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MOSSBAUER STUDY OF HYDRATED IRON SULFATES\*

by

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\* S.I.A. and L.I. dedicate this paper to Prof. J. Danon who gave relevant contributions to this work until his premature death in October 30, 1989.

## Summary

The hydrated iron sulfates amarantite  $\text{Fe}(\text{SO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ , copiapite  $(\text{Mg}, \text{Al})\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$  and ungemachite  $\text{K}_3\text{Na}_9\text{Fe}(\text{SO}_4)_6(\text{OH})_3 \cdot 9\text{H}_2\text{O}$  were studied by Mössbauer Spectroscopy (MS) in connection with Differential Scanning Calorimetry (DSC). The effect of the dehydration on the hyperfine parameters at the Fe sites was investigated. For amarantite, the Mössbauer spectrum remained practically unchanged, while the  $\text{Fe}^{3+}$  quadrupole splittings for copiapite and ungemachite increased. The  $\text{Fe}^{2+}$  quadrupole splitting of ungemachite was also unchanged. We have found out the anisotropy of the recoilless absorption probability for the  $^{57}\text{Fe}$  Mössbauer gamma ray in amarantite. The three minerals were found to be highly hygroscopic after the dehydration consequent of the DSC measurements.

**Key-words:** Mössbauer spectroscopy; Hyperfine interactions; Hydrated iron sulfates

-1-

## 1. Introduction

Amarantite  $\text{Fe}(\text{SO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$ , copiapite  $(\text{Mg,Al})\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$  and ungemachite  $\text{K}_3\text{Na}_9\text{Fe}(\text{SO}_4)_6(\text{OH})_3 \cdot 9\text{H}_2\text{O}$  have been studied to the mineralogical point of view [1,2,3]. Since the second half of the sixties, Mössbauer Spectroscopy has been used to investigate the minerals [4]. The convenience of such technique has to do with the easy use of the isotope  $^{57}\text{Fe}$  and the existence of a great number of iron compounds in the earth. In non-magnetic systems, the information obtained by Mössbauer spectroscopy stems from the isomer shift, which measures the electron density at the probe nucleus, and from the electric quadrupole interaction, which is sensitive to deviations of the charge distribution around the nucleus from cubic symmetry. The recoil-free fraction is another important parameter which will be considered in this paper. It depends on the gamma ray energy and the lattice properties.

In this work, the Mössbauer effect of amarantite, copiapite and ungemachite was investigated. The minerals were obtained from Sierra Gorda, Chile (amarantite and copiapite) and from Tintic Standard Mine, USA (ungemachite). Amarantite was also gotten from Saghand Mine, Iran. We have also investigated these minerals by Differential Scanning Calorimetry and could observe the effect of their dehydration in the Mössbauer spectra.

## 2. Experiments and Results

The three minerals were studied by Mössbauer Spectroscopy (MS), in absorber experiments, with a  $^{57}\text{Co}:\text{Rh}$  source at room temperature. Some measurements at liquid nitrogen and helium were made in order to check the existence of magnetic effects. As magnetic splittings were not found, we believe that the Fe ions are low spin.

Differential Scanning Calorimetry (DSC) was also used to investigate the dehydration of the samples in connection with the MS measurements. The DSC experiments were made in the temperature range 50.0 to 500.0°C at a rate of 10°C per minute.

X-Ray analyses were also made in order to identify the minerals.

### A - Amaranthite $\text{Fe}(\text{SO}_4)(\text{OH})\cdot 3\text{H}_2\text{O}$ .

Amarantite is triclinic [2]. Two sites of iron ions occupy the center of distorted octahedrals of oxygen ions, some of which belong to water molecules [2,3]. Our X-Ray analyses are in agreement with the lattice parameters and the structure proposed by Cesbron [2] for this mineral.

DSC measurements (Fig 1-a) show four endothermic peaks, the deeper one being at 112°C and the others at 184°C, 237°C and 318°C. These peaks indicate successive loss of water molecules. The last exothermal peak, at 518°C, seems to be due to oxydation. The hygroscopic nature of amaranthite [2] was observed by the increase of weight which took place during the 24 hours after the thermal analysis. X-Ray measurements here

-3-

then revealed that the rehydrated sample was in an amorphous state.

We have not observed the formation of hohmannite  $\text{Fe}_2(\text{SO}_4)_2(\text{OH})_2 \cdot 7\text{H}_2\text{O}$  reported in the literature as due to the absorption of water in a greater amount than that lost [2].

The Mössbauer spectra of amarantite exhibit a single  $\text{Fe}^{3+}$  doublet at room temperature (Fig. 2). From this and also considering the structures of similar compounds [3,5,6,7] we assume that the two iron sites are equivalent.

Using the mineral coming from Chile, we have arranged eight small needle shaped single crystal samples (about  $5 \times 0.5 \times 0.5$  mm) as a Mössbauer absorber in which plane one could only define the crystal longitudinal direction. This was supposed to be the c axis [3]. The Mössbauer results at room temperature of this partially oriented single crystalline amarantite (gamma ray perpendicular to c axis) is shown in Fig. 3 and Tab. 2. A powder sample was also investigated (Fig. 2a and Tab 2).

The ratio of the areas of the Mössbauer peaks corresponding to the two quadrupole transitions for a single crystal is [8]:

$$\frac{a_3}{a_1} = \frac{\sum_{i \text{ sites}} p_3(\theta_i \phi_i) f(\theta_i \phi_i)}{\sum_{i \text{ sites}} p_1(\theta_i \phi_i) f(\theta_i \phi_i)} \quad (1)$$

where  $\theta_i \phi_i$  define the direction of the incident photon relative to the principal axis of the electric field gradient (EFG) at the Fe nuclear site  $i$ ,  $p_n(\theta_i \phi_i)$  is the relative absorption probability for transition  $n$  ( $n=1,3$ )

and  $f(\theta, \phi_1)$  is the recoilless absorption probability.

If the EFG is axially symmetric (the asymmetry parameter  $\eta=0$ ), the area ratio is reduced to the know expression:

$$\frac{a_3}{a_1} = \frac{3(1+\cos^2\theta)f(\theta)}{(5-3\cos^2\theta)f(\theta)} \quad (2)$$

where  $\theta$  is the orientation angle of the incident radiation relative to the z principal axis of the EFG. If we assume that in amarantite the EFG z principal axis coincides with the c axis, then, for the partially oriented single crystal sample one has  $\theta=90^\circ$ . So, if for a moment one assumes that f is isotropic, one gets from expression 2  $(a_3/a_1)_{\text{theor.}}=0.6$ . This is compared with our experimental result  $(a_3/a_1)_{\text{exper.}}=0.72\pm 0.04$ . This rough agreement between the theoretical and the experimental area ratios allows us to conclude that the so-called electric field gradient  $q>0$  (the nuclear quadrupole moment Q of  $^{57}\text{Fe}$  is positive).

For a powder absorber all orientations of the EFG principal axis relative to the incident photon direction are possible. Therefore, expression 1 becomes:

$$\frac{a_3}{a_1} = \frac{\int_{4\pi} p_3(\theta\phi)f(\theta\phi)d\Omega}{\int_{4\pi} p_1(\theta\phi)f(\theta\phi)d\Omega} \quad (3)$$

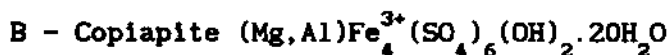
An area ratio different from 1 found for the powder amarantite

-5-

( $a_3/a_1=0.90\pm 0.03$ ; Tab 2) indicates that  $f$  is in fact anisotropic. This anisotropy known in the literature as Goldanskii Effect [9,10,11] was also observed in our previous work [12].

Now one can qualitatively ascribe to the angular dependence of  $p_3$  and  $p_1$  the great difference between the areas of the two peaks of the partially oriented single crystal sample ( $a_3/a_1=0.72\pm 0.04$ ; Tab 2).

We have measured the Mössbauer spectra of the powder sample, at room temperature, immediately after the DSC experiment, in order to study the effect of losing water. No change was observed (Figs. 2a and 2b; Tab 1) indicating that the water molecules which are lost in the heating process are probably relatively far from the distorted octahedra centered in the Fe atoms.

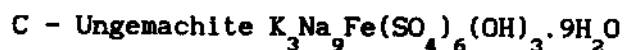


The samples were prepared from a specimen coming from Chile. X-Ray measurements have confirmed the lattice parameters found in the literature, indicating a triclinic structure for this mineral [13].

DSC analyses (Fig. 1b) show three endothermic peaks, indicating that the water molecules are lost at  $102^\circ\text{C}$ ,  $154^\circ\text{C}$  and  $170^\circ\text{C}$ . We found out that copiapite is also highly hygroscopic: 24 hours later the sample had recovered the lost water, reaching an amorphous state revealed by X-Ray measurements.

Mössbauer spectra at room temperature of the powder copiapite exhibit two  $\text{Fe}^{3+}$  doublets (Fig. 4a; Tab 1a). The spectra taken before and

immediately after the DSC measurements (Fig. 4b) are slightly different, indicating that the  $H_2O$  molecules involved in the dehydration have some interaction with the Fe ions, affecting the hyperfine parameters.



The light green sample comes from Tintic Standard Mine, Utah, USA.

As for the other minerals, X-Ray measurements were done in order to confirm the lattice parameters and the hexagonal structure [13].

The DSC analyses present two deep endothermic peaks indicating that most of the water is expelled at  $127^{\circ}C$  and the rest at  $227^{\circ}C$  (Fig. 1c). This mineral has also reached an amorphous state connected to the hygroscopic process, 24 hours after the DSC experiment.

Mössbauer measurements of ungemachite revealed the existence of two  $Fe^{3+}$  and one  $Fe^{2+}$  doublets. By comparing the spectra obtained before and immediately after the DSC experiment (Fig. 5; Tab 1), one finds significant differences involving the hyperfine parameters for the  $Fe^{3+}$  doublets, while the  $Fe^{2+}$  doublet remained unchanged. The more efficient electrostatic shielding done by the three filled  $t_{2g}$  electronic orbitals of  $Fe^{2+}$  may explain the insensibility of the hyperfine parameters measured in the  $Fe^{2+}$  ion [10].



-7-

### 3. Final Remarks

As far as we know, this is the first Mössbauer study of the minerals amarantite, copiapite and ungemachite.

The dehydration produced during the DSC measurements doesn't modify the  $\text{Fe}^{3+}$  Mössbauer hyperfine parameters of amarantite, while for copiapite one has slight changes. In this respect, ungemachite shows an interesting marked change of the  $\text{Fe}^{3+}$  doublets, while the  $\text{Fe}^{2+}$  doublet remains unaltered probably due to the more efficient electrostatic shielding done by three filled  $t_{2g}$  electronic orbitals.

The three iron sulfates are highly hygroscopic and reach amorphous states when they re-absorb water after the DSC measurements.

The single  $\text{Fe}^{3+}$  doublet of amarantite has made possible to observe the anisotropy of the Mössbauer recoil-free fraction in this mineral. We could also find out that the electric field gradient  $q$  at the  $\text{Fe}^{3+}$  site in amarantite is positive.

### Acknowledgements

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## Figure and Table Captions

- Fig. 1 - Differential Scanning Calorimetry curves for amarantite(a), copiapite(b) and ungemachite(c).
- Fig. 2 - Mössbauer spectra, at 300K, of powder amarantite before(a) and immediately after(b) the dehydration.
- Fig. 3 - Mössbauer spectrum, at 300K, of a partially oriented single crystalline amarantite, the incident photon being perpendicular to the c axis.
- Fig. 4 - Mössbauer spectra, at 300K, of powder copiapite before(a) and immediately after(b) the dehydration.
- Fig. 5 - Mössbauer spectra, at 300K, of powder ungemachite before(a) and immediately after(b) the dehydration.
- Tab. 1 - Isomer Shifts(IS), Quadrupole Splittings(QS), half widths( $\Gamma$ ) and doublet relative areas(A) for the three minerals before(a) and immediately after(b) the dehydration. The number between parenthesis is the absolute error for the last figure of each quantity.
- Tab. 2 - Comparative Mössbauer results, at 300K, for powder and crystalline (partially oriented) amarantite. The I's are the line intensities. The indices 1 and 3 refers to the left and right Mössbauer peaks, respectively.  $(a_3/a_1)_{\text{exper.}} = I_3 \Gamma_3 / I_1 \Gamma_1$ . The other symbols are explained in caption of Tab. 1.

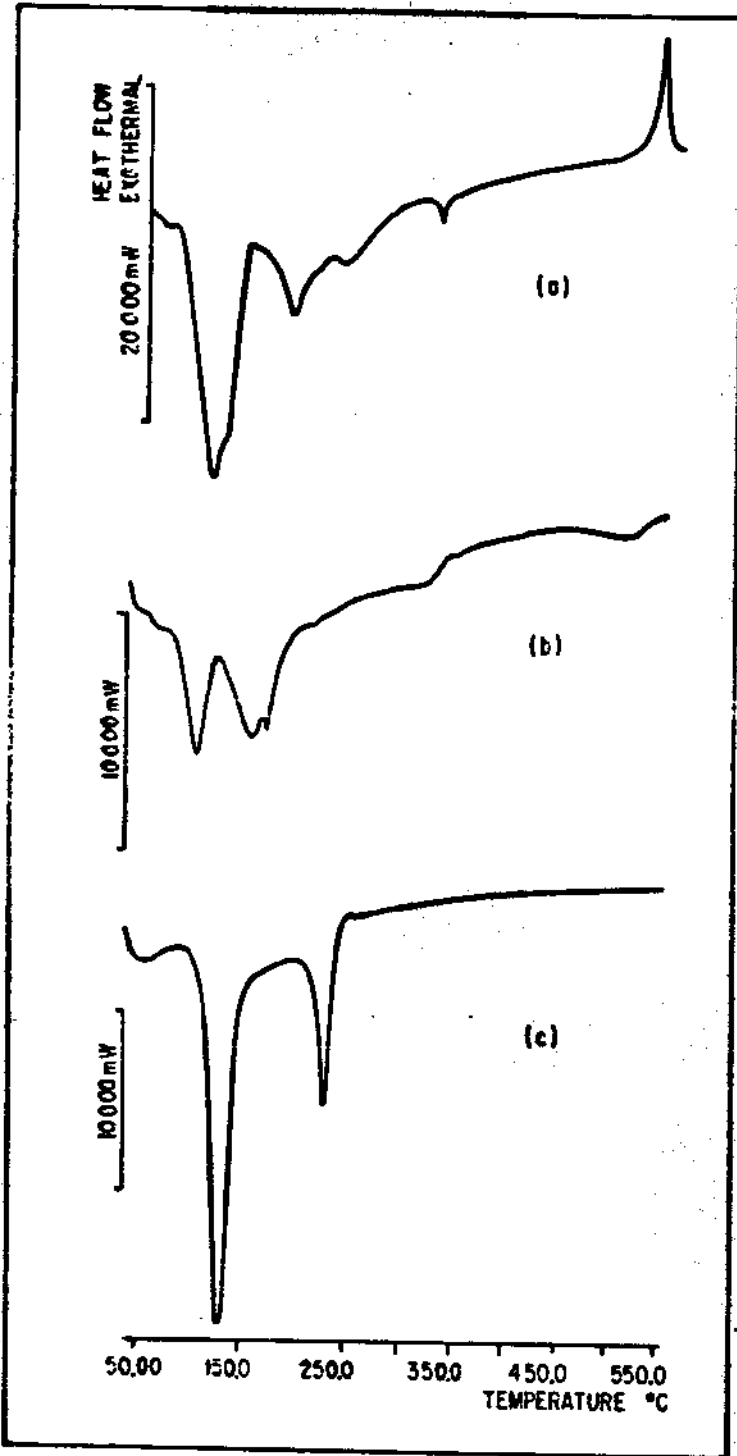


Fig. 1

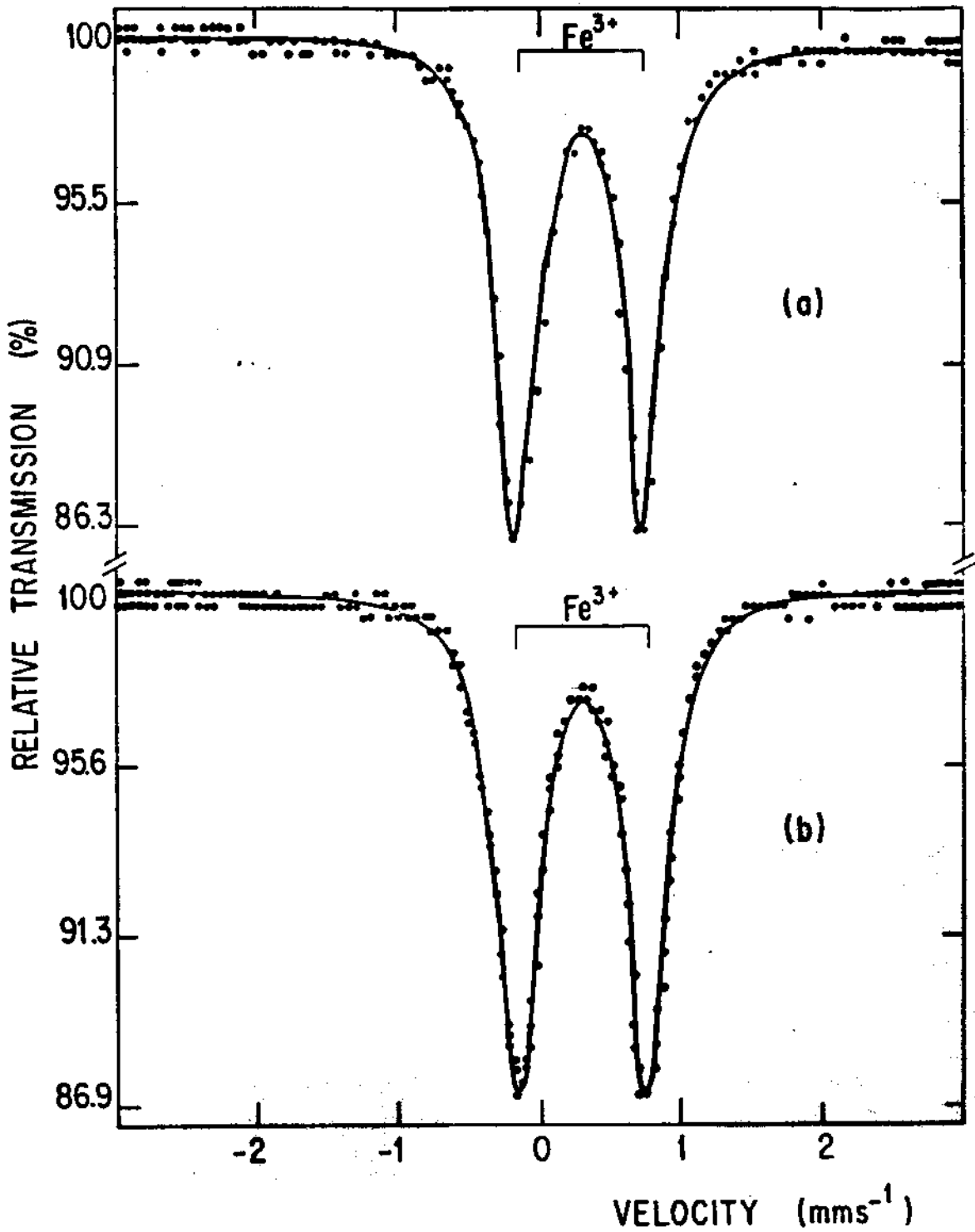


Fig. 2

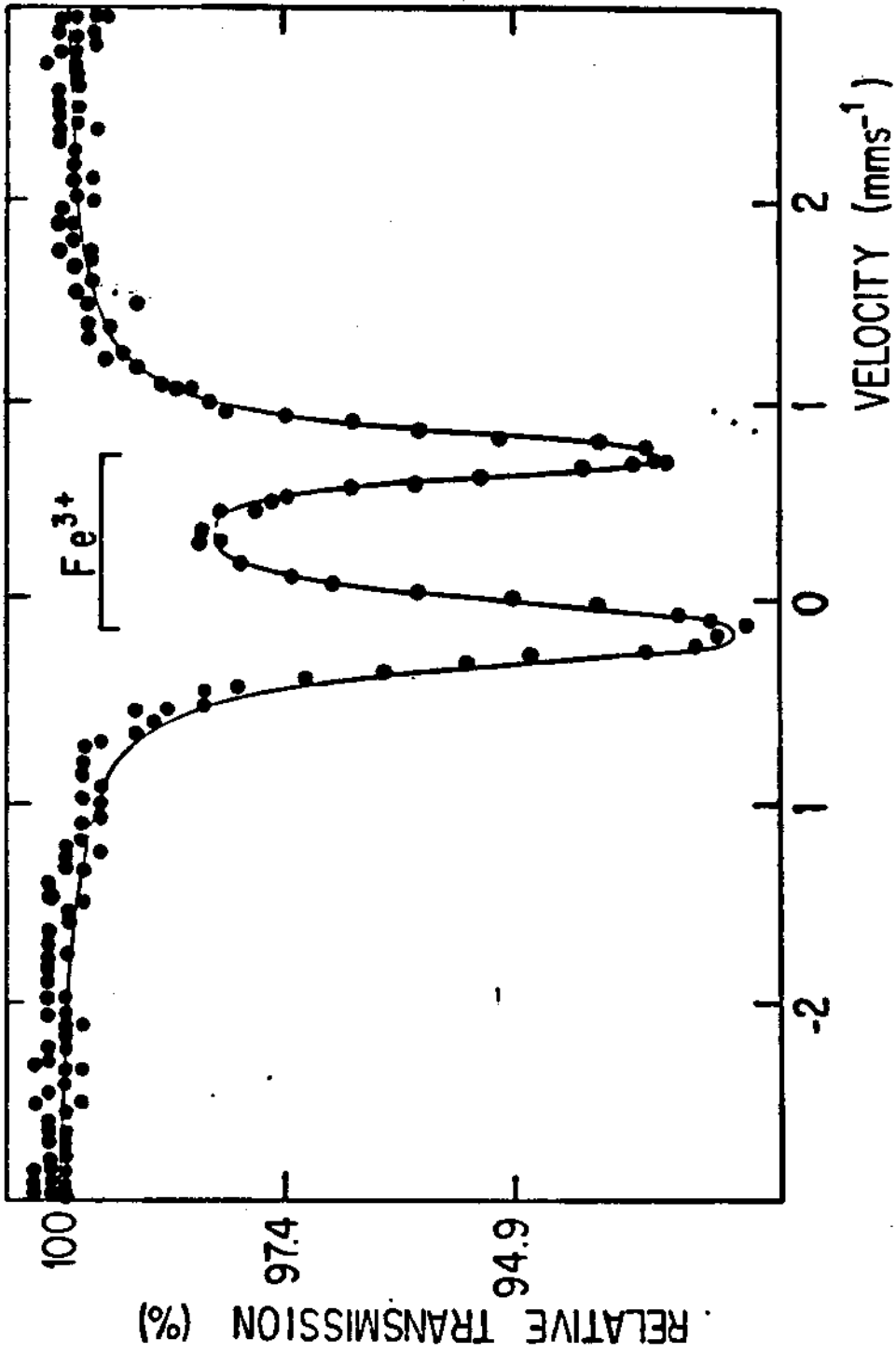


Fig. 3

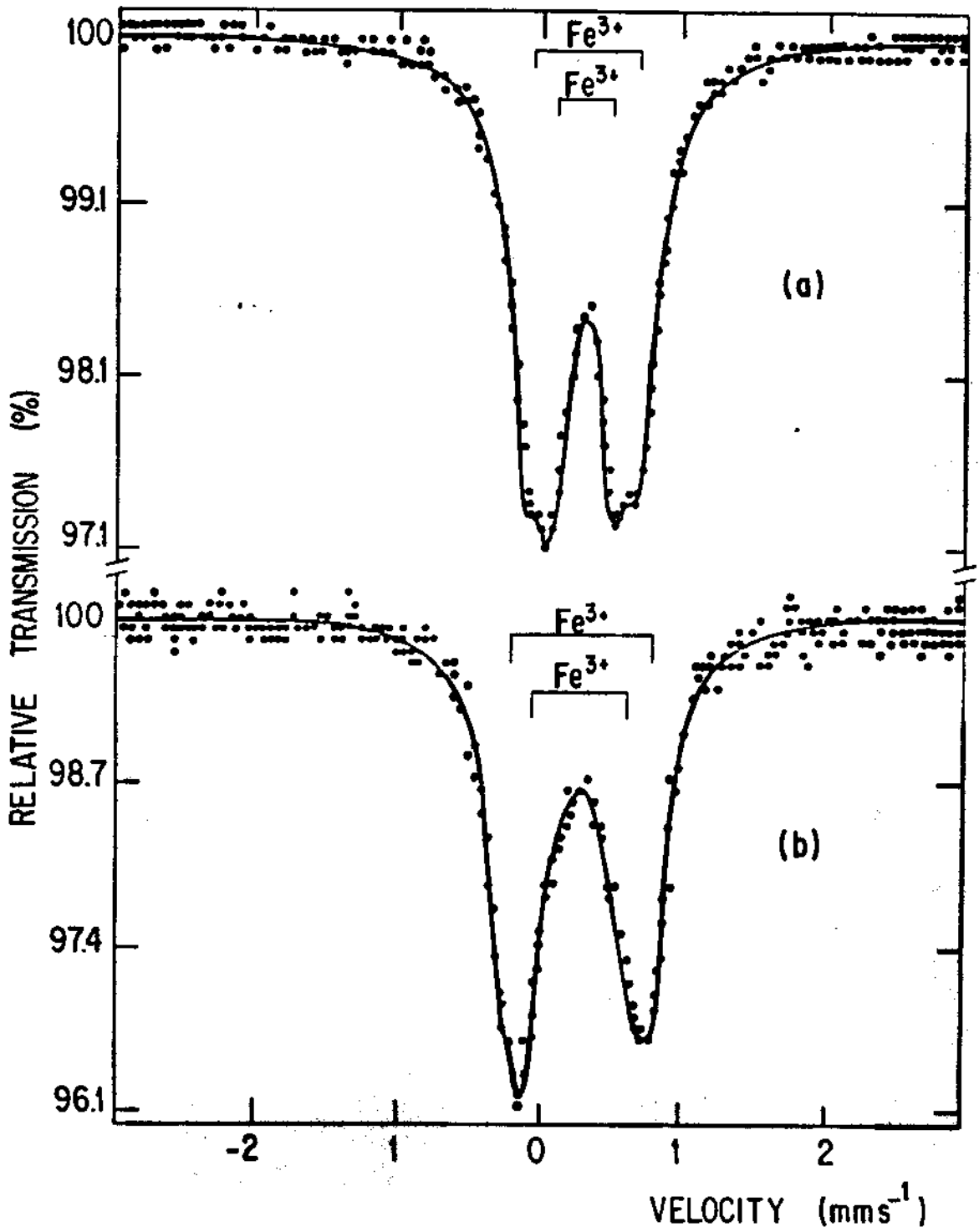


Fig. 4

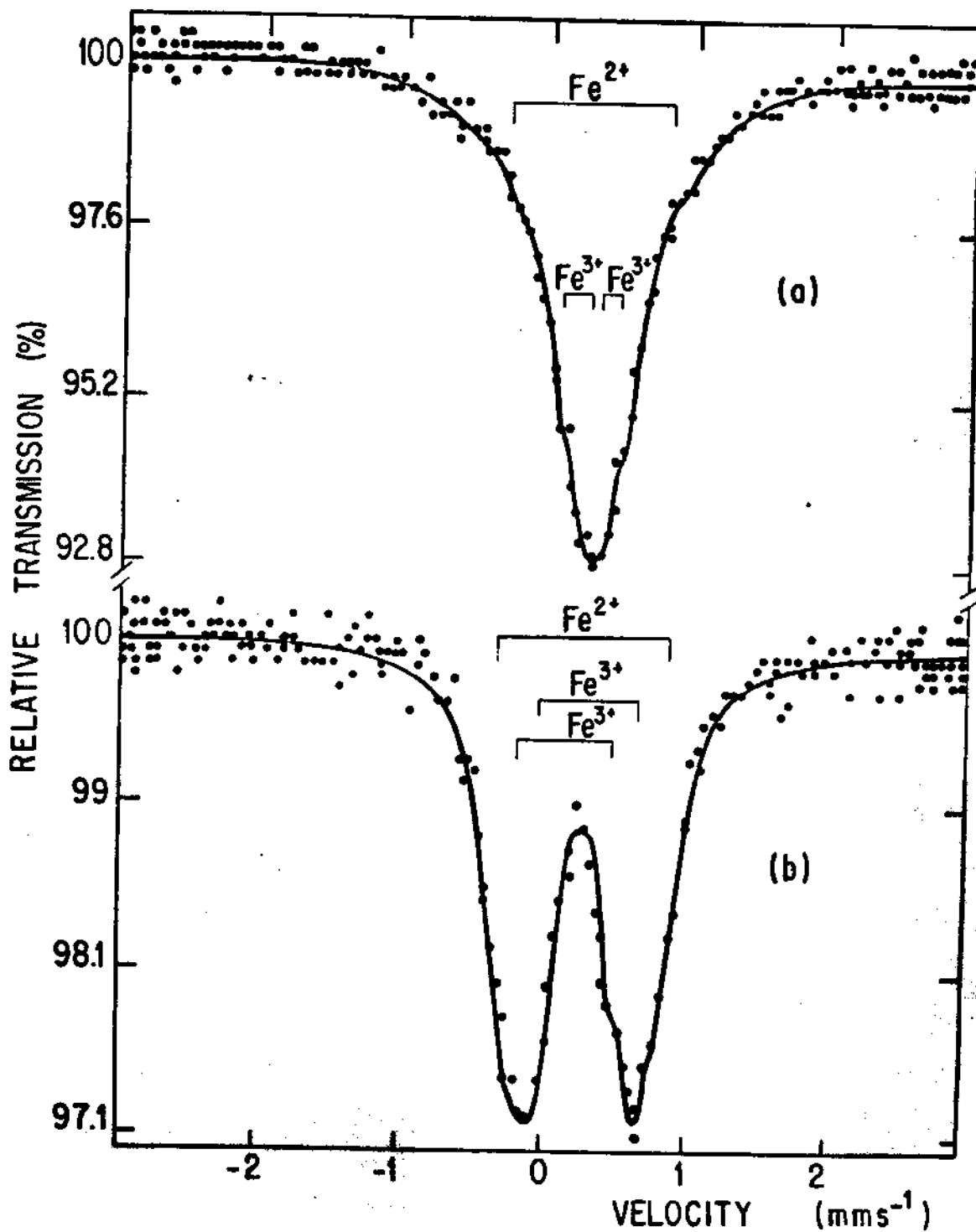


Fig. 5

SAMPLE	IS ( $\text{mms}^{-1}$ )	QS ( $\text{mms}^{-1}$ )	$\Gamma$ ( $\text{mms}^{-1}$ )	A (%)
AMARANTITE	0.316 (1)	0.879 (1)	0.304 (2)	-
COPIAPITE	0.304 (2)	0.39 (1)	0.26 (1)	37
	0.311 (2)	0.75 (1)	0.34 (1)	63
UNGEMACHITE	0.19 (3)	0.18 (4)	0.4 (1)	34
	0.42 (1)	0.14 (5)	0.48 (8)	48
	0.27 (5)	1.1 (4)	1.0 (2)	18

(a)

SAMPLE	IS ( $\text{mms}^{-1}$ )	QS ( $\text{mms}^{-1}$ )	$\Gamma$ ( $\text{mms}^{-1}$ )	A (%)
AMARANTITE	0.314 (1)	0.900 (1)	0.334 (1)	-
COPIAPITE	0.255 (3)	0.58 (2)	0.40 (1)	40
	0.292 (1)	0.952 (4)	0.303 (6)	60
UNGEMACHITE	0.32 (1)	0.69 (3)	0.31 (3)	50
	0.15 (2)	0.66 (3)	0.26 (4)	24
	0.26 (1)	1.16 (5)	0.31 (4)	26

(b)

Table 1



HYPERFINE PARAMETERS	NEEDLES ( $\theta=90^\circ$ )	POWER
$\Gamma_1$ (mms <sup>-1</sup> )	0.352 (5)	0.323 (3)
$\Gamma_3$ (mms <sup>-1</sup> )	0.299 (6)	0.289 (1)
$I_1$ (%)	7.28 (7)	13.0 (1)
$I_3$ (%)	6.18 (7)	13.1 (1)
IS (mms <sup>-1</sup> )	0.311 (1)	0.317 (1)
EQ (mm <sup>-1</sup> )	0.871 (2)	0.880 (1)
$(a_3/a_1)$ exper.	0.72 (4)	0.90 (3)

Table 2

## References

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