



## Mössbauer Spectra of the Acid Mine Drainage Mineral Schwertmannite from the Sokolov Basin, Czech Republic

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<sup>57</sup>Fe Mössbauer spectra were taken at room temperature, 78 K and 5 K for a pure schwertmannite sample from Lomnice. All were satisfactorily fitted to the sum of two components. A thermal scan gave a magnetic ordering temperature of 109 K, the highest observed for this mineral.

### 1. Introduction

Mankind has been mining sulphidic ores for at least 5000 years (the copper age) and the effects of the subsequent acid sulphide oxidation can be seen in many areas. The minerals which are precipitated depend on the local conditions, principally the pH, the redox potential, Eh, and the concentrations  $[\text{SO}_4^{2-}]$  and  $[\text{Fe}^{2+}]$ . The principal outcomes are jarosite,  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ , goethite,  $\alpha\text{-FeOOH}$ , schwertmannite, approximately  $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ , and ferrihydrite, approximately  $\text{Fe}_5\text{HO}_8.4\text{H}_2\text{O}$ . The last two are always poorly crystalline, producing poor XRD data, and Mössbauer spectroscopy is one of the best means of identification, together with their characteristic colours (e.g. [1]). The schwertmannite sample studied here was a particularly well-formed sample [2] from the Lomnice pit (locality 6) in the Sokolov Basin, Czech Republic, where the effluent pH undergoes seasonal variation of 3.0-3.7.

Characterization of any natural or man-made material by Mössbauer spectroscopy requires a set of spectra showing its possible variations, usually as a function of temperature. In this paper, we present <sup>57</sup>Fe Mössbauer spectra taken at the three common temperatures of room temperature, 78 K and 5 K. The magnetic ordering temperature in the ferric oxyhydroxides is also strongly influenced by the crystallinity, so it is of interest to determine how high this may be in a well-crystallized sample.

### 2. Results

#### 2.1 Conventional Mössbauer Spectra

The room temperature Mössbauer spectrum is shown in Fig. 1 and is seen to be an asymmetric doublet similar to, but even more asymmetrical than, that of ferrihydrite, presumably due to the incorporation of the larger sulphate ions. The asymmetry is caused by the range of environments in which the  $\text{Fe}^{3+}$  ion can be found. Although octahedrally coordinated to oxygen ions, these oxygen ions can be a simple  $\text{O}^{2-}$ , or part of  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , or  $\text{SO}_4^{2-}$  entities. There are thus a great many possible  $[\text{FeO}_6]$  arrangements, with each one having its own isomer shift (IS) and quadrupole splitting (QS). In such circumstances, there is commonly a correlation between the IS and the QS which causes the composite spectrum of all these individual subspectra to be asymmetrical.

The spectrum has been fitted, using Voigtians, to two quadrupole split doublets (Fig. 1) and the parameters are given in Table 1. An alternative fit to one doublet with a correlation between the IS and QS did not produce as good a fit.

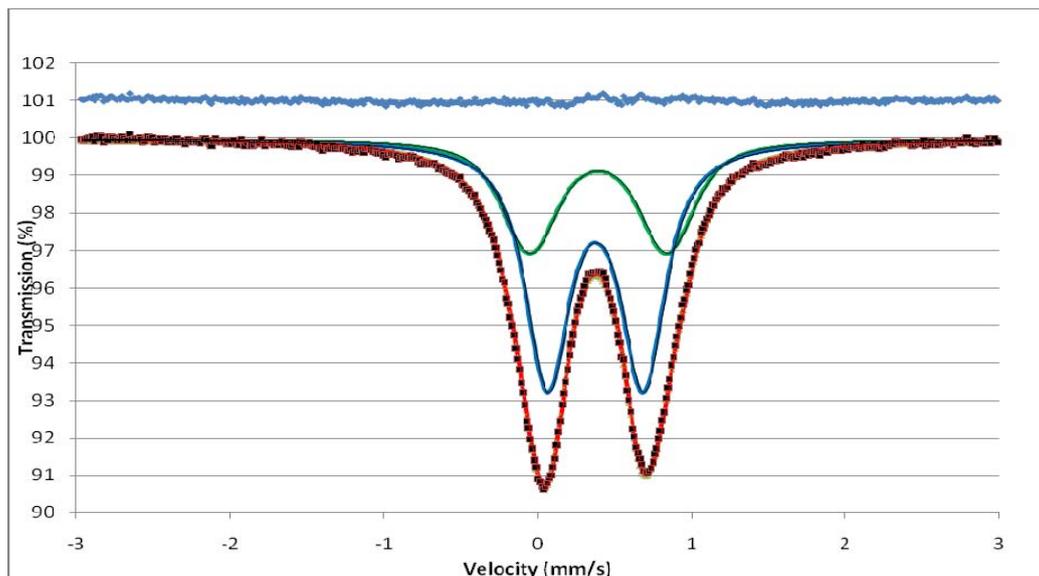


Fig. 1. Room temperature Mössbauer spectrum of schwertmannite sample showing the fit to two Voigtian doublets. The top line shows the difference between the data and the fit

Table 1. Parameters from least squares fit to the room temperature spectrum.

Doublet	IS (mm/s)	QS (mm/s)	$\sigma$ (QS) (mm/s)	Area (%)	$\Gamma$ (mm/s)
1	0.39(1)	0.89(8)	0.18(4)	35	0.30
2	0.37(1)	0.62(9)	0.09(1)	65	0.30

The spectrum at 78 K (Fig. 2) shows strong evidence of magnetic ordering but does not give a clean sextet. In the original paper on the identification of schwertmannite [3], it was noted that there was a distribution of ordering temperatures due to variation in crystallinity, but this spectrum appears to have magnetic relaxation as well. The fit shown has used three doublets and a broad line to approximate the spectrum, from which the maximum probability hyperfine field has been estimated to be 34.6 T.

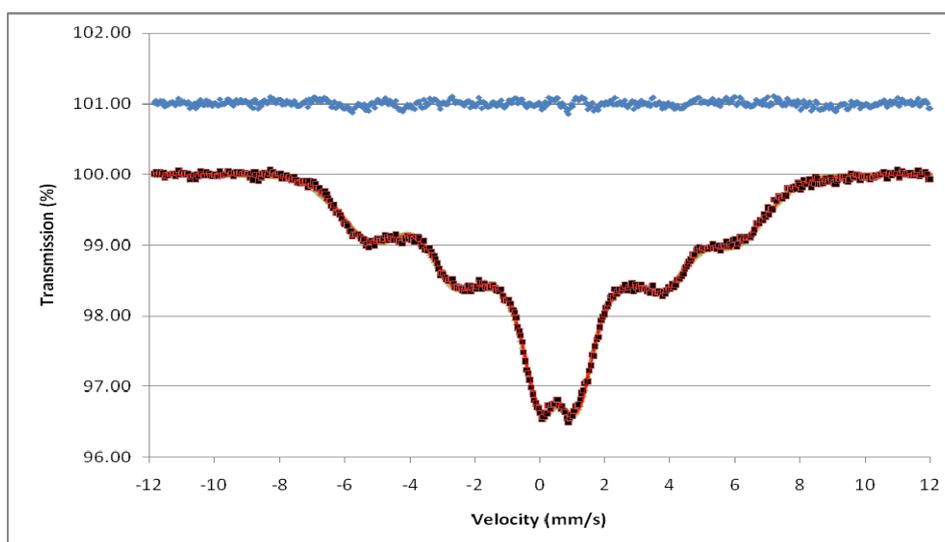


Fig. 2. Mössbauer spectrum at 78 K of the schwertmannite sample.



The spectrum at 4.2 K (Fig. 3) shows complete sextet structure indicating that the sample is now completely magnetically ordered. However, as in the room temperature spectrum, there is a range of hyperfine parameters, making the spectrum quite difficult to fit. Consistent with the room temperature spectrum, it has been fitted to two sextets with Voigtian lines, each sextet having separate correlations between the IS and the hyperfine field (HFF),  $\delta_1$ , and the QS and HFF,  $\epsilon_1$ . The parameters are given in Table 2.

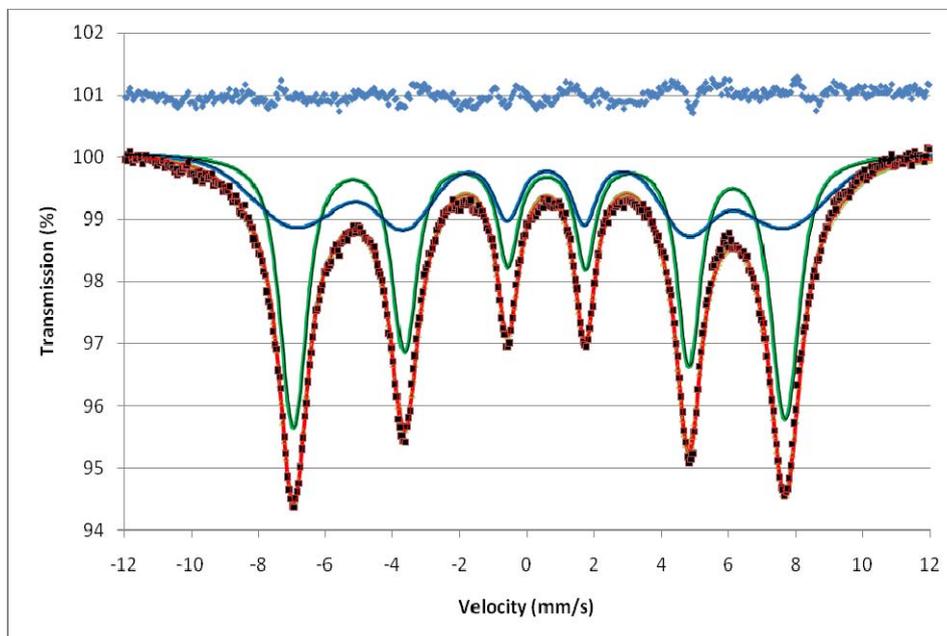


Fig. 3. Mössbauer spectrum at 5 K of the schwertmannite sample.

Table 2. Parameters from least squares fit to the 5 K spectrum.

$\langle IS \rangle$ mm/s	$\delta_1$ mm/s	$\langle QS \rangle$ mm/s	$\epsilon_1$ mm/s	HFF T	$\sigma(\text{HFF})$ T	Area %	$\Gamma$ mm/s
0.47	-0.09	-0.11	0.23	45.3	1.3	59	0.73
0.48	-0.03	-0.08	0.03	45.0	7.0	41	0.73

## 2.2. Thermal Scan

Because there is a strong overlap of the source line with the left hand line of the quadrupole split doublet, a series of counts, each taken for a fixed time as the temperature is changed, will show a slowly varying count rate due to the thermal shift, punctuated by a much more rapid change as the sample starts to become magnetically ordered and the spectrum splits out into a sextet.

A thermal scan was run over the range from room temperature down to 80 K, as shown in Fig. 4. Both the high temperature and low temperature sections are well fitted by a linear relation and the intersection of these lines occurs at 109 K, which we take to be the magnetic ordering temperature. This is comparable to the highest known ferrihydrite ordering temperature, which is close to 115 K [4].

## 3. Discussion and conclusions

The spectra observed here are similar, but not identical, to those previously published. The room temperature spectrum is well fitted to the two Voigtian doublets, without a correlation between the IS and QS, but a single IS-QS correlated doublet was not so



successful. There is a reasonable consistency between the relative areas of the two components of the room temperature (65%:35%) and 5 K spectrum (59%:41%) and that of the original investigation [3] of approximately 60%:40%. However, there is, as yet, no real understanding of the origin of these two components, in terms of possible different sites, or whether it simply provides sufficient parameters to fit the spectra. In this investigation, there seems to be some difference in the parameter range of the two sites as measured by the standard deviations of the QS and HFF, a distinction which does not seem to have occurred with previous samples.

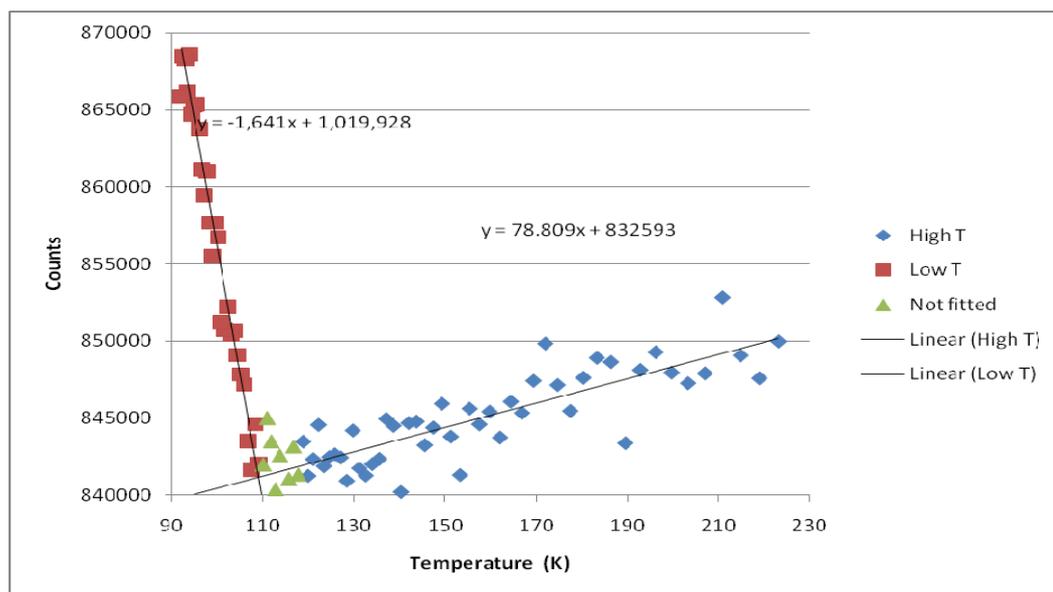


Fig. 4. Zero velocity thermal scan of the schwertmannite sample showing the magnetic ordering temperature at 109 K.

We note that the peaks in the 5 K spectrum seem less “pointy” than those in [3] and also some other published spectra, but the reason for this is not clear. Rounding of the peaks is usually indicative of a broader distribution of parameters. This sample has the highest magnetic ordering temperature yet measured for schwertmannite, and this shows it to probably be the most crystalline and yet the HFF values in Table 2 are slightly smaller than those in ref. 2. However we must be careful to distinguish between crystallinity and homogeneity, the latter being responsible for parameter broadening. It may be that the seasonal range of pH which occurs during formation results in an annual variation in the  $\text{SO}_4^{2-}$  concentration in the material. Additional problems arise from the existence of structurally incorporated and adsorbed  $\text{SO}_4^{2-}$ , removal of the latter being complicated by the fact that recurring washing may also affect structural  $\text{SO}_4^{2-}$ .

### Acknowledgments

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### References

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