of tin in the inverse spinel-related structure remains
essentially unchanged as it is oxidized to structurally-related γ-Fe_2O_3. Changes
in the magnetic hyperfine field distributions in the tin-119 Mössbauer spectra
recorded *in situ* between 285 and 500 K show that at the higher temperatures
some of the tin-doped Fe_3O_4 is converted to structurally-related tin-doped
γ-Fe_2O_3. Comparison with data recorded from similar materials by ^{57}Fe
Mössbauer spectroscopy show that the phase transition is sensitive to the partial
pressure of oxygen and the period of time at the elevated temperatures. The
changes in the magnetic hyperfine field distributions show that conversion of
tin-doped Fe_3O_4 to tin-doped γ-Fe_2O_3 is largely completed at 600 K and occurs
without the segregation of tin. At 700 K some tin segregates to form tin dioxide
as the conversion of tin-doped Fe_3O_4 to tin-doped γ-Fe_2O_3 is completed. At
higher temperatures the inverse spinel-related γ-Fe_2O_3 phase is converted to
the corundum-related α-Fe_2O_3 structure.

1. Introduction

The iron oxide of composition Fe_3O_4 adopts an inverse spinel-related structure and is oxidized
by mild heating in air to structurally-related γ-Fe_2O_3 before being converted by thermal
treatment at higher temperature to corundum-related α-Fe_2O_3. Our studies of tin-doped Fe_3O_4
have shown that it is also converted by mild thermal treatment in air to tin-doped γ-Fe_2O_3
and subsequently to tin-doped α-Fe_2O_3 [1]. Our examinations by extended x-ray absorption

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fine structure (EXAFS) [2, 3] showed that in both inverse spinel-related phases tin adopts the octahedral, as opposed to tetrahedral, sites and that, as expected, in tin-doped α-Fe_2O_3 tin is also octahedrally coordinated [4]. Furthermore, [57]Fe Mössbauer spectroscopy at temperatures exceeding 298 K showed [5, 6] that the magnitude of the magnetic hyperfine fields at the iron sites in the tin-doped inverse spinel-related phases changes in a systematic way and gives Curie temperatures with values less that those reported for pure Fe_3O_4 and γ-Fe_2O_3 [7, 8]. However, the situation at the tin site as determined initially by [119]Sn Mössbauer spectroscopy was more complex. Although tin was incorporated in all materials as Sn^{4+}, the initial results suggested that whereas the maximum in the average magnetic hyperfine field distributions in the spectrum for tin-doped Fe_3O_4 at 298 K occurred [5] at about 20 T, the maximum in the average magnetic hyperfine field distribution in the spectrum for tin-doped γ-Fe_2O_3 at 298 K occurred [6] at about 14 T. The maximum in the average magnetic hyperfine field distribution in the [119]Sn Mössbauer spectrum recorded from tin-doped α-Fe_2O_3 at 298 K also occurred at 14 T [4].

In order to examine the changes in the magnetic hyperfine field distribution on the tin site during these oxidation and phase transformations, and in order also to develop a deeper appreciation of the factors which influence the oxidation of spinel-related tin-doped Fe_3O_4 to tin-doped γ-Fe_2O_3 and its subsequent transformation to the corundum-related structure, we have examined *in situ* the changes in the magnetic hyperfine field distribution by [119]Sn Mössbauer spectroscopy and the changes in the local coordination of tin by tin K-edge x-ray absorption spectroscopy.

2. Experimental details

Tin-doped Fe_3O_4 of composition $Fe_{2.9}Sn_{0.1}O_4$ was prepared by heating stoichiometric quantities of powdered tin(IV) oxide, iron(III) oxide, and metallic iron in a sealed evacuated quartz ampoule at 900 °C for 24 h and allowing the product to cool as the furnace returned to room temperature.

Tin-119 Mössbauer spectra were recorded with a conventional constant acceleration Mössbauer spectrometer using an approximately Ca [119]SnO$_3$ source. The spectra were recorded *in situ* at elevated temperatures using a specially designed furnace [9]. The sample thickness was 100–150 mg cm^{-2}. The linewidth (FWHM) of the Ca [119m]SnO$_3$ calibration spectrum was 1.00 mm s^{-1} with an isomer shift of 0.11 mm s^{-1} relative to that of metallic iron at 298 K.

The tin K-edge x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) were recorded at the Synchrotron Radiation Source, Daresbury Laboratory, UK, with an average current of 200 mA at 2 GeV. The data were collected at 298 and 498 K using a Daresbury Laboratory furnace on Station 9.2 with an Si(220) double crystal monochromator that was detuned to 70% of the maximum intensity to remove the harmonic. Ion chambers were filled with noble gases so as to absorb about 20% and 80% of the beam in the first and second chambers, respectively. The energy resolution of the monochromator is about 0.5 eV at the tin K-edge. The samples were examined in transmission mode as pressed discs. The x-ray absorption edge positions were identified at the points of greatest slope on the edge. The monochromator was calibrated with a metallic tin foil, the x-ray absorption edge of which was recorded at 29 200 eV. The raw EXAFS data were reduced using the SRS programs EXCALIB and EXBROOK. EXAFS analyses were performed using the program EXCURV98 [10]. Phase shifts using muffin-tin potentials were calculated *ab initio* using Hedin–Lundqvist exchange potentials and von Barth ground state potentials. The fit index R is defined by $R = \sum_i [(1/(\sigma_i)(|\text{experiment}(i) - \text{theory}(i)|)] \times 100\%$ where $1/(\sigma_i) = ([k(i)]^3 / \sum_i [k(i)]^3 |\text{experiment}(i)|)$ where $k(i)$ is the wavevector amplitude for the ith point.
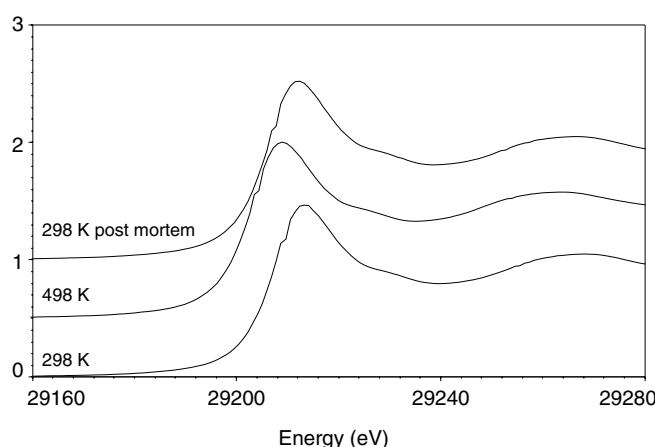
Figure 1. Tin K-edge XANES recorded from $Fe_{2.9}Sn_{0.1}O_4$ (a) *ex situ* at 298 K, (b) *in situ* at 498 K, (c) *ex situ*, *post mortem* at 298 K.

Table 1. X-ray absorption edge positions.

Sample	Edge position (eV $\pm$ 0.2)
Sn metal	29 200
$Fe_{2.9}Sn_{0.1}O_4$, *ex situ*, 298 K	29 208.2
$Fe_{2.9}Sn_{0.1}O_4$, *in situ*, 498 K	29 205.8
$Fe_{2.9}Sn_{0.1}O_4$, *ex situ, post mortem*, 298 K	29 208.3

3. Results and discussion

3.1. Tin K-edge XANES and EXAFS

The tin K-edge XANES recorded from the tin-doped Fe_3O_4 at 298 K, *in situ* at 498 K, and *ex situ* after re-cooling to 298 K are shown in figure 1. The x-ray absorption edge positions are collated in table 1. The results show that whilst the x-ray absorption edge positions of the preheated and *post mortem* samples were identical within the errors, the position of the x-ray absorption edge recorded from the material *in situ* at 498 K was shifted by about 2.5 eV to lower energy, indicative of increasing electron density on the Sn^{4+} site.

The tin K-edge EXAFS recorded from tin-doped Fe_3O_4 before thermal treatment, *in situ* at 498 K, and *ex situ* following thermal treatment, are shown in figure 2. The best fit parameters are collected in table 2. The data recorded *ex situ* before thermal treatment are similar to those previously recorded from a material of identical composition [2, 3] and interpreted in terms of tin occupying the octahedral site in inverse spinel-related Fe_3O_4. The results recorded from the materials *in situ* during treatment at 498 K and *ex situ* following thermal treatment are, within the errors, identical. Our previous work [11] has demonstrated the sensitivity of EXAFS to the detection of small differences in the octahedral environment of cations in spinel-related structures. Hence we conclude that in the system under examination here tin does not undergo detectable changes in its octahedral coordination by oxygen during the thermal treatment.

3.2. ^{119}Sn Mössbauer spectroscopy

The ^{119}Sn Mössbauer spectra recorded *in situ* from $Fe_{2.9}Sn_{0.1}O_4$ at temperatures between 285 and 750 K are collected in figure 3. Although the Sn^{4+} ion is nonmagnetic, its nucleus can
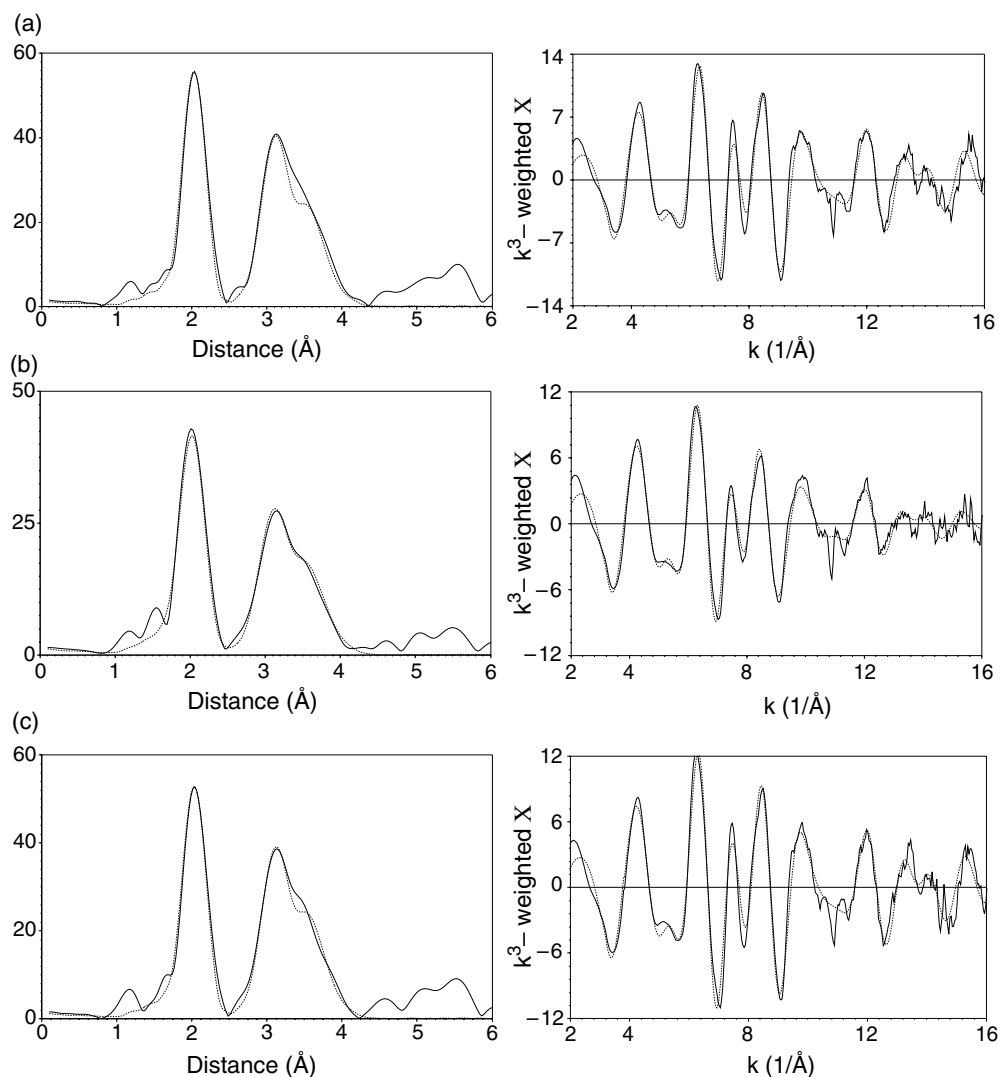
Figure 2. Tin K-edge EXAFS (i) and phase shifted Fourier transforms (ii) recorded from $Fe_{2.9}Sn_{0.1}O_4$ (a) *ex situ* at 298 K, (b) *in situ* at 498 K, (c) *ex situ*, *post mortem* at 298 K. The experimental data are shown by the solid curve.

sense a magnetic hyperfine field by supertransferred hyperfine interaction (STHI) with the iron ions in the spinel structure. The ^{119}Sn Mössbauer parameters, obtained by fitting the spectra with several broad-lined discrete sextets, are collected in table 3. The spectra were also fitted with magnetic hyperfine field distributions as shown in figure 4.

The spectrum recorded from the material before heating (figure 3(a)) was best fitted with a magnetic hyperfine field distribution in which the dominating sextet pattern with a magnetic hyperfine field of about 20–22 T accounted for about 81% of the spectral area. The remaining approximately 19% of the spectrum was assigned to a broad line sextet (about 12–15 T) (table 3) and a doublet, accounting for less than 1% of the spectral area, corresponding to a paramagnetic contribution. The spectrum recorded *in situ* at 400 K (figure 3(b)) showed a similar structure.

Table 2. Best fit parameters to the tin K-edge EXAFS recorded from $Fe_{2.9}Sn_{0.1}O_4$.

Treatment	Fit index R	Atom type	Coordination number	Tin–atom distance (Å) $\pm 1\%$	$2\sigma^2$ (Å^2) $\pm 10\%$
Ex situ 298 K	25.43	O	6	2.054	0.006
		Fe	6	3.107	0.012
		Fe	6	3.553	0.016
In situ 498 K	24.75	O	6	2.054	0.010
		Fe	6	3.106	0.016
		Fe	6	3.565	0.020
Ex situ	25.81	O	6	2.057	0.006
Post mortem		Fe	6	3.107	0.012
298 K		Fe	6	3.552	0.016

A sextet of magnetic hyperfine field of about 18 T accounted for approximately 55% of the spectral area, with the remainder of the spectrum being associated with two broadened sextets. The spectrum recorded from the material heated at 500 K (figure 3(c)) was also amenable to fitting to three sextets, but with a dramatically different ratio between the spectral areas of the three components as compared to the data recorded at 400 K. The component with largest magnetic hyperfine field of about 14 T accounted for only about 11% of the spectrum but that with intermediate magnetic hyperfine field (about 12 T) accounted for about 61% of the spectral area. The material was then cooled to 285 K and the spectrum recorded *in situ* (figure 3(d)).

An appreciation of these changes in the spectra over the temperature range 285–500 K may be approached by considering the magnetic hyperfine field distributions shown in figure 4. The magnetic hyperfine field distribution recorded *in situ* at 400 K was shifted to a lower average magnetic hyperfine field as compared to that initially recorded *ex situ* at 285 K. Furthermore, the pattern of the distribution was different, and a new maximum in the distribution around 13 T emerged. This process developed further in the spectrum recorded *in situ* at 500 K such that when the material was cooled and the spectrum recorded *in situ* at 285 K the main structure of the distribution was dramatically different from that initially recorded from the material at 285 K. The spectrum showed the magnitude of the component with largest magnetic hyperfine field (about 20 T) to have diminished to account for only about 7% of the spectral area (table 3) and with a concomitant increase in the components around 10–15 T. The results suggest the conversion of the tin-doped Fe_3O_4 to a new phase. The ^{119}Sn Mössbauer parameters of the new emerging phase are similar [6] to those of tin-substituted γ-Fe_2O_3 and indicate that, at temperatures up to 500 K, some tin-substituted Fe_3O_4 is oxidized to tin-substituted γ-Fe_2O_3. Further cycling of the material from 285 to 500 and back to 285 K (spectra not shown) did not produce any further changes in the spectra. The results bring into question the reasons why the Fe_3O_4 to γ-Fe_2O_3 phase transition at temperatures below about 600 K was not seen in earlier experiments where the Curie temperature ($T_c = 770$ K) of $Fe_{2.9}Sn_{0.1}O_4$ was determined [5] or in similar studies by ^{57}Fe Mössbauer spectroscopy of the Fe_3O_4 to γ-Fe_2O_3 phase transition at 680 K [1]. In the first case the partial pressure of oxygen was lower than 0.01 Pa (10^{-7} atm) to inhibit oxidation processes, whereas in this work the partial pressure of oxygen was maintained at about 1 Pa (10^{-5} atm as the air pressure in the furnace was about 5×10^{-5} atm). In the second case, the time domain is of importance since the small amount of tin required a longer period of time to record reasonable ^{119}Sn Mössbauer spectra than was required to record the ^{57}Fe Mössbauer spectrum from the corresponding sample. Hence the '*in situ*' conditions used here were very different from those used previously [1, 5]. It would also appear from this work
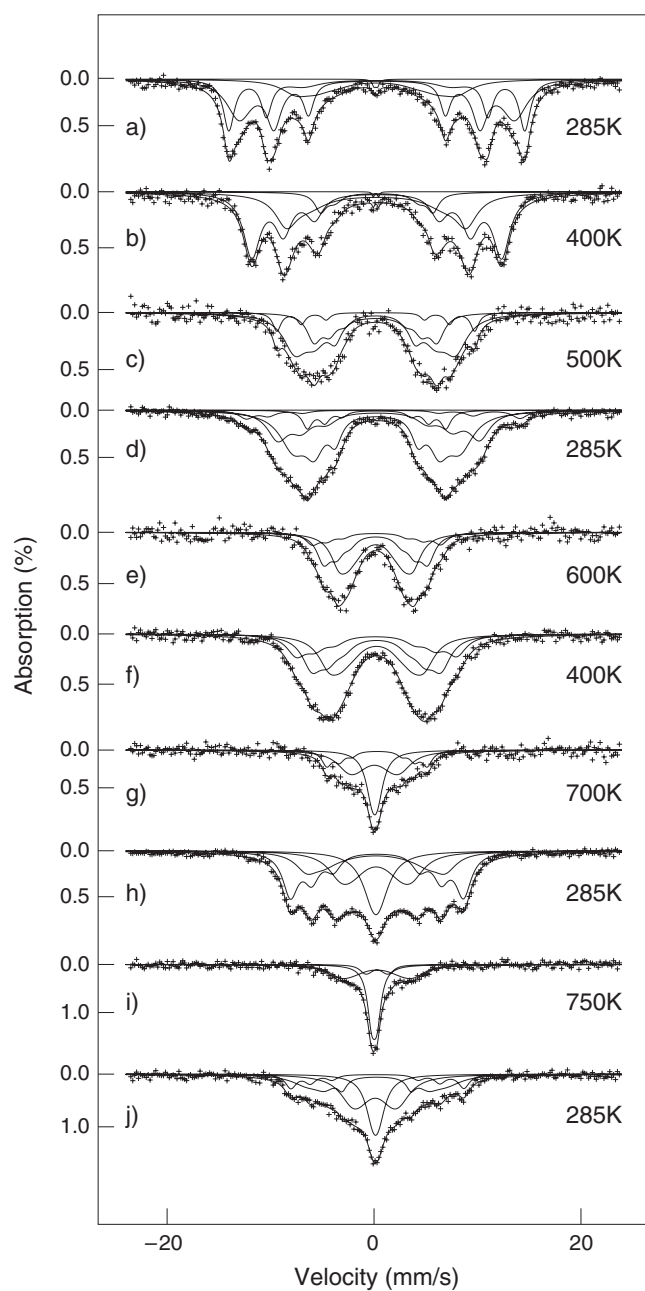
Figure 3. ^{119}Sn Mössbauer spectra recorded *in situ* from $Fe_{2.9}Sn_{0.1}O_4$ between 285 and 750 K.

vide supra, that EXAFS is unable to sense the small changes in the octahedral environment of tin in the spinel-related Fe_3O_4 phase as it is oxidized to structurally-related γ-Fe_2O_3. The increase in electron density on the tin site at 498 K detected by XANES would have been expected to give a small increase in the magnitude of the magnetic hyperfine field. However, the ^{119}Sn Mössbauer spectrum recorded at 500 K showed that this effect, which would be small in magnitude, cannot be resolved from the dominating reduction of the magnetic hyperfine field induced by the higher temperature.

Table 3. ^{119}Sn Mössbauer parameters recorded from $Fe_{2.9}Sn_{0.1}O_4$.

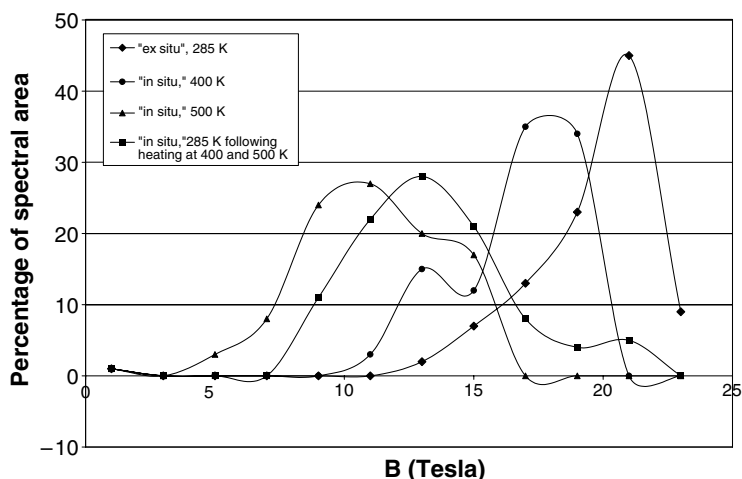|	Sextet 1				Sextet 2				Sextet 3			Sextet 4			Doublet			
Temp. (K)	$\delta \pm 0.05$ (mm s^{-1})	$\Delta \pm 0.05$ (mm s^{-1})	$H \pm 1$ (T)	Area (%)	$\delta \pm 0.05$ (mm s^{-1})	$\Delta \pm 0.05$ (mm s^{-1})	$H \pm 1$ (T)	Area (%)	$\delta \pm 0.1$ (mm s^{-1})	$H \pm 1$ (T)	Area (%)	$\delta \pm 0.1$ (mm s^{-1})	$H \pm 1$ (T)	Area (%)	$\delta \pm 0.02$ (mm s^{-1})	$\Delta \pm 0.02$ (mm s^{-1})	Area (%)	Average value of δ (mm s^{-1})
285	0.30		22	30	0.30		20	51	0.2	12	19							0.28
400	0.25		18	55	0.20		13	34	0.3	8	11							0.25
500	0.15	0.00	14	11	0.10		12	61	0.1	9	28							0.12
285	0.30	0.10	20	7	0.35	0.10	15	31	0.2	12	53	0.2	10	9				0.29
600	0.20	0.05	9	15	0.15		8	34	0.2	5	51							0.18
400	0.15	0.07	12	24	0.25		9	38	0.2	7	38							0.22
700	0.30		7	22	0.05		4	44							0.08	0.49	34	0.10
285	0.25	0.05	13	35	0.20		10	21	0.2	5	24				0.18	0.51	19	0.21
750	0.25		6	41	0.30		2	12							0.02	0.51	47	0.15
285	0.20	0.10	13	13	0.35		10	28	0.1	4	37				0.16	0.51	22	0.17

Figure 4. The magnetic hyperfine field distribution obtained from $Fe_{2.9}Sn_{0.1}O_4$ following sequential treatment at 285, 400, 500 and 285 K.

The spectrum recorded *in situ* at 600 K (figure 3(e)) could be fitted to either a distribution of magnetic hyperfine fields in the range about 5–9 T or to three broad lined sextets with line width from 2.5 to 3.5 mm s^{-1} (table 3). The spectrum recorded subsequently at 400 K (figure 3(f)) showed no evidence of a high magnetic field component (18 T in figure 3(b)) and no evidence of a paramagnetic doublet (<1%), and thereby confirms the substantial transformation of tin-doped Fe_3O_4 to tin-doped γ-Fe_2O_3 without exsolution of tin as tin dioxide.

The spectrum recorded *in situ* at 700 K (figure 3(g)) showed a further reduction in the magnitude of the hyperfine magnetic field of the two sextet components (about 4–7 T) and the appearance of a doublet accounting for approximately 34% of the spectral area. The development of the quadrupole split absorption may, in principle, be related to either (a) the exsolution of tin from the spinel-related structure to form tin dioxide, or (b) that due to small particle sizes a superparamagnetic transition occurs at this temperature, or (c) that given the broad nature of the spectral lines, the doublet represents a component with a hyperfine magnetic field smaller than about 2 T.

To investigate these possibilities the material was cooled to 285 K, and the resulting spectrum (figure 3(h)) was found to exhibit interesting features. Firstly, the spectrum clearly demonstrates the presence of a quadrupole split absorption accounting for about 19% of the spectral area (table 3) with ^{119}Sn Mössbauer parameters characteristic of tin dioxide ($\delta = 0.15$ mm s^{-1} and $\Delta = 0.5$ mm s^{-1}) [12]. The result demonstrates that, at temperatures around 700 K, the onset of segregation of tin from the spinel-related structure occurs. Secondly, the resolution of the magnetic hyperfine components of the spectrum (figure 3(h)) is far superior to that observed in the spectrum recorded previously at 285 K (figure 3(d)). The clearly resolved component with magnetic hyperfine field of about 13 T and accounting for about 35% of the spectral area is characteristic of tin-substituted γ-Fe_2O_3 [6, 12], and demonstrates significant oxidation of the original tin-substituted Fe_3O_4. In a similar study of a sample with a composition of $Fe_{2.8}Sn_{0.2}O_4$ the same effect was observed after heat treatment at 600 K. In that case the sample was examined by ^{57}Fe Mössbauer spectroscopy, and showed only a component related to tin-doped γ-Fe_2O_3. No evidence for the existence of Fe_3O_4- or the formation of α-Fe_2O_3-related phases was detected. Hence, we conclude that heating to 700 K under the conditions used here leads to complete conversion of tin-doped Fe_3O_4 to tin-doped
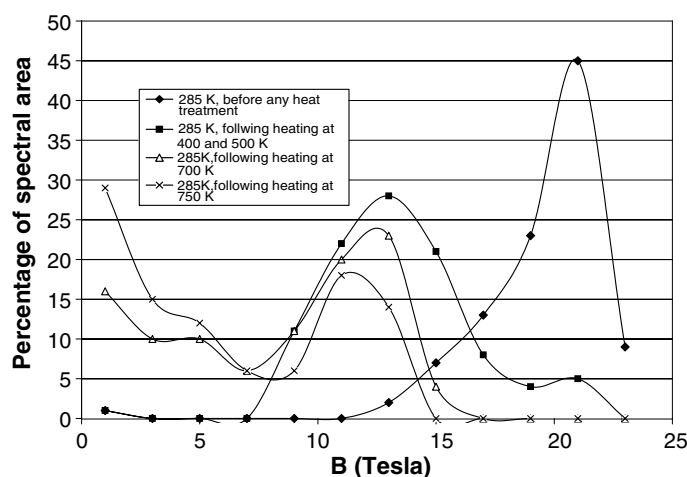
Figure 5. The magnetic hyperfine field distribution obtained from spectra recorded at 285 K from Fe$_{2.9}$Sn$_{0.1}$O$_4$ at different stages during the heat treatment.

γ-Fe$_2$O$_3$ with segregation of some tin to form tin dioxide. The material was finally heated at 750 K (figure 3(i)) and cooled to 285 K (figure 3(j)). The results show a development of the paramagnetic component in the spectrum, demonstrating further exsolution of tin as tin dioxide at 750 K together with enhanced complexity in the magnetic components of the spectra. Previous studies by ^{57}Fe Mössbauer spectroscopy of the same sample at elevated temperature [1] have shown that at about 700 K the spinel-related tin-substituted γ-Fe$_2$O$_3$ begins to convert to the corundum-related tin-doped α-Fe$_2$O$_3$. Hence we associate the more complex nature of the magnetically split components in the ^{119}Sn Mössbauer spectrum recorded from the material following heating at 750 K to the partial conversion of tin-doped γ-Fe$_2$O$_3$ to tin-doped α-Fe$_2$O$_3$. The changes in the magnetic hyperfine field distributions observed in the spectra during the whole thermal treatment are recorded in figure 5. The results confirm the major change in the magnetic hyperfine field distribution pattern during thermal treatment at 400–500 K. The data also show that further heating at 700 K results in a sharpening of the maximum peak at about 11–13 T and the development of a paramagnetic component which is represented as the maximum at about 1 T. The well defined sextet with a magnetic hyperfine field of about 13 T (and line width of 1.8 mm s^{-1}) contributes to the steep right-hand slope of the maximum at about 11–13 T in the distribution assigned to the data recorded at 700 K.

The variation of the magnetic hyperfine field of the main spectral components recorded from Fe$_{2.9}$Sn$_{0.1}$O$_4$ with increasing temperature are shown in figure 6. The development of the magnetic hyperfine field at the tin site is depicted with two series which overlap within the temperature range 400–500 K, indicating that the transition from Fe$_3$O$_4$ to γ-Fe$_2$O$_3$ occurs within this temperature window. For comparison the magnetic hyperfine field recorded by ^{57}Fe Mössbauer spectroscopy [5] is also shown (scaled down by 0.5) and gives a Curie temperature of about 770 K, i.e. 70 K below that of pure Fe$_3$O$_4$. The results from ^{119}Sn Mössbauer spectroscopy of a sample of composition of Fe$_{2.95}$Sn$_{0.05}$O$_4$ in the temperature range 25–500 K are also shown in figure 6.

The values of B_{max} determined from the ^{119}Sn Mössbauer spectra of Fe$_{2.95}$Sn$_{0.05}$O$_4$ and Fe$_{2.9}$Sn$_{0.1}$O$_4$ follow the same pattern from 285 to 500 K, with the latter having a slightly lower field (about 1 T). Clearly this field decreases more rapidly with temperature than that sensed by the iron ions. The increase in the lattice parameters due to increasing temperature may have a greater effect on the supertransferred hyperfine interaction at the tin sites than on the
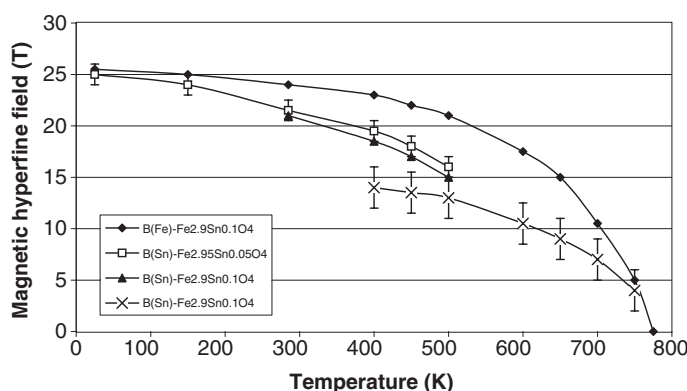
Figure 6. Variation of magnetic hyperfine field with temperature in $Fe_{2.9}Sn_{0.1}O_4$ as sensed by the Fe and Sn ions (Fe data scaled down by 0.5).

spin density at the iron nuclei. The variation of the magnetic hyperfine field with temperature following the Fe_3O_4 to γ-Fe_2O_3 transition approaches the same Curie temperature as that derived from ^{57}Fe Mössbauer spectroscopy. The spectrum recorded at 800 K did not show any magnetic component.

4. Conclusion

Tin K-edge EXAFS indicate that when tin-doped Fe_3O_4 is heated to 498 K there is no change in local coordination around tin. ^{119}Sn Mössbauer spectroscopy shows that at 500 K some of the tin-doped Fe_3O_4 is oxidized to structurally-related tin-doped γ-Fe_2O_3. Heating to elevated temperatures initiates further oxidation and subsequently exsolution of tin from the spinel-related structure to form tin dioxide and the conversion of the spinel-related phase to corundum-related α-Fe_2O_3. Comparison with previous studies by ^{57}Fe Mössbauer spectroscopy demonstrates that the oxidation processes and phase transition are sensitive to oxygen partial pressure and are time- as well as temperature-dependent. The interpretation of the ^{119}Sn Mössbauer spectra is more complex than originally thought, and the results demonstrate the sensitivity of *in situ* ^{119}Sn Mössbauer spectroscopy when complemented by *in situ* x-ray absorption measurements at elevated temperature to subtle changes in the magnetic hyperfine field at tin and the environment of tin which accompanies oxidation and phase transformations in the iron oxide matrix.

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