MOSSBAUER STUDY OF FERRO-GALLIC INKS FROM MANUSCRIPTS OF THE XIIth AND XVth CENTURIES

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Abstract. - Mössbauer spectra of ferro-gallic inks of ancient and damaged manuscripts of the XIIth and XVth Centuries reveal the presence of large amounts of ferrous oxalate. This compound was also found to be formed after artificial ageing of recently prepared inks. Superparamagnetic or amorphous phases containing Fe^{3+} ions are also observed and are likely related to the black colour of the ink.

Black inks used in ancient manuscripts were frequently of the ferro-gallic nature. According to ancient recipes /1/ such types of inks were prepared from ferrous sulphate, from a tannic substance of the gallo-tannic family and from a gum as binding agent. We examined by means of Mössbauer spectroscopy and X-ray diffraction both fragments of ancient manuscripts and recent ink samples of this type.

I. ANCIENT MANUSCRIPT STUDIES

1) Missel of Colmar. This missel dated from 1469 belongs to the library of the Protestant Consistory of Colmar, France. A large part of the paper sheets of this manuscript are very much damaged, possibly as a consequence of the decomposition of the inks used in writing. Mössbauer absorbers were made from fragments of the damaged part of the manuscript, by assembling together about 25 to 50 paper sheets. The spectra were recorded at various temperatures between 295 and 1.4K using a source of ^{57}Co in Rh and the percentage of resonant absorption was found to be between 1 and 3%.

The room temperature spectrum (T=295K, Fig.1) is made of 2 quadrupole doublets arising from Fe^{2+} and Fe^{3+} ions, whose relative proportions are respectively 45 ± 1 and 55 ± 1 %.

The magnetic hyperfine interaction appears below 20K for the Fe^{2+} fraction, giving a low symmetry hyperfine pattern (lines i,j,k,l,m,n,o, p, T=4.2K, Fig.1) from which all hyperfine parameters were derived by computer fitting (Table 1). The phase containing the Fe^{2+} ions was then identified as ferrous oxalate FeC_2O_4, $2H_2O$ /2/.

At the lowest temperatures the Fe^{3+} fraction is present as a quadrupole doublet (lines g,h, Fig.1) and a Zeeman sextet (lines a,b,c,d, e,f) whose relative proportions are temperature dependent. The intensity ratio (Fe^{3+} magnetic)/(Fe^{3+} total) drops from 39±3% at 1.4K to 20±2% at 10K and decreases slowly at higher temperatures. Such a behaviour is typical for the presence of a superparamagnetic phase, probably with very small particle size or even amorphous. This interpretation is also supported by the large Fe^{3+} linewidth observed at room temperature and by the fact that an external field of 5.5 Tesla markedly increases the magnetic fraction of the Fe^{3+} spectrum at 4.2K and aligns the corresponding moments.

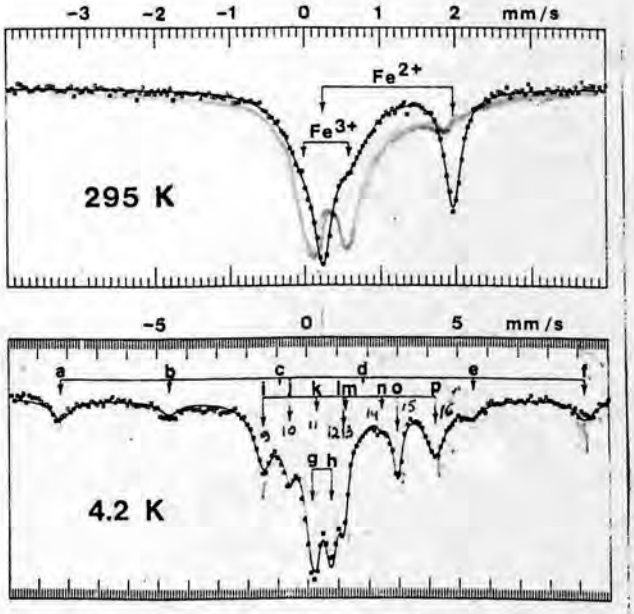

Fig.1 - Missel of Colmar : Mössbauer spectra and fitted curves. Line indexation at 4.2K : a,b,..., f : Fe^{3+} Zeeman sextet ; g,h : Fe^{3+} doublet, i,j,...,p : Fe^{2+} octet.

Two X-ray diffraction spectra have also been recorded from this manuscript, one from

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T (K)	IS mm/s	G mm/s	QS mm/s	H (KG)	η	θ deg	P %	comments
295	0.27	0.68	0.59	-	-	-	55	Fe^{3+}para
	1.08	0.28	1.73	-	-	-	45	Fe^{2+}para
4.2	0.41	0.64	0.64	-	-	-	39	Fe^{3+}para
	0.42	0.74	-	542	-	-	15	Fe^{3+}magn.
	1.23	var.	-2.04	150	0.6	79	46	Fe^{2+}magn.
1.4	0.41	0.78	0.68	-	-	-	33	Fe^{3+}para
	0.42	0.79	-	536	-	-	20	Fe^{3+}magn.
	1.23	var.	-2.04	150	0.6	79	47	Fe^{2+}magn.

Table 1 - Missel of Colmar : fitted parameters

IS : isomer shift (ref. $^{57}Co/Rh$)
G : full line width at mean height
QS : quadrupole splitting
H : hyperfine field
η : electric field gradient asymmetry parameter
θ : angle between H and EFG principal axis
P : relative area

cut out and ground black letters, the other from ground fragments of blank paper. Compared to this latter spectrum, the former contains additional lines belonging to the compounds SO_4Ca, $2H_2O$ (gypsum) and α FeC_2O_4, $2H_2O$ (ferrous oxalate). The presence of ferrous oxalate which is thus detected by both techniques in the ink is interesting as it supports previous assumptions concerning the probable formation of oxalic acid from the gallic acid decomposition /3/, and it may be connected to the degradation of parts of the manuscript ; furthermore a vapour chromatographic analysis has shown that the gallic acid was no longer present in the damaged parts of the missel /1/. As for the gypsum, it probably results from the action of the ferrous sulphate of the ink on some calcium compound present in the paper. However we have not been able to detect the presence of such a compound (CO_3Ca for example) in the X-ray spectrum of the blank paper.

2) Syriac manuscript. We also investigated by Mössbauer spectroscopy damaged fragments of a syriac manuscript of the XIIth century. The spectra recorded at 295 and 4.2K look very much like the corresponding spectra of the missel of Colmar : almost half the total absorption intensity is due to ferrous oxalate and the remaining part is due to Fe^{3+} ions which mainly contribute a quadrupole doublet. The fraction of Fe^{3+} ions which gives a magnetic hyperfine sextet at 4.2K is however less important and its lines are broader than in the missel of Colmar, which could indicate that the size of the superparamagnetic particles is smaller.

II. RECENTLY PREPARED INK STUDIED. We prepared ink samples following ancient recipes, from 3g of gall-nuts, 3g of gum-arabic and variable quantities of SO_4Fe, $7H_2O$ ranging from 3g to 0.15g for 100 ml of distilled water. Romm temperature Mössbauer spectra (Fig.2) were recorded after drying the samples.

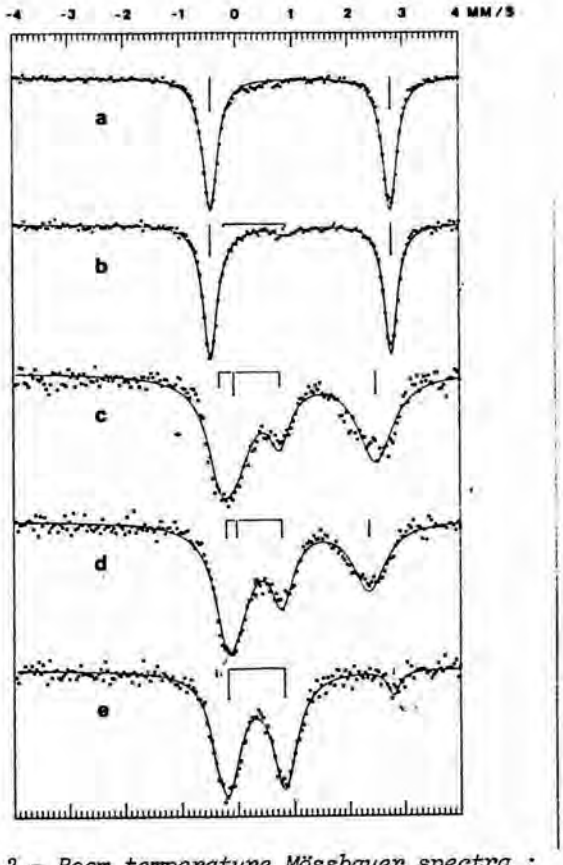

Fig.2 - Room temperature Mössbauer spectra : a : SO_4Fe, $7H_2O$; b,c,d,e : recently prepared ink samples from solutions containing respectively 3, 1.5, 1, 0.15g SO_4Fe, $7H_2O$ per 100 ml water. Linked arrows : Fe^{3+} doublet. Separate arrows : Fe^{2+} doublet.

In contrast with the manuscript spectra, no ferrous oxalate component appears in the spectra of these recent ink samples. The predominant Fe^{2+} quadrupole doublet which is observed in the sample having the highest iron concentration (Fig.2b) is obviously due to SO_4Fe, $7H_2O$ whose spectrum is given for comparison in Fig.2a. Distributions of Fe^{2+} quadrupole splitting values are observed in spectra 2c and 2d. The relative Fe^{3+} proportion increases for decreasing iron contents and becomes predominant in the spectrum 2e of the most dilute sample. The phase containing these Fe^{3+} ions, which is probably responsible for the black colour of the ink, has been shown to be amorphous by X-ray diffraction experiments. The corresponding quadrupole splitting (Table 2) is somewhat larger than for the Fe^{3+} paramagnetic fraction in the missel of Colmar and no Fe^{3+} magnetic fraction has been observed down to 1.4K.

An interesting observation was made concerning the evolution of the small Fe^{2+} contribution of spectrum (2e) after ageing the sample at 60C in a 90% relative humidity atmosphere during 3 weeks : whereas the Fe^{2+} doublet before ageing had hyperfine characteristics close to those of SO_4Fe, $7H_2O$, the Fe^{2+} doublet in the ageed sample clearly corresponds to ferrous oxalate, as

	IS mm/s	G mm/s	QS mm/s	P %	comments
before ageing	0.31 1.18	0.53 0.27	1.00 3.19	90±2 10±2	Fe^{3+} para SO_4Fe, $7H_2O$
after ageing	0.31 1.08	0.49 0.22	0.94 1.72	87±2 13±2	Fe^{3+} para FeC_2O_4, $2H_2O$

Table 2 - Fitted parameters at T=295K of recently prepared ink samples (from 0.15g SO_4Fe, $7H_2O$ in 100 ml water) before and after ageing.

was observed with the ancient manuscripts. Alternatively, a biological degradation of the gallic acid by sowing the ink solution by Aspergillus niger spores led to a complete oxydization of iron into the Fe^{3+} form.

Further experimental studies are planed in order to establish possible correlations between the degradation state of the manuscripts, the percentage of ferrous oxalate which appears in the ink and the initial concentration of ferrous sulphate in the ink preparation and to study in more details the possible influence of biological degradation.

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