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^{57}Fe Mössbauer effect studies of Sm_2Fe_{17} under different heat treatment conditions

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Room-temperature ^{57}Fe Mössbauer spectra have been measured in Sm_2Fe_{17} under different heat treatment conditions. The details of fitting these spectra is exhaustively discussed. The spectra of Sm_2Fe_{17} are split into seven inequivalent magnetic sites. An identical result was obtained by using two fitting modes. The following has been indicated from the results for all samples. Firstly for these samples containing α-Fe sextets and paramagnetic doublets, by choosing an appropriate annealing system, the smallest amount of impurities might be obtained, i.e. an approximately single-phase Sm_2Fe_{17} compound was obtained. Secondly the overall weighted average fields were all approximately equal. This was thought to arise because the different heat treatment conditions caused no change in the near-neighbour coordination of iron atoms. Thirdly the 6c site and 18 h site had the largest and the smallest hyperfine fields, respectively.

1. Introduction

In R_2Fe_{17} (R = rare-earth metal) compounds, the magnetic moments of Fe are almost as large as those in iron metal; therefore they are possible candidates for permanent magnetic materials. Unfortunately, their Curie temperatures are rather low and none of them possesses uniaxial anisotropy at room temperature [1]. So the binary 2:17 compounds cannot be used for hard magnetic materials. The magnetic properties of R_2Fe_{17} are very sensitive to composition. Partial substitution of iron in $R_2M_xFe_{17-x}$ (M = Al [2], Si [3, 4], Ni [5], Co [6], etc.), whether they have a magnetic moment or not, will raise the Curie temperature T_C, but the easy-magnetization direction (EMD) of R_2Fe_{17} cannot be changed. Interstitial atoms are more effective in raising T_C in $R_2Fe_{17}M_y$ (M = H [7–9], C [10–16], N [17–19]). When M = C or N, $Sm_2Fe_{17}M_y$ has easy-axis anisotropy at room temperature.

In most cases, samples of the R_2Fe_{17} compounds always contain unreacted α-Fe; e.g., when a casting method is used after an anneal, there is a small amount of free iron in Sm_2Fe_{17}, which was pointed out in [19–21], a few per cent of elemental iron in some cases [22] and in Sm_2Fe_{17} [23] and some traces of α-Fe in the Nd and Sm compounds [24]. Also, when the mechanical alloying method is employed, there is also α-Fe in Sm_2Fe_{17} after grinding and inappropriate crystallization conditions [25]. (Note that some workers use the term free iron and elemental iron for α-Fe).

In subsequent research, the ternary or polynary compounds of R_2Fe_{17} will be produced by adding other elements. If α-Fe exists as an impurity in these, it will prevent us from obtaining a higher coercivity. Because it is a soft magnetic phase with respect to the magnetic properties, which can act as a nucleation site for reverse magnetic domains [26], and its magnetization is easily reversed under an external small opposite magnetic field, a cascade of demagnetization processes is obtained within adjacent grains [27]. At the same time, a trace of α-Fe makes the experimental determination of the magnetic properties complicated.

In order to avoid α-Fe precipitation, a small excess of Sm was added when Sm_2Fe_{17} was being prepared, but the appropriate amount of Sm was difficult to control. A high-pressure nitrogenation process was adopted by Isnard *et al.* [28], which permitted a lower reaction temperature. This will allow samples of higher purity with almost no α-Fe to form. It has been reported [29] that minor additions (about 2 at%) of group NB–VB–VIB elements significantly reduce the amount of α-Fe precipitated in the starting materials. Not only could it eliminate a long homogenization process, but also it will ensure a good performance and effect on the intrinsic magnetic properties. The addition of Ga can help to stabilize the rhombohedral Th_2Zh_{17}-type structure and to reduce the soft magnetic impurity phases such as α-Fe in $Sm_2Fe_{14}Ga_3C_{1.5}$ [27] and $Gd_2Fe_{17-x}Ga_xC_2$ [30]. In other words, it is not easy to eliminate α-Fe completely in R_2Fe_{17} and its series of compounds.

In this paper, we measured the hyperfine parameters of Sm_2Fe_{17} at room temperature by ^{57}Fe Mössbauer spectroscopy. The phases in the samples

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were analysed under different heat treatment conditions and the details of fitting the spectra are discussed.

2. Experimental procedure

The Sm_2Fe_{17} alloy was prepared by arc melting starting materials with a purity of better than 99.5%. Then the ingots were annealed in a vacuum at a temperature of 950–1050 °C for 6–10 h. They were then pulverized into fine powder and prepared as Mössbauer absorbers of 13 mg cm^{-2} thickness.

The transmission ^{57}Fe Mössbauer spectra were observed at room temperature on a constant-acceleration Promeda spectrometer, with a 15 mCi source of cobalt-57 in palladium. The velocity scale was calibrated using an α-Fe absorber of 25 μm thickness at room temperature. The spectra were measured using 512 channels and were analysed by the program AWMI [31] (so called because it consists of an algorithm without matrix inversion), on a IBM PC/XT microcomputer.

3. Fitting of Mössbauer spectra

The R_2Fe_{17} compounds are known to crystallize with either the rhombohedral Th_2Zh_{17} structure type ($R\,\bar{3}m$) or the hexagonal Th_2Ni_{17} structure type ($P6_3/mmc$) for the lighter and heavier rare-earth metals, respectively. They have different stackings of the layers along C (Fig. 1). Both are represented by hexagonal cells, with $Z = 3$ and $Z = 2$, respectively [18, 32, 33]. Sm_2Fe_{17} is the rhombohedral Th_2Zh_{17} structure type.

As the magnetization is oriented in the basal plane along [1 0 0] in Sm_2Fe_{17}, the Mössbauer spectra are analysed with seven inequivalent magnetic sites. These are labelled 6c, $9d_6$, $9d_3$, $18f_{12}$, $18f_6$, $18h_{12}$ and $18h_6$, with relative intensities in the ratios 6 : 6 : 3 : 12 : 6 : 12 : 6 [20, 34].

Five samples were investigated: sample 1, treated in vacuum at 1050 °C for 10 h; sample 2, treated in vacuum at 950 °C for 10 h; sample 3, treated in vacuum at 1050 °C for 6 h; sample 4, treated in vacuum at 950 °C for 6 h; sample 5, cast and not treated, for comparison with treated samples.

We used constraints similar to those adopted in [34]. One linewidth was used for sextets in all spectra. The isomer shifts were made equal for the two magnetically inequivalent sites originating from the same crystallographic site. The values of hyperfine field for 9d, 18f, and 18h were adopted from [34]. The above constraint condition was called the CCI mode. In order to compare the effect of different fitting methods, we also adopted an unconstrained fitting to the hyperfine parameters, which was called the CC2 mode. The Mössbauer spectra fitted are given in Figs 2 and 3. Our spectra are similar to those reported in [20, 24].

The linewidth of sextets in all spectra was chosen as 0.25 mm s^{-1}. The value is smaller than or equal to those found in [20] and in [34], respectively. In as much as there is enough range within the envelope of the central doublet of uncertain origin, we extend the constraint to its linewidth. The practical fitting values are 0.20–0.26 mm s^{-1}.

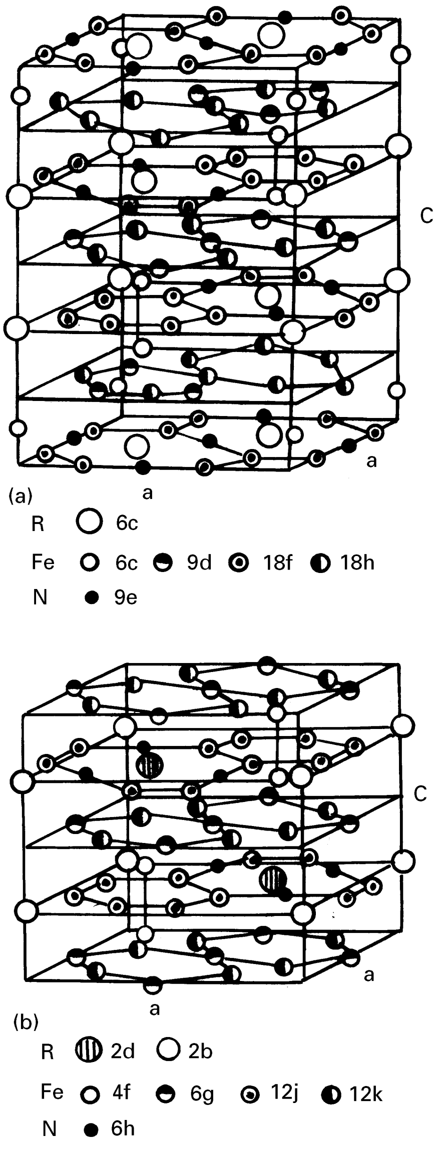

Figure 1 Structures of (a) the rhombohedral and (b) hexagonal varieties of R_2Fe_{17}. The octahedral interstices which may be occupied by nitrogen are the 9e and 6h sites indicated as full circles.

Because the 6c site has only one magnetically inequivalent site and the largest hyperfine field, and its peaks 1 and 6 are away from those of other sextets, the 6c site hyperfine parameters are fitted freely. In all samples (Table I), the fields for 6c and the weighted average fields of 18h have the largest and the smallest values, respectively. This is identical with the results in [24, 34]. In the same sample, the field values of the corresponding site and the related contents of the main phase, impurity and α-Fe (see Section 4) are approximately equal using the CC1 and CC2 modes. It is thought that spectra of good quality were obtained by the fitting.

In all the spectra, the isomer shifts of the 6c site have the largest values and the sequence in size for the isomer shifts is 6c > 18h > 18f > 9d. In the CC2 model, the isomer shifts of the pairs are not equal, but their weighted averages follow the above sequence.

It can be seen from Table I that the assignment that we found for each site is close to that given in [34] on

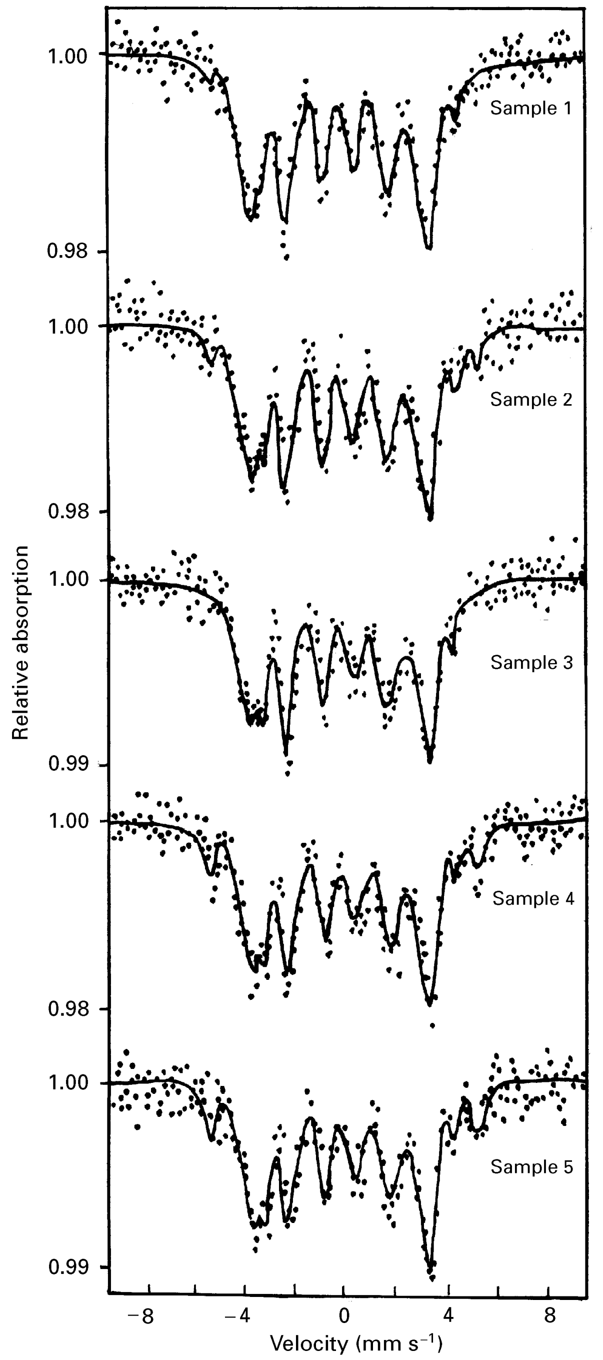

Figure 2 The Mössbauer spectra of Sm_2Fe_{17} using the CC1 mode.

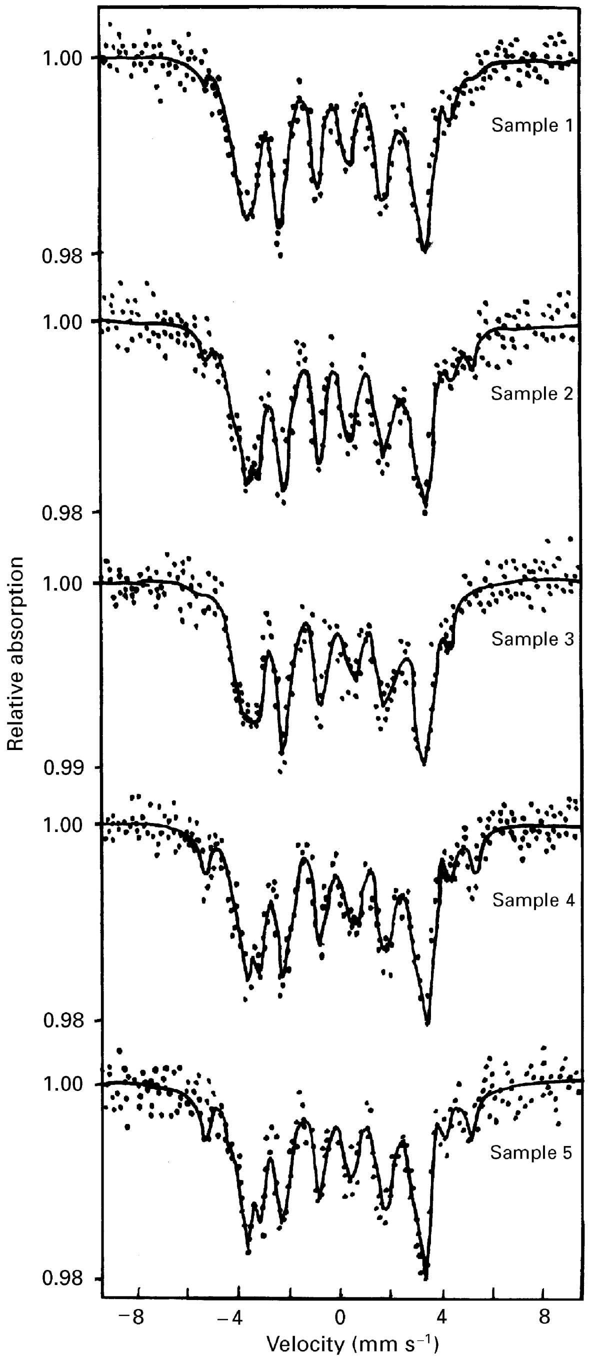

Figure 3 The Mössbauer spectra of Sm_2Fe_{17} using the CC2 mode.

the basis of the data and sequence in size of the hyperfine fields and isomer shifts.

4. Results and discussion

The experimental results can be seen in Table II, where the second term represents the sum of the α-Fe sextet and paramagnetic doublet.

From the fitting, we find that the spectra of Sm_2Fe_{17} all contain the α-Fe sextet. Our result is in agreement with those of many researchers (see Section 1). In the CC1 mode, we adopted the values in [34] for the hyperfine fields of the pairs in order that the related contents of the main phase and impurity for our samples can be compared with the reported values under approximately the same fitting condition. In Table II, the smallest content of α-Fe is 2.34%. In [33], values of α-Fe between 2% and 7% were found for the spectra of R_2Fe_{17} compounds. Our content is approximately equal to the low limit in [34] and is less than that (approximately 9%) in [20]. In addition, a central doublet of uncertain origin is added to all spectra, where the contents are 2.70–5.40%. Other researchers [24, 35] also showed the doublet to exist in their fitting spectra.

The origin of α-Fe mainly stems from the preparation process. Ideal annealing conditions may eliminate much of the α-Fe but cannot completely do this. The origin of the doublet could be that some portions of the samples become paramagnetic, when the measurement temperature (about 295 °K) is close to the Curie temperature (385 °K [26], 389 °K [18], 413 °K [19] or 423 °K [13]) of Sm_2Fe_{17} [35].

TABLE I Mössbauer spectra hyperfine fields H and isomer shifts IS (relative to room-temperature α-Fe) for Sm_2Fe_{17}

Sample			6c	$9d_6$	$9d_6$	$18f_{12}$	$18f_8$	$18h_{12}$	$18h_6$	Weight average	α-Fe
1	CC1	H (kOe)	274.3	214.0	219.0	206.0	236.0	202.0	195.0	217.0	330.3
		IS ($mm\,s^{-1}$)	0.061	− 0.177	− 0.177	− 0.097	− 0.097	− 0.087	− 0.087	− 0.089	
	CC2	H (kOe)	273.9	212.9	220.0	208.6	235.9	201.7	199.3	217.8	325.8
		IS ($mm\,s^{-1}$)								− 0.087	
2	CC1	H (kOe)	271.1	214.0	219.0	206.0	236.0	202.0	195.0	216.7	330.3
		IS ($mm\,s^{-1}$)	0.098	− 0.177	− 0.177	− 0.097	− 0.097	− 0.087	− 0.087	− 0.085	
	CC2	H (kOe)	271.6	208.3	218.3	207.8	239.8	204.9	187.5	216.7	328.0
		IS ($mm\,s^{-1}$)								− 0.091	
3	CC1	H (kOe)	265.1	214.0	219.0	206.0	236.0	202.0	195.0	216.0	330.3
		IS ($mm\,s^{-1}$)	0.083	− 0.175	− 0.175	− 0.095	− 0.095	− 0.085	− 0.085	− 0.085	
	CC2	H (kOe)	265.2	212.0	216.7	205.9	237.4	205.0	203.2	217.4	339.7
		IS ($mm\,s^{-1}$)								− 0.062	
4	CC1	H (kOe)	271.0	214.0	219.0	206.0	236.0	202.0	195.0	216.6	330.3
		IS ($mm\,s^{-1}$)	0.064	− 0.174	− 0.174	− 0.094	− 0.093	− 0.084	− 0.084	− 0.086	
	CC2	H (kOe)	270.7	211.3	218.6	207.7	233.9	203.6	197.7	217.1	331.4
		IS ($mm\,s^{-1}$)								− 0.064	
5	CC1	H (kOe)	268.9	214.0	219.0	206.0	236.0	202.0	195.0	216.4	330.3
		IS ($mm\,s^{-1}$)	− 0.016	− 0.173	− 0.173	− 0.093	− 0.093	− 0.083	− 0.083	− 0.095	
	CC2	H (kOe)	267.2	211.0	218.6	205.3	231.2	205.0	200.6	216.5	328.2
		IS ($mm\,s^{-1}$)								− 0.097	

TABLE II Related contents of the phases in Sm_2Fe_{17}. Δ = CC2–CC1 (CC1 and CC2 are the two fitting modes)

Sample	Main phase (%)			Impurity (%)		α-Fe (%)		
	CC1	CC2	Δ	CC1	CC2	CC1	CC2	Δ
1	92.68	92.43	− 0.25	7.32	7.57	3.68	3.81	0.13
2	85.42	85.47	0.05	14.58	14.53	9.18	9.20	0.02
3	92.95	92.87	− 0.08	7.05	7.13	2.34	2.36	0.02
4	82.76	82.56	− 0.20	17.25	17.45	13.40	13.75	0.35
5	81.62	81.64	0.02	18.38	18.36	15.68	15.64	− 0.04

It can be seen from Table II that the values in the CC1 and CC2 columns corresponding to the main, impurity and α-Fe phases are very close to each other for the same sample. As the results obtained using the two modes are almost the same, therefore they are thought to be correct.

From the data in Table II, the impurity and α-Fe contents of sample 5 (the cast sample) have the largest values. The reason is apparent, namely because it does not undergo the homogenization treatment. The impurity and α-Fe contents of samples 1 and 3 are both less than about half of those of samples 2 and 4, respectively. This indicates that the treatment at 1050 °C is better than that at 950 °C. However, the contents in sample 3 are slightly less than those of sample 1 and the contents of sample 4 are greater than those of sample 2. This indicates that the higher temperature needs a shorter time within our chosen treatment range.

It will be seen from Table I that the overall weighted average fields are all approximately equal. This is thought to arise because the different heat treatment conditions did not change the near-neighbour coordination of iron atoms in Sm_2Fe_{17}.

It is common knowledge that, the larger the number of near-neighbour iron atoms, the higher is the hyperfine field. The number of nearest-neighbour atoms for the 6c, 9d, 12f and 18h sites are (1, 3, 6, 3, 1), (2, 0, 4, 4, 2), (2, 2, 2, 4, 2), and (1, 2, 4, 2, 3), respectively [24]. It is understood that the 6c dumbbell site and 18h site should have the largest and the smallest hyperfine fields since they have the most and the fewest iron atoms, and the fewest and the most rare-earth neighbours, respectively.

5. Conclusions

1. The spectra of Sm_2Fe_{17} are split into seven inequivalent magnetic sites. Identical results were obtained using the two fitting modes, i.e., for the same sample, the field values of the corresponding site and the related contents of the main, impurity and α-Fe phases are approximately equal.

2. For our preparation technology, all samples at room temperature contain α-Fe sextets and paramagnetic doublets. By choosing an appropriate annealing temperature and an approximate annealing time, the smallest amount of the impurity phase may be obtained. Within our research range, the smallest α-Fe and the impurity contents are 2.34% and 7.05%, respectively.

3. For all samples, the overall weighted average fields were all approximately equal. It was thought the different heat treatment conditions did not result in any change in near-neighbour coordination of the iron atoms in Sm_2Fe_{17}.

4. The 6c site and 18h site have the largest and the smallest hyperfine field, respectively, for all samples.

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