# Mössbauer spectra of $Fe^{3+}$-poor schorls: reinterpretation on the basis of the ordered structure model

## Mössbauerovská spektra skorylů chudých $Fe^{3+}$: reinterpretace na základě uspořádaného strukturního modelu (Czech summary)

*(2 text-figs.)*

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Mössbauer spectra of tourmalines are usually interpreted assuming a disordered distribution of octahedral ions, particularly of $Fe^{2+}$ and $Al^{3+}$, between Y and Z structural sites (Hermon et al. 1973, Korovushkin et al. 1979, Ferrow et al. 1988). Sometimes, as it is in the case of Fe-elbaites, such assumptions are baseless on the ground of crystallochemistry. The analyses of statistical relationships between mean bond lengths and cation populations of Y and Z octahedra of tourmalines with Al > 6 apfu have shown a significant effect of ionic substitutions in neighbouring cation sites (particularly within the triad of the Y octahedra) on the mean sizes of both structural sites. As a result, disordering of octahedral ions may have much lesser significance or be completely absent. The paper presents a possibility of crystallochemical interpretation of quadrupole splitting doublets in the Mössbauer spectra of $Fe^{3+}$-poor schorls. The proposed interpretation is based on an analysis of frequency of $Fe^{2+}$ occurrences within particular ion groups in the Ist and IInd coordination shells. If $Fe^{2+}$ occurs as a central ion in Y octahedra, the O(3) site is occupied by $(OH)^-$, and differences in the Ist coordination shell result from substitution of ($OH^-$, $F^-$, $O^{2-}$) ions in the O(1) site. In the IInd coordination shell, the variability of ions is basically limited to cations of the remaining two Y octahedra. Groups of ions, which may occur around $Fe^{2+}$, have eventually been arranged into five sets of different variants, revealing crystallochemical similarity within each set and, as it can be supposed, affecting the $Fe^{2+}$ ion in the same way. The results are characterized by very good concurrence of spectroscopic and chemical data, i.e. the contributions of quadrupole splitting doublets of $Fe^{2+}$ ions to a whole spectrum and calculated shares of $Fe^{2+}$ in specific groups of ions of the Ist and IInd coordination shells related to total Fe. By the same virtue, the presence of numerous doublets of quadrupole splitting in the Mössbauer spectra of tourmalines can be fully explained on a basis of crystallochemical properties, without assuming a random distribution of octahedral ions.

*Key words*: tourmaline, schorl, Mössbauer spectrum, crystallochemical interpretation, the ordered structure model

## Introduction

The Mössbauer effect was first applied in studies of tourmalines by deCoster et al. (1963). In the next years, the method was frequently used in solving some structural problems of these minerals (*e.g.* Hermon et al. 1973, Korovushkin et al. 1979, Ferrow et al. 1988). It is particularly useful in obtaining information on distribution of $Fe^{2+}$ and $Fe^{3+}$ ions between nonequivalent octahedral lattice positions, referred to as Y and Z sites (Fig. 1). It is generally accepted in all papers that $Fe^{2+}$ occupies mainly Y site, but some of it is also incorporated in Z site. According to structure refinement (*e.g.* Grice - Ercit 1993) for different varieties of $Fe^{2+}$,$Fe^{3+}$-tourmalines, there are no substantial amounts of these ions in Z sites. But Mössbauer spectroscopy usually indicates significant amounts of $Fe^{2+}$ ions in Z octahedra estimated at 20-30 % (sometimes even more) of total Fe. Taking this into consideration, it seems essential to answer the question whether it is possible to interpret Mössbauer spectra of tourmalines without assuming a disordered distribution of $Fe^{2+}$ ions between Y and Z octahedra.

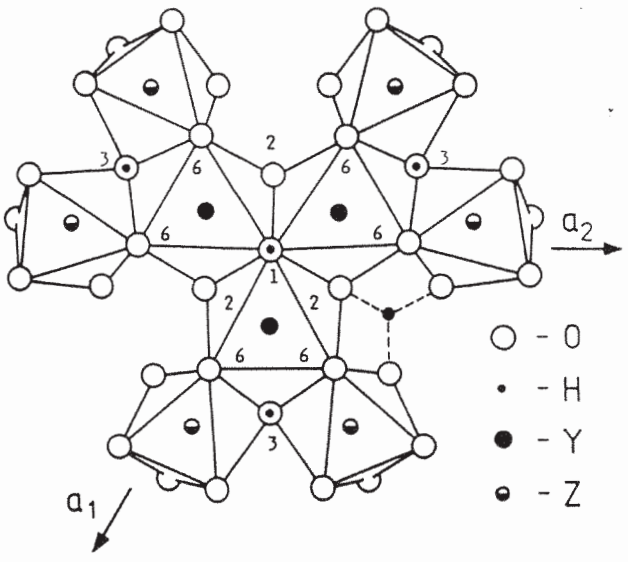


Fig. 1. The complex of Y and Z octahedra in the tourmaline structure, view perpendicular to *c*-axis (numbers denote anion sites)

## Methods

Chemical composition of the tourmalines studied was determined using classic methods of weight analysis, supported by volumetric and instrumental methods. $SiO_2$ and $H_2O(+)$ were determined by weight ($H_2O+$ as losses on ignition above 500 °C with a correction to oxidizing $Fe^{2+}$ iron); $Al_2O_3$, $Fe_{total}$ as FeO, CaO and MgO complexometrically (EDTA); $B_2O_3$, $TiO_2$ and F colorimetrically (the carmin acid method, the peroxide method and the Zr-ER method, respectively); $Na_2O$ and $K_2O$ by flame photomet-

ry, while $Li_2O$, MnO, ZnO and CaO (for the latter it was cross-checking) by ASA. Ratios of FeO and $Fe_2O_3$ were calculated from Mössbauer data. Chemical formulae of formal units were calculated on the basis of 31 ions of (O,OH,F).

Mössbauer spectra were recorded at room temperature using a constant acceleration spectrometer. Absorbers were prepared in the form of discs with a surface density of 5 mg Fe/cm$^2$. $^{57}$Co(Rh) was applied as a source of γ-radiation. Spectra were resolved with a computer program that fits Lorentz curves using the least squares method. Isomeric shift was calibrated against α-Fe.

Mössbauer spectra of every tourmaline studied were fitted into 3-5 doublets of $Fe^{2+}$ ions and one doublet of $Fe^{3+}$ ions, or one doublet of iron with the mixed valence state ($Fe^{2.5+}$). The choice of the variant of the spectrum resolutions presented here stemmed from the best fitting parameters ($\chi^2$ and MISFIT) of the theoretical spectrum to the experimental data and from satisfactory Mössbauer parameters of the subspectra (IS, QS, Γ). Initial constraints were limited to a minimum, considering particularly fixing of specific values but this took place only in the case of very weak lines (*e.g.* for the $Fe^{3+}$ quadrupole a value of IS = 0.35 mm/s was fixed as it was found in the spectra of thermally oxidized tourmalines). Also in single cases, when three lines (narrow, wider and again narrow) appeared next to each other, they could be joined with their half widths. IS and QS of doublets of $Fe^{2+}$ ions were not fixed. Eventually, the effects of gradual freeing of initially constrained parameters were tested. Iron contents in specific arrangements of ions of the Ist and IInd coordination shells were calculated for $Fe^{2+}$ ions. In the calculations it was assumed that the amounts of $Fe^{3+}$ ions and of mixed valence state ($Fe^{2.5+}$) ions are the same as the ones obtained from resolution of Mössbauer spectra.

## Discussion of the problem

It has been accepted in interpretation of the Mössbauer spectra of tourmalines that $Fe^{2+}$ and $Fe^{3+}$ ions can occupy both octahedral sites, by analogy to the interpretation of the results of crystal structure refinement of buergerite (Barton 1969) and VIS or IR spectroscopy as well (*e.g.* Mattson - Rossman 1984, 1987). As a consequence of this, practically all tourmalines studied by this method were interpreted as structures with a disordered distribution of $Fe^{2+}$ and $Fe^{3+}$ ions. In recent years, the analysis of the order-disorder phenomenon in the structure of tourmalines was considerably expanded on a basis of structural parameters determined in crystal structure refinement (Hawthorne et al. 1993, Hawthorne 1996). Applying a particular reasoning and analysis of the relationships between mean sizes of Y or Z octahedral sites and a mean radius of a complex octahedral ion in these positions, he showed a Mg,Al-disorder in dravites. In crystal structure refinement of tourmalines available in literature, the presence of $Fe^{2+}$ ions in Z sites is acceptable, but $Fe^{2+}$ always occurs in these sites only in trace amounts (*e.g.* Grice - Ercit 1993) which, what is more important, are significantly lower than those evaluated in Mössbauer spectroscopy.

Attempts to analyse the statistical relationships among mean sizes of structural sites in the tourmaline structure and cation populations in these sites (Pieczka, 1997), and also chemical composition versus unit cell parameters (Pieczka, *in prep.*) indicate the lack of significant statistical disordering of $Fe^{2+}$ ions between Y and Z sites. This fact does not exclude an incorporation of small amounts of these ions into Z octahedra, but this phenomenon does not need to be statistically significant. At the same time, these analyses point to a possible disordering of $Fe^{3+}$ and $Al^{3+}$ ions between Y and Z octahedra. Likewise, a simple trend analysis of thermally-induced changes of lattice parameters between the original tourmaline with $Fe^{2+}$ and its oxidized form with $Fe^{3+}$ (*a* parameter descreases, *c* parameter slightly increases) indicates also the presence of the $Fe^{2+}$ ion in Y octahedra. Further analysis of approximate thermally-induced changes of mean sizes of Y and Z sites gives a distinct decrease of Y octahedra sizes, with a simultaneous small increase only of Z octahedra sizes (Pieczka - Kraczka 1996). This is possible only when $Fe^{2+}$ ions are present in Y sites, otherwise Z octahedra would have to shrink ($r_{Fe2+(HS)} = 0.78$ Å -> $r_{Fe3+(HS)} = 0.645$ Å)!.

Among the Mössbauer spectra of $Fe^{2+}$-rich tourmalines, three categories may be distinguished considering the complexity of their shapes:

1) the simplest spectra of schorls with Al ≥ 6 apfu and $Fe^{3+} \approx 0$ apfu, with symmetrical or almost symmetrical intensities of both branches;
2) spectra of schorls with Al ≥ 6 apfu and $Fe^{3+} > 0$ apfu, revealing more distinct asymmetry of intensities of both branches;
3) spectra of $Fe^{2+}$- and $Fe^{3+}$-tourmalines with a deficit of aluminium in their structure, i.e. those with Al < 6 apfu and $Fe^{3+} >> 0$ apfu, revealing very distinct asymmetry of the shapes.

Considering the character of presented research aimed at visualisation of rules pertinent to interpretation of the Mössbauer spectra of tourmalines, only the simplest spectra of the most common tourmalines of the group (1) have been discussed in this paper. It must be mentioned, however, that the proposed interpretation model, including also "charge-transfer" mechanism, was applied in explanation of slightly more complicated spectra of the group (2) tourmalines (Pieczka - Kraczka 1994, 1996), and a spectrum of Fe-elbaite as well (Pieczka - Kraczka 1995). As an example, the spectra of four tourmalines, numbered S35, S49, N3 and N5 will be considered; the samples differ in the chemical composition of their Y, O(1) and O(3) sites population. The crystallochemical formulae of the tourmalines in question are as follows:

**(S35) - Al-schorl from Strzegom (Poland)**

$(Na_{0.498}K_{0.013}Ca_{0.067}\square_{0.422})(Fe^{2+}_{1.831}Al_{0.599}$
$Mg_{0.390}Fe^{3+}_{0.075}Mn_{0.037}Ti_{0.072}Zn_{0.016}Li_{0.014})$
$Al_{6.000}B_{3.001}(Si_{5.933}Al_{0.067})O_{27}(OH_{3.186}O_{0.454}F_{0.360})$

**(S49) - Al-schorl from the Izera Mts. (Poland)**

$(Na_{0.619}K_{0.024}Ca_{0.074}\square_{0.283})(Fe^{2+}{}_{2.117}Al_{0.351}$
$Mg_{0.348}Ti_{0.072}Fe^{3+}{}_{0.070}Mn_{0.012}Li_{0.010}Zn_{0.010})$
$Al_{6.000}B_{3.005}(Si_{5.849}Al_{0.151})O_{27}(OH_{3.254}F_{0.483}O_{0.263})$

**(N 3) - Al-schorl from Överhogdal (Sweden)**

$(Na_{0.779}K_{0.061}Ca_{0.042}\square_{0.118})(Fe^{2+}{}_{1.652}Al_{0.499}$
$Mg_{0.495}Ti_{0.055}Fe^{3+}{}_{0.264}Mn_{0.023}Li_{0.006}Zn_{0.005})$
$Al_{6.000}B_{2.998}(Si_{5.942}Al_{0.058})O_{27}(OH_{3.010}F_{0.269}O_{0.721})$

**(N 5) - Al-schorl from Erzgebirge (Germany)**

$(Na_{0.606}K_{0.017}Ca_{0.016}\square_{0.361})(Fe^{2+}{}_{1.855}Al_{0.735}$
$Mg_{0.237}Ti_{0.066}Fe^{3+}{}_{0.058}Mn_{0.026}Li_{0.005}Zn_{0.011})$
$Al_{6.000}B_{3.003}Si_{5.996}O_{27}(OH_{3.414}O_{0.554}F_{0.032})$

A quadrupole doublet of a Mössbauer spectrum is described by: isomeric shift (IS), which depends mainly on the investigated ion and its coordination, and quadrupole splitting (QS), whose value depends on the local gradient of electrical field. The latter must depend obviously on the high- or low-spin state of ions (HS-LS) which in turn is influenced by the type of chemical bonds (ionic *vs* covalent bond), and in practice by the mutual relationships of the two bond types. Assuming this, Mössbauer spectra of tourmalines cannot be interpreted without taking into consideration changes occurring within the closest neighbourhood of $Fe^{2+}$ and $Fe^{3+}$ ions, i.e. the ligands of the Ist coordination shell. This reasoning is supported by the fact that the Ist coordination shell of the $Fe^{2+}$ ion in Y octahedron is strongly differentiated in its anion composition: 4 of its 6 lattice sites are filled with oxygen, and the remaining two [O(1) and O(3)] with diversified ions. These ions include usually $(OH)^-$, at O(1) also $F^-$, and if the substitution of the deprotonation type takes place, at least one of the two possible $(OH)^-$ sites are occupied by oxygen. The authors dealing with Mössbauer investigations of minerals with a single possible variant of the Ist coordination shell around $Fe^{2+}$ or $Fe^{3+}$ ions (*e.g.* spinels - Bancroft et al., 1983) pointed to a significant effect of varying cations in the IInd coordination shell onto QS of individual components of quadrupoles. This phenomenon may be common in tourmalines in which numerous different forms of substitution are associated with a simultaneous replacement of ions in the Ist and IInd shells of their closest neighbours. To simplify further considerations and calculations, we have concentrated only on octahedral ions the most frequent in Mg-Fe-Al-tourmalines, i.e. $Mg^{2+}$, $Mn^{2+}$, $Fe^{2+}$, $Fe^{3+}$, $Al^{3+}$ and $Ti^{4+}$. These ions can be arranged into 21 variants in which at least one $Fe^{2+}$ ion occupies the triad of Y octahedra, and also 21 variants with at least one $Fe^{3+}$, respectively. Since the amount of $Fe^{3+}$ in the group of tourmalines studied in this work is rather low (3-4 % of the total Fe for the samples S35, S49, N5 and about 14 % for the sample N3), the analysis of crystallochemical differentiation around this ion has been omitted. When $Fe^{2+}$ occurs as a central ion, the O(3) site is occupied by $(OH)^-$, and the variability within the Ist coordination shell results from substitution of $(OH^-,F^-,O^{2-})$ ions in the O(1) site. Considering the mentioned possibilities of the arrangement of ions, the specific part of the tourmaline structure that seems to be directly responsible for the shape of Mössbauer spectra may be schematically presented as follows:

$Fe^{2+}/4O(OH)_{(3)}(OH,F,O)_{(1)}/(Y,Y)$
central / Ist coordination shell / variable components in ion IInd coordination shell

For any estimation on the contribution of $Fe^{2+}$ ions to the total iron content for every group of ions in the tourmaline structure, it is necessary to calculate probabilities of occurring different variants of the Ist and IInd coordination shells. If crystallochemical data are available, substitutions within the O(1) site are relatively easy to be calculated quantitatively. Considerably more difficult is the quantitative analysis associated with the variability around $Fe^{2+}$ ions within the IInd coordination shell. The mentioned 21 possible variants of the structure of the Y octahedra triad, out of which at least one contains $Fe^{2+}$, may be subdivided into four groups taking into account crystallochemical criteria (valency, effective ionic radius, electronegativity):

| I | II | III | IV |
|---|---|---|---|
| | | | $Fe^{2+}(Fe^{3+},Al,Ti)$ |
| $Fe^{2+}Fe^{2+}Fe^{2+}$ | $Fe^{2+}Fe^{2+}Fe^{3+}$ | $Fe^{2+}Fe^{2+}(Al,Ti)$ | $(Fe^{3+},Al,Ti)$ |
| $Fe^{2+}Fe^{2+}Mg$ | $Fe^{2+}MgFe^{3+}$ | $Fe^{2+}Mg(Al,Ti)$ | |
| $Fe^{2+}Fe^{2+}Mn$ | $Fe^{2+}MnFe^{3+}$ | $Fe^{2+}Mn(Al,Ti)$ | |
| $Fe^{2+}MgMg$ | | | |
| $Fe^{2+}MgMn$ | | | |
| $Fe^{2+}MnMn$ | | | |

As ions within each of the four groups are similar considering their crystallochemical properties, it may be accepted that their effects exerted on the $Fe^{2+}$ ion are similar. Going from the group I to IV, the ions become gradually more diversified within the triad of Y octahedra, and thus they should affect the $Fe^{2+}$ ion in a more complicated way. If the structure of these ionic arrangements is expressed in the most generalized manner:

I) $Fe^{2+}R^{2+}R^{2+}$
II) $Fe^{2+}R^{2+}Fe^{3+}$
III) $Fe^{2+}R^{2+}(Al,Ti)$
IV) $Fe^{2+}(Fe^{3+},Al,Ti)(Fe^{3+},Al,Ti)$

and all possible variants of the Ist coordination sphere are considered, it is possible to calculate maximum 12 different combinations of ion groups, representing simultaneously changes within the Ist and IInd coordination shell of the closest neighbours of $Fe^{2+}$ ions. They are as follows:

1) $Fe^{2+}$ 4O2(OH) $R^{2+}R^{2+}$
2) $Fe^{2+}$ 4O(OH)F $R^{2+}R^{2+}$
3) $Fe^{2+}$ 5O(OH) $R^{2+}R^{2+}$
4) $Fe^{2+}$ 4O2(OH) $R^{2+}Fe^{3+}$
5) $Fe^{2+}$ 4O(OH)F $R^{2+}Fe^{3+}$
6) $Fe^{2+}$ 5O(OH) $R^{2+}Fe^{3+}$
7) $Fe^{2+}$ 4O2(OH) $R^{2+}$(Al,Ti)
8) $Fe^{2+}$ 4O(OH)F $R^{2+}$(Al,Ti)
9) $Fe^{2+}$ 5O(OH) $R^{2+}$(Al,Ti)

10) $Fe^{2+}$ 4O2(OH) ($Fe^{3+}$,Al,Ti)($Fe^{3+}$,Al,Ti)
11) $Fe^{2+}$ 4O(OH)F ($Fe^{3+}$,Al,Ti)($Fe^{3+}$,Al,Ti)
12) $Fe^{2+}$ 5O(OH) ($Fe^{3+}$,Al,Ti)($Fe^{3+}$,Al,Ti)

The practice indicates, however, that the most complex Mössbauer spectra of $Fe^{2+}$-tourmalines with the lowest $Fe^{3+}$ content, characterized by a distinct broadening of their both branches toward the centre of a spectrum, cannot be resolved into more than six doublets of quadrupole splitting (*vide* Korovushkin et al. 1979). Considering this, it is necessary to combine at least some of the variants, taking into account crystallochemical criteria (valency, effective ionic radius, electronegativity), providing for them a similar degree of geometrical deformation and similar local electric field gradient. Considering the rules stated above, the following groups have been distinguished for the tourmalines analysed:

I) $Fe^{2+}/O_4(OH)_2/R^{2+}(R^{2+},Fe^{3+})$
II) $Fe^{2+}/O_4(OH)F/R^{2+}R^{2+}$
III) $Fe^{2+}/O_4(OH)_2/R^{2+}(Al,Ti)$
IV) $Fe^{2+}/O_4(OH)F/R^{2+}(Fe^{3+},Al,Ti)$
$Fe^{2+}/O_4(OH)_2/(R^{3+}, Ti)(R^{3+},Ti)$
V) $Fe^{2+}/O_4(OH)(F,O)/(R^{3+}, Ti)(R^{3+},Ti)$
$Fe^{2+}/O_5(OH)/R^{2+}(R^{2+},Fe^{3+},Al,Ti)$

The doublets of quadrupole splitting associated with variants 1) and 2) should be characterized by high values of QS, and their positions in Mössbauer spectra should be well defined. The lines of doublets with smaller QS become more diffused (the fact is clearly associated with the increase of their half width $\Gamma$ and their low intensities). This situation may be regarded as resulting from superposition of numerous weak components, attributed to ionic groups slightly more complicated crystallochemically. Having established the variants of ions distribution within the Ist and IInd coordination shells around $Fe^{2+}$ and chemical composition of a tourmaline sample, it is possible to calculate at first probabilities of finding each variant in the structure of tourmaline in question, and then the contribution of $Fe^{2+}$ ions to the total iron content in each variant. Assuming that a Mössbauer spectrum reflects a specific crystallochemical state of $Fe^{2+}$ ions, these contributions may be compared with contributions of component doublets of quadrupole splitting.

## Results and conclusions

Resolutions and crystallochemical interpretations of quadrupoles in Mössbauer spectra of investigated $Fe^{3+}$-poor

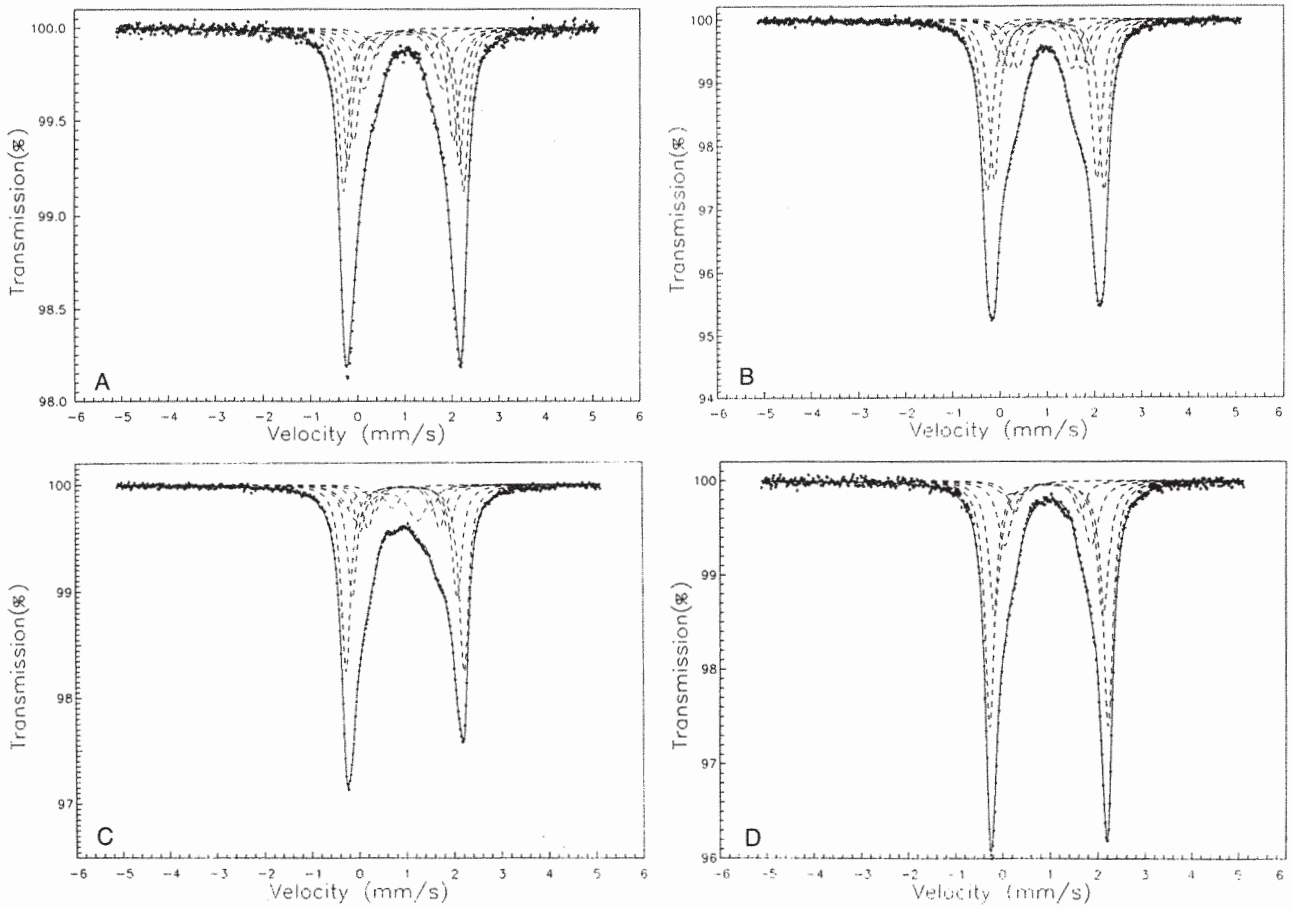


Fig. 2. Mössbauer spectra of tourmalines studied.
A - Strzegom (Poland); B - Izera Mts (Poland); C - Överhogdal (Sweden); D - Erzgebirge (Germany);
(*full line* - recorded spectrum, *dashed lines* - resolved subspectra)

schorls (Fig. 2 A-D) are presented in Table 1. These results, likewise those partly presented earlier (Pieczka - Kraczka 1994, 1995, 1996), indicate a high concordance between data of Mössbauer spectroscopic data and calculations made on the basis of the composition of a given tourmaline.

Korovushkin et al. (1979) examined the effects of temperature on QS and differentiated on this basis six distinguished doublets of quadrupole splitting of $Fe^{2+}$ ions into two groups, attributed to Y and Z octahedra. In the opinion of the present authors, however, the $Fe^{2+}$ ions do not need to occur in two different octahedra. The same effect may be explained by gradual changes, in the nearest neighbourhood of $Fe^{2+}$ there begin to appear additional oxygen ions [at the O(1) site], as well as ions of $Al^{3+}$, $Fe^{3+}$ and $Ti^{4+}$ in the II coordination shell. When analysing the five presented earlier variants of the nearest neighbourhood structure of $Fe^{2+}$ ions, there may be noticed a gradual differentiation of ligands of the Ist coordination shell from $(OH,F)^-$ toward $O^{2-}$, and also of cations of the IInd coordination shell from bivalent ions towards groups containing trivalent ions and even $Ti^{4+}$. These substitutions, must also affect the geometrical distortion and local electric field gradient within the Y octahedra. It seems even more probable as the triad of Y octahedra share common ligands - O(1) and O(2), while the mean bond lengths of Y-O changes from about 2.08-2.04 Å for variants of the nearest neighbourhood of $Fe^{2+}{}_Y$ ions corresponding to doublets I and II, up to about 2.00-1.96 Å for variants of the nearest neighbourhood of $Fe^{2+}{}_Y$ ions corresponding to doublets IV and V. Although the classical Y octahedron is built of four oxygens, $OH^- = O(3)$ and $(OH,F)^- = O(1)$, still the O(1) site in naturally occurring tourmalines is filled with oxygen in some percent to about 20 % of Y octahedra. The Ist coordination sphere of the Y ions changes distinctly in such a case [4O - $(OH)_{(3)}$ - $O_{(1)}$], becoming similar to a surrounding typical of Z site. It may be thus concluded that the really wide range of variability of the QS parameter of $Fe^{2+}{}_Y$ ions in the model proposed (from about 2.5 to about 1.2 mm/s) may be associated with lar-

Table 1. Resolutions and interpretations of Mössbauer spectra of schorls from Strzegom and Izera Mts (Poland), Överhogdal (Sweden) and Erzgebirge (Germany)

| Sample | $\chi^2$ | MIS-FIT | IS mm/s | QS mm/s | Γ mm/s | A % | $A_{CALC}$ % | Interpretation |
|---|---|---|---|---|---|---|---|---|
| S35 | 1.088 | 0.010 | 1.08 | 2.54 | 0.24 | 27 | 31 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}(R^{2+},Fe^{3+})$ |
| | | | 1.08 | 2.37 | 0.25 | 23 | 20 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}R^{2+}$ |
| | | | 1.08 | 2.11 | 0.30 | 23 | 18 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}$(Al,Ti) |
| | | | 1.08 | 1.68 | 0.41 | 17 | 16 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}(Fe^{3+}$,Al,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_4(OH)_2/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | 1.08 | 1.17 | 0.34 | 6 | 11 | Y-oct.: $Fe^{2+}/O_4(OH)(F,O)/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_5(OH)/R^{2+}(R^{2+},Fe^{3+}$,Al,Ti) |
| | | | 0.35 | 0.46 | 0.38 | 4 | | Y-oct.: $Fe^{3+}/O_4$(OH,O)(OH,F,O) |
| S49 | 1.053 | 0.000 | 1.08 | 2.47 | 0.25 | 30 | 29 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}(R^{2+},Fe^{3+})$ |
| | | | 1.08 | 2.17 | 0.27 | 30 | 31 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}R^{2+}$ |
| | | | 1.09 | 1.86 | 0.34 | 11 | 9 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}$(Al,Ti) |
| | | | 1.08 | 1.53 | 0.34 | 12 | 14 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}(Fe^{3+}$,Al,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_4(OH)_2/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | 1.08 | 1.13 | 0.34 | 12 | 2 | Y-oct.: $Fe^{2+}/O_4(OH)(F,O)/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_5(OH)/R^{2+}(R^{2+},Fe^{3+}$,Al,Ti) |
| | | | 0.35 | 0.36 | 0.33 | 3 | | Y-oct.: $Fe^{3+}/O_4$(OH,O)(OH,F,O) |
| | | | 0.76 | 1.30 | 0.29 | 2 | | Y-oct: $Fe^{2.5+}/O_4$(OH,O)(OH,F,O) |
| N3 | 1.101 | 0.003 | 1.08 | 2.48 | 0.24 | 34 | 35 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}(R^{2+},Fe^{3+})$ |
| | | | 1.08 | 2.21 | 0.25 | 21 | 13 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}R^{2+}$ |
| | | | 1.08 | 1.86 | 0.27 | 10 | 12 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}$(Al,Ti) |
| | | | 1.07 | 1.51 | 0.27 | 9 | 13 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}(Fe^{3+}$,Al,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_4(OH)_2/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | 1.07 | 1.19 | 0.27 | 5 | 7 | Y-oct.: $Fe^{2+}/O_4(OH)(F,O)/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_5(OH)/R^{2+}(R^{2+},Fe^{3+}$,Al,Ti) |
| | | | 0.35 | 0.97 | 0.40 | 7 | | Y-oct.: $Fe^{3+}/O_4$(OH,O)(OH,F,O) |
| | | | 0.72 | 1.28 | 0.50 | 14 | | Y-oct: $Fe^{2.5+}/O_4$(OH,O)(OH,F,O) |
| N5 | 1.112 | 0.010 | 1.08 | 2.49 | 0.24 | 43 | 47 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}(R^{2+},Fe^{3+})$ |
| | | | 1.08 | 2.28 | 0.29 | 29 | 32 | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}R^{2+}$ |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}$Al |
| | | | 1.06 | 1.82 | 0.36 | 17 | 8 | Y-oct.: $Fe^{2+}/O_4(OH)_2/R^{2+}$Ti |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_4(OH)F/R^{2+}(Fe^{3+}$,Al,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_5($ OH$)/R^{2+}R^{2+}$ |
| | | | 1.05 | 1.38 | 0.31 | 7 | 9 | Y-oct.: $Fe^{2+}/O_4(OH)(OH,F,O)/(R^{3+}$, Ti)$(R^{3+}$,Ti) |
| | | | | | | | | Y-oct.: $Fe^{2+}/O_5(OH)/R^{2+}(Fe^{3+}$,Al,Ti) |
| | | | 0.35 | 0.40 | 0.47 | 4 | | Y-oct.: $Fe^{3+}/O_4$(OH,O)(OH,F,O) |

IS - isomeric schift against α-Fe, QS - quadrupole splitting, Γ - half width at half maximum, A - quadrupole abundance, $A_{CALC.}$ - quadrupole abundance of $Fe^{2+}$ ions calculated from crystallochemical formula

ge oscillations of electric field gradient in specific variants of the triplet of Y octahedra. In our opinion, it is just the parameter responsible for low QS values of the dublets IV and V, and - sometimes - for significant broadening of both arms of the spectrum towards its centre.

It should be stressed that besides the commonly accepted model of interpretation of Mössbauer spectra of tourmalines based on disordering of $Fe^{2+}$ and $Al^{3+}$ ions between Y and Z octahedra, the spectra of practically all tourmalines (also elbaites), not only schorls, can be interpreted in a much simpler way, i.e. without the necessity of assuming such type of distribution of above mentioned ions. The model of interpretation proposed here correlates well with both crystallochemical data and structural parameters, assessed by other independent methods.

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## Mössbauerovská spektra skorylů chudých $Fe^{3+}$: reinterpretace na základě uspořádaného strukturního modelu

Mössbauerovská spektra turmalínů jsou obyčejně interpretována za předpokladu neuspořádaného rozmístění oktaedrických kationtů, především $Fe^{2+}$ a $Al^{3+}$ mezi strukturními pozicemi Y a Z (Hermon et al. 1973, Korovuškin et al. 1979, Ferrow et al. 1988). Na základě krystalochemie, jako je to v případě Fe-elbaitů, nemají takové předpoklady žádný základ. Statistická analýza vztahů mezi středními délkami vazeb a kationty v oktaedrických pozicích Y a Z u turmalínu s Al > 6 apfu ukázala výrazný efekt substituce iontů sousedních pozic kationtů (zvlášť oktaedrů v pozici Y) na střední velikost obou strukturních pozic. Proto má neuspořádanost oktaedrických iontů mnohem menší význam nebo zcela chybí. Tento článek prezentuje možnost krystalochemické interpretace kvadrupólového rozštěpení dvojic ve spektrech turmalínů s nízkým obsahem $Fe^{3+}$. Navrhovaná interpretace je založena na analýze frekvence výskytů $Fe^{2+}$ v určité skupině iontů v I. a II. koordinační slupce. Pokud se $Fe^{2+}$ vyskytuje jako centrální ion v Y oktaedru, pozice O(3) je obsazena $(OH)^-$ a rozdíly v I. koordinační slupce jsou výsledkem substituce ($OH^-$, $F^-$, $O^{2-}$) v pozici O(1). Ve II. koordinační slupce je variabilita iontů omezena na kationty ve dvou zbývajících Y oktaedrech. Skupiny iontů, které se mohou vyskytovat okolo $Fe^{2+}$, mohou být uspořádány do pěti skupin různých variant, rozrazujících krystalochemickou podobnost v každé skupině. Výsledky jsou charakterizovány dobrým souhlasem spektroskopických a chemických dat, např. příspěvek kvadrupólového rozštěpení dvojic $Fe^{2+}$ iontů na celé spektrum a vypočítaných podílů $Fe^{2+}$ ve specifických skupinách iontů I. a II. koordinační slupky ve vztahu k $Fe_{tot}$. Přítomnost mnoha dvojic kvadrupólového štěpení v mössbauerovských spektrech turmalínů může být úplně vysvětlena na základě krystalochemických vlastností, bez předpokladu náhodného rozmístění oktaedrických iontů.