

## Mossbauer Spectroscopy of the Reaction Products Following Thermal Decomposition of $K_4Fe(CN)_6 \cdot 3H_2O$

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The reaction of  $K_4FeO_2$  (obtained through thermal decomposition of  $K_4Fe(CN)_6 \cdot 3H_2O$ ) with air humidity in the remaining alkaline medium after the thermal attack, produces small particles of  $\gamma-Fe_2O_3$ .

A reação de  $K_4FeO_2$  (obtido através da decomposição térmica de  $K_4Fe(CN)_6 \cdot 3H_2O$  em contato com a umidade do ar no meio alcalino remanescente após o ataque térmico, produz pequenas partículas de  $\gamma-Fe_2O_3$ .

We have reported in a previous paper<sup>1</sup> the thermogravimetric, room temperature Mossbauer effect and X-ray comparative study of the thermal decomposition of  $K_4Fe(CN)_6 \cdot 3H_2O$ . It was shown that the heating of 2000 mg of the compound in air at a rate of  $2^\circ C/min$  produced at  $900^\circ C$  and  $1000^\circ C$  mainly  $K_4FeO_2$  (Fig. 1a and 2a) with a small contribution of  $Fe_3O_4$  (around 2% for the sample heated up to  $900^\circ C$  and even less for the one heated up to  $1000^\circ C$ ), and a more appreciable contribution (20 and 13%, respectively) of a paramagnetic compound thought to be the hydration product  $\beta-FeOOH$  (Table 1). Available data in the literature for both compounds are also quoted in Table 1. In the present note we report some results on the reaction products of the above mentioned samples. The sample obtained by heating up to  $900^\circ C$  and which had been encapsulated under Ar, was opened in air and immediately a one day room temperature measurement was performed (Fig. 1b), which therefore is an integration of the Mossbauer spectra of the final reaction products and the intermediate steps. The spectrum has been adequately fitted on the assumption of small amounts of  $Fe_3O_4$  (some 2-5%) plus unreacted  $K_4FeO_2$ , superimposed to a typical paramagnetic spectrum, well differentiated from the original  $\beta-FeOOH$ . The  $1000^\circ C$  sample, on the contrary, was left open for a similar period of time and then the room temperature Moss-

sbauer spectrum was taken. Therefore the spectrum represents the final (or nearly) reaction products (Fig.2b). Only one paramagnetic compound is found, whose parameters (Table 2) coincide well within the experimental error with those of the paramagnetic fraction of the former sample. To further elucidate the nature of this compound both samples were measured at liquid helium temperature, and identical magnetically split spectra were found (Fig.1c and 2c). The corresponding parameters are shown in Table 2. As we suspected the reaction product to be  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) in accordance with the statement in the literature<sup>9,10</sup> that the hydrolysis of  $\text{KFeO}_2$  and  $\beta\text{-FeOOH}$  produces maghemite, we synthesized the compound<sup>11,13</sup> so as to be able to compare their Mossbauer spectra. The sample thus produced has shown an identical spectrum at  $4.2^\circ\text{K}$  within the experimental error. For the sake of comparison, Table 3 shows the values found in the literature for  $\gamma\text{-Fe}_2\text{O}_3$  at different temperatures. Using the  $\theta_F$  value of the literature<sup>20</sup>,  $675^\circ\text{C}$ , and the Brillouin curve for  $S = 5/2$ , together with the room temperature effective fields for both sublattices, we obtain values for the low temperature effective fields in the range  $498\text{-}515$  kOe. Therefore we conclude that effectively the reaction of  $\text{KFeO}_2$  via  $\beta\text{-FeOOH}$  in an alkaline medium, such as what remains after the thermal decomposition of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ , produces  $\gamma\text{-Fe}_2\text{O}_3$ . Furthermore we may venture to indicate that the approximate particle size is in the range near  $6$  nm in accordance with Krupyaniskii and Suzdalev<sup>12</sup>. Besides, support is found for their statement that there is essentially no line broadening and washing out of the spectrum due to superparamagnetism as had been found by Coey and Khalafalla<sup>13</sup>. Our slightly lower QS values may suggest that our particles are more spherelike than those in reference 12. Therefore thermal decomposition of  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  in the  $900\text{-}1000^\circ\text{C}$  range and further reaction in air may provide an alternative method for the production of controlled size particles of  $\gamma\text{-Fe}_2\text{O}_3$ . We may recall that this transformation of  $\beta\text{-FeOOH}$  differs from the one found by Dézsi et al.<sup>22</sup> who report the conversion to  $\alpha\text{-Fe}_2\text{O}_3$  at  $670^\circ\text{K}$ .

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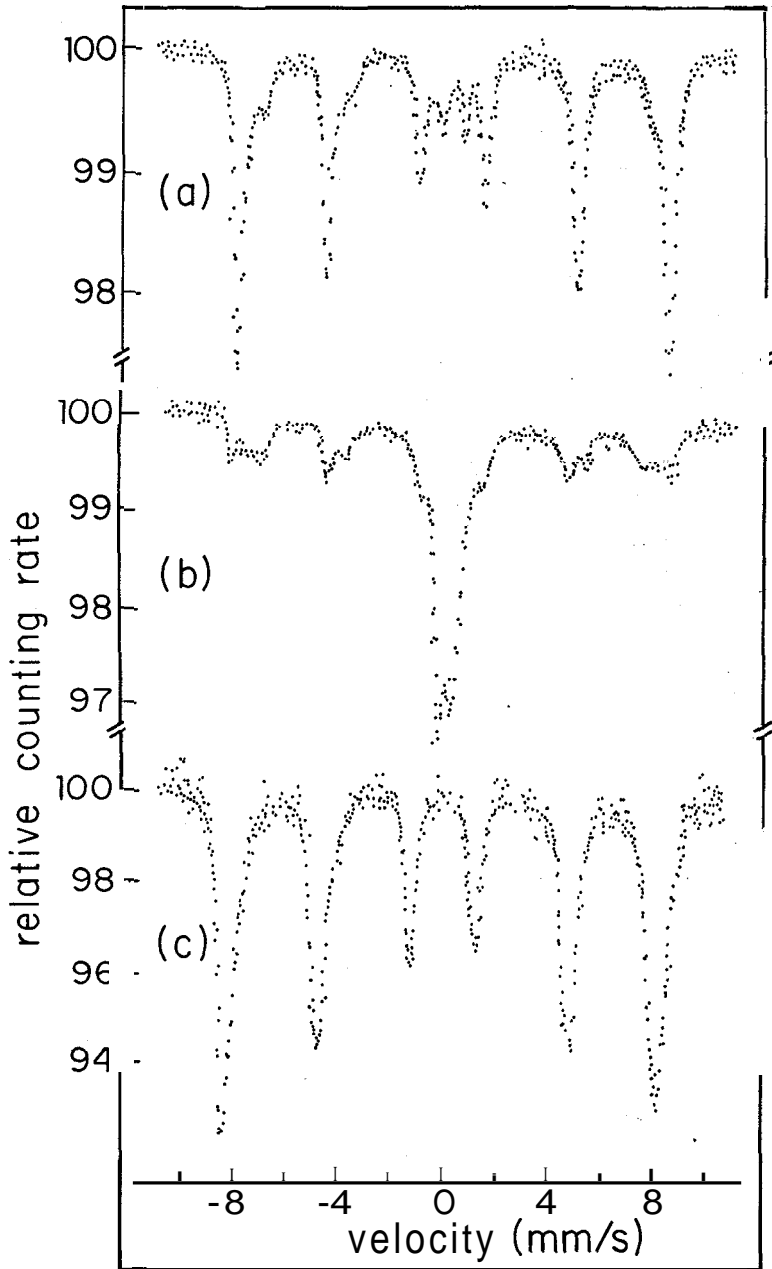


Fig.1 - Mössbauer absorption spectra of the products of the thermal decomposition of  $K_4Fe(CN)_6 \cdot 3H_2O$  in air at a velocity of  $2^\circ C/min$  up to  $900^\circ C$ . a) sample under Ar, room temperature; b) sample opened in air, room temperature; c) same as b),  $4.2^\circ K$ .

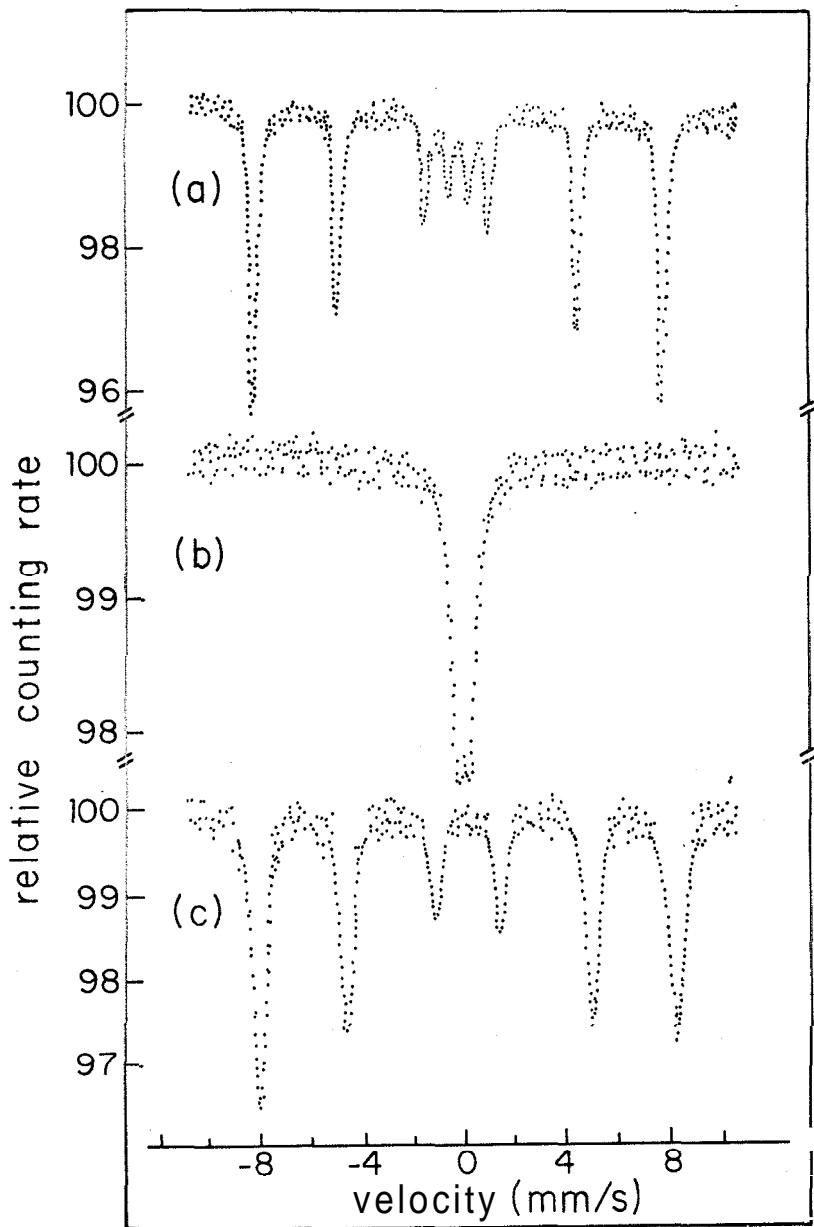


Fig.2 - Mössbauer absorption spectra of the products of the thermal decomposition of  $K_4Fe(CN)_6 \cdot 3H_2O$  in air at a velocity of  $2^\circ C/min$  up to  $1000^\circ C$ . a) sample under Ar, room temperature; b) sample opened in air, room temperature; c) same as b),  $4.2^\circ K$ .

Table 1 - Room temperature Mössbauer parameters of the main products of the thermal decomposition of  $K_4Fe(CN)_6 \cdot 3H_2O$  up to 900 and 1000°C, and comparison with available data in the literature for these compounds.

	900°C			1000°C			Ref.
	$IS^{a,b,c}$	$QS^{a,b}$	$H_{eff}^{a,d}$	$IS^{a,b,c}$	$QS^{a,b}$	$H_{eff}^{a,d}$	
KFeO <sub>2</sub>	0.24(3)	0.03(3)	500(5)	0.21(3)	0.04(3)	500(5)	1
	0.18(3)	0	505(5)				2,8
	0.18 §	0.16 §	496(5)				7
β-FeOOH	0.35(3)	0.73(3)	-	0.35(5)	0.70(3)	-	1
	0.33(1)	0.68(1)	-				3
	0.33(6)	0.62(6)	-				4
	0.39(2)	0.62(2)	-				21
	-	0.64(5)	-				5
	0.38 §	0.70(1)	-				6

a) Error of the last figure quoted within brackets

b) In mm/s

c) Isomer shift data referred to Fe

d) In kOe

§ Estimated from text and/or drawings

Table 2 - Room temperature and liquid helium Mössbauer parameters of the main reaction product of  $K^+eO_2$  and β-FeOOH. Sample originated on the thermal treatment of  $K_4Fe(CN)_6 \cdot 3H_2O$  up to 900 and 1000°C.

	900°C			1000°C			
	$IS^{a,b,c}$	$QS^{a,b}$	$H_{eff}^{a,d}$	$IS^{a,b,c}$	$QS^{a,b}$	$H_{eff}^{a,d}$	
R.T.	0.41(4)	0.55(3)	-	0.36(4)	0.48(4)	-	Present work
4.2°K {	0.22(6)	0.05(5)	502(6)	0.30(6)	0.00(5)	504(6)	} Present work
	0.40(3)	0.10(3)	513(6)	0.44(4)	0.09(3)	513(6)	

$a, b, c, d$  - see footnotes of Table 1.

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Table 3 - Data from the literature for the Mossbauer parameters of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>

Temp.	$IS^{a,b,c}$	$H_{eff}^{a,d}$	Particle Size	Ref.	
Room	0.29(9)	0.90(9)	-	less than 6 nm	12
	broad triangular absorption peak		7,4 nm	13	
	0.27(9)	0	505(5)	6-30 nm	12
	0.27(9)	0.63(9)	-		
	0.33(1)	0.09(1)	501,4 (0,7)	bulk	3
	0.27(4)	0	488(5)	"micron-sized"	14
	0.41(4)	0	499(5)		
	0.41(5)	0	505(20)	bulk	15
	0.32(9)	0.06§	496(20)	acetate magnetic tape	16
	0.26	-	499	bulk=95,5 nm	13,17
	0.37	-	505		
	0.18(3)	-	502(4)		
	0.40(3)	-	503(4)	bulk	18
85°K	0.31	0	515(2)	bulk	15
	-	-	512(10)§		
5°K	-	-	526(10)	5-75 nm	19
	-	-	520(10)§		
4.2°K	-	-	532(10)	bulk	18

$a, b, c, d, §$  - see footnotes on table 1.

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