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ANALYSIS OF THE MÖSSBAUER SPECTRA OF SEVERAL IRON-RICH TOURMALINES (SCHORLS)

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Résumé.- On a appliqué systématiquement un procédé d'ajustement des spectres Mössbauer dans le cas de cinq tourmalines du type dravite-schorl étudiées à des températures comprises entre 4.2 K et 600 K. Aucune supposition a priori n'a été faite concernant le nombre de sites de fer et leur occupation relative. Le meilleur ajustement a été obtenu avec quatre doublets quadrupolaires, bien que les paramètres de certains de ces doublets indiquent la possibilité de recouvrement. On discute de modèles pouvant expliquer l'origine de ces doublets.

Abstract.- The Mössbauer spectra of five tourmalines in the dravite-schorl series at temperatures in the range 4.2K to 600K have been subjected to a systematic fitting procedure. No prior models of numbers of iron sites or their relative occupations were assumed. It was found that a fitting scheme containing four quadrupole doublets was adequate to fit the spectra of all of the samples over the whole temperature range, although the parameters of some of these doublets indicated that they may contain more than one overlapping component. Possible models for the origins of these doublets are briefly discussed.

1. Introduction. - It has long been recognized /1/ /2/ that obtaining meaningful information by computer fitting the Mössbauer spectra of many iron-containing minerals is a far from trivial task. This is both because of the multiplicity of iron sites that can occur in a particular material, which often give rise to spectra with strongly overlapping absorption peaks, and because of variability in the composition of samples obtained from different locations. In this paper the Mössbauer spectra of a number of iron-containing tourmalines, and an attempt to categorize them by systematic computer fitting, are reported.

Tourmaline is a ring silicate with a rhombohedral unit cell /3/. Iron is commonly believed to occur in two inequivalent sites, both of which are octahedrally coordinated and have C_1 point symmetry. The b-site is occupied by Fe and Mn in schorl and by Mg in dravite, and is coordinated to four oxygens and two hydroxyl ions. Thus it has been postulated /4/ that it may occur in cis- and trans-configurations. The c-site is occupied predominantly by Al^{3+} ions and is coordinated to five oxygens and one hydroxyl ion. The samples whose spectra will be reported here are solid solutions in the dravite-schorl series, so the b-sites contain mainly Fe, Mn and Mg. b-sites are arranged in equilateral triangles about the rhombohedral axis, separated by

$\sim 3.18 \text{ \AA}$. The general formula is /3/ $Na(Mg, Fe, Mn, Li, Al)_3 Al_6 [Si_6 O_{18}] (BO_3)_3 (OH, F)_4$.

^{57}Fe Mössbauer spectra of tourmaline samples have been reported by several authors (e.g. /5-8/ and references contained therein) and a variety of different spectra and effects have been observed. The aim of this work was to study a number of samples that gave rather different-looking Mössbauer spectra and to try to systematize the fitting procedures subject only to the requirements of the experimental data, i.e. no prior models of numbers of sites or their occupations were assumed.

2. Experimental. - Five dravite-schorl samples from various localities were obtained. Their places of origin, identification and iron contents are given in table I.

Table I : Sample identification

Sample identification	Place of origin	FeO concentration (mole%)
HR	Harts Range, Northern Territory, Australia.	10.3
Y	Yinnietharra, West Australia	13.6
Pa	Patagonia, Arizona, USA	18.1
Um	Umberatana, South Australia	4.1
He	Heemskirk, Tasmania, Australia	15.7

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Reasonably complete chemical analyses were made of all samples using an electron microprobe and details of the results may be obtained from the authors.

Mössbauer spectra were obtained with a computer-controlled electromechanical spectrometer /9/ with sample temperatures in the range 4.2K to 600K. The samples used were mostly powders but single crystal slices of some samples were run as well. The powders were prepared by grinding with a mortar and pestle and then intimately mixing with boron nitride to ensure an even distribution of sample within the sample holder, and to minimize preferred orientation effects. Care was taken to keep the ^{57}Fe isotopic thickness low enough that saturation effects on the absorption were negligible.

$^{57}\text{CoRh}$ and $^{57}\text{CoPd}$ sources were used at room temperature. The spectrometers were calibrated using iron foil absorbers in conjunction with the data of Violet and Pipkorn /10/.

The spectra were fitted by a standard least-squares technique based on the work of Powell /11/. Linear parameters were obtained exactly at each iteration using linear least-squares methods and consequently initial estimates of them were not required. Partial derivatives with respect to the non-linear parameters were obtained numerically. Line-shapes used were generally Lorentzian, but in some cases pseudo-Lorentzians /12/ were also used to account for inhomogeneous broadening, etc. The widths of the two peaks of each doublet were taken to be the same.

3. Results.— Spectra of powder samples of the five tourmalines are shown in figure 1. Apart from some obvious features in common the spectra look quite different.

The aim of the fitting procedure was to fit all of the spectra obtained from these samples in the temperature range 4.2K to 600K with as small a number of subspectra (doublets and/or single peaks) as possible subject to the conditions that the parameters of each subspectrum should show only small variations between samples and should have a smooth temperature dependence. For all of the samples it was found that a scheme containing four quadrupole doublets was sufficient to give a good description of the spectra over the entire temperature range (excluding the low temperature region in samples that exhibited magnetic order). The values of the parameters of these doublets at 300K are given in table II. Also given are the relative intensities of the doublets, normalized to unity, in each of the samples at 300K. The fits with these parameters and

intensities are the solid lines in figure 1.

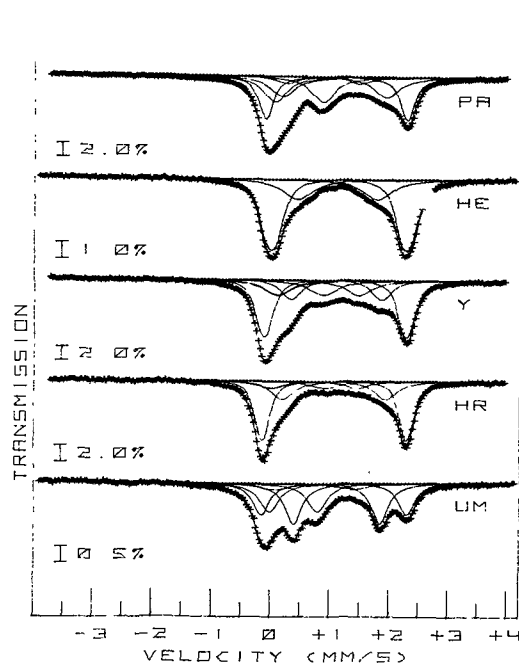


Fig. 1 : Mössbauer spectra of powder samples of the five tourmaline samples studied. The samples were at 300K. The solid lines are the fits using the four-doublet scheme described in the text using the parameters listed in table II. The component doublets are also shown. The source was $^{57}\text{CoRh}$ at room temperature.

4. Discussion.— Use of a four doublet fitting scheme does not necessarily imply that there are only four components in the spectra, and in fact evidence was found that some of the doublets consist of two overlapping components, but it indicates the amount of information that can be unambiguously obtained from these spectra. It is therefore suggested that further components can only be meaningfully included in fitting these spectra if suitable constraints, derived from independent data, can be applied to some parameters.

Of the four doublets described in table II, N° 1 and 2 have almost identical centre shifts at all temperatures, and these are consistent /13/ with their origin being Fe^{2+} in sites of octahedral coordination. Doublet 1 was dominant in all samples and is therefore very likely to arise from Fe^{2+} in the b-sites. The width of its peaks was in the range 0.3–0.4 mm s^{-1} and was only weakly temperature dependent in all samples, indicating some inhomogeneous broadening, possible originating in different occupations of neighbouring b-sites as suggested by Belov et al. /5/.

While the centre shift of doublet 2 was always

very similar to that of N° 1, its splitting and linewidth were somewhat more sample-dependent than those of doublet 1.

Table II : Parameters derived from the four doublet fitting scheme at 300K.

Doublet N°	Parameter	HR	Y	Samples Pa	Um	He
1	$\delta^{(1)}$	1.09	1.09	1.09	1.08	1.10
	$\Delta^{(2)}$	2.43	2.40	2.39	2.46	2.26
	$\Gamma^{(3)}$	0.30	0.35	0.30	0.33	0.41
	$A^{(4)}$	0.49	0.41	0.32	0.26	0.68
2	δ	1.08	1.10	1.05	1.13	1.07
	Δ	1.74	1.52	1.74	1.45	1.28
	Γ	0.47	0.41	0.51	0.34	0.57
	A	0.26	0.17	0.27	0.35	0.32
3	δ	0.47	0.50	0.46	0.40	-
	Δ	0.92	0.77	0.82	0.81	-
	Γ	0.63	0.61	0.42	0.39	-
	A	0.14	0.22	0.32	0.28	0
4	δ	0.73	0.79	0.86	0.75	-
	Δ	1.44	1.36	1.21	1.34	-
	Γ	0.48	0.54	0.42	0.64	-
	A	0.11	0.20	0.09	0.11	0

(1) δ is centre shift with respect to an Fe foil absorber (in mms^{-1}).

(2) Δ is the splitting of the two peaks of the doublet (in mms^{-1}).

(3) Γ is the full width at half height of each peak of the doublet (in mms^{-1}).

(4) A is the area of the doublet, with the total spectrum area normalized to unity.

This may indicate that this doublet contains more than one component. In sample He, for example, its splitting was significantly less than in other samples. This sample, in fact, gave spectra that in all respects were very similar to those reported by Scorzelli et al. /6/ for a black tourmaline : the area of doublet 2 increased as the temperature was raised. There are certain inconsistencies with their proposed explanation however. For example, sample He had an excess of Al to fill the c-sites and a balancing deficiency of Fe, Mg and Mn to fill the b-sites, so there seems to be no reason for there to be a significant concentration of Fe^{2+} ions in c-sites. Also the effect on the isomer shift of their proposed electron exchange process is not clear.

Doublet 2 in the other samples, however, seems to be more intense when the Al content is insuffi-

cient to fill the c-sites (as in samples Pa and Um), so it may contain a component arising from Fe^{2+} in c-sites, as has been suggested before /8/.

Doublet 3 appears from its centre shift /13/ and small quadrupole splitting to arise from Fe^{3+} , but its peaks are very broad in some samples ($\sim 0.6 \text{ mms}^{-1}$) in Y and HR so there may well unresolved components due to Fe^{3+} in both b- and c-sites. While Fe^{3+} would normally be expected, from valence considerations, to be in the c (Al^{3+}) site, the larger doublet 3 linewidths in Y and HR coupled with the fact that these samples contained more Al than required to fill the c-sites (and insufficient Fe, Mg and Mn to fill the b-sites) certainly indicates that Fe^{3+} is likely to occupy b-sites as well as c-sites.

Doublet 4 has a centre shift almost exactly

mid-way between those for Fe^{2+} (doublets 1 and 2) and Fe^{3+} (doublet 3), and may be, at least partly, due to neighbouring $\text{Fe}^{2+} - \text{Fe}^{3+}$ pairs between which there is fast electron hopping. Such a process has been suggested by Pollak and Bruyneel /4/ and there is optical evidence /14/ for such iron pairs on b-sites. In the Y and HR samples, for which it was suggested above that Fe^{3+} occurred in b-sites, this doublet is quite strong and its intensity increases with increasing temperature, which is additional evidence in favour of this assignment. In the Um and Pa samples, however, where there is less evidence for Fe^{3+} in b-sites, the intensity of doublet 4 is weaker and almost independent of temperature. This suggests that there is another mechanism contributing to doublet 4. A possibility is Fe^{2+} in a site of tetrahedral coordination /13/ and in this context it may be relevant to note that both the Um and Pa samples had a slight Si deficiency. Doublet 4 was not detectable in the He sample, which was neither deficient in Si nor contained any detectable Fe^{3+} .

5. Conclusions.— In this paper the emphasis has been placed on the method of analysis of the Mössbauer spectra of a group of schorl samples. Conclusions drawn from the results of such an analytical method must be based on comparisons of the parameters obtained for various samples and their temperature dependences, and such comparisons have indicated the presence of overlapping doublets in some cases. Further comparisons utilizing the results of chemical analyses can throw further light on the origins of the observed spectral features.

A more complete account of this work, in which interpretations of the spectra based on the above considerations will be emphasized, will be published later.

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