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

Mössbauerovská spektra skorjúch 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 is the case of Fe-eldrites, 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 apfs have shown a significant effect of ionic substitutions in neighboring cation sites (particularly within the trioctahedra) 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 schorl. The proposed interpretation is based on an analysis of frequency of Fe$^{3+}$ occurrences within particular ion groups in the 1st and 11a coordination shells. If Fe$^{3+}$ occurs as a central ion in Y octahedra, the O(3) site is occupied by (OH$^-$), and differences in the 1st coordination shell result from substitution of (OH$^-$, F$^-$, O$^{2-}$) ions in the O(1) site. In the 11a 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$^{3+}$, have eventually been arranged into five sets of different variants, revealing a crystallochemical similarity within each set and, as it can be supposed, affecting the Fe$^{3+}$ ion in the same way. The results are characterized by very good concurrence of spectrscopic and chemical data, i.e. the contributions of quadrupole splitting doublets of Fe$^{3+}$ ions to the whole spectrum and calculated shares of Fe$^{3+}$ in specific groups of ions of the 1st and 11a 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.

Keywords: 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 particu-
larly useful in obtaining information on distribution of Fe$^{3+}$ 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 - Excit 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$^{3+}$ ions in Y 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.

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$_2$O(+) were determined by weight (H$_2$O as losses on ignition above 500 °C with a correction to oxidizing Fe$^{2+}$-iron); Al$_2$O$_3$, Fe$_{total}$ as FeO, CaO and MgO complexometrically (EDTA); B$_2$O$_3$, TiO$_2$ and F colorimetrically (the carmin acid method, the peroxide method and the Zr-ER method, respectively); Na$_2$O and K$_2$O by flame pho-
ry, while Li₂O, MnO, ZnO and CaO (for the latter it was cross-checking) by ASA. Ratios of FeO and Fe₂O₃ were calculated from Mössbauer data. Chemical formulae of formal units were calculated on the basis of 31 ions of (OH,Fe,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/cm². ⁵⁷Co(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 Fe²⁺ ions and one doublet of Fe³⁺ ions, or one doublet of iron with the mixed valence state (Fe²⁺Fe³⁺). The choice of the variant of the spectrum resolution presented here stemmed from the best fitting parameters (χ² 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 Fe³⁺ 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 Fe²⁺ 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 1st and 1nd coordination shells were calculated for Fe²⁺ ions. In the calculations it was assumed that the amounts of Fe³⁺ ions and of mixed valence state (Fe²⁺Fe³⁺) 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 Fe²⁺ and Fe³⁺ 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 Fe²⁺ and Fe³⁺ 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 Fe²⁺ ions in Z sites is acceptable, but Fe²⁺ 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 Fe²⁺ 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 Fe³⁺ and Al³⁺ ions between Y and Z octahedra. Likewise, a simple trend analysis of thermally-induced changes of lattice parameters between the original tourmaline with Fe²⁺ and its oxidized form with Fe³⁺ (a parameter decreases, c parameter slightly increases) indicates also the presence of the Fe²⁺ 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 - Krazcka 1996). This is possible only when Fe²⁺ ions are present in Y sites, otherwise Z octahedra would have to shrink (r₁Fe²⁺=0.78 Å -> r₁Fe³⁺=0.645 Å).

Among the Mössbauer spectra of Fe²⁺-rich tourmalines, three categories may be distinguished considering the complexity of their shapes:

1) the simplest spectra of schorls with Al ≥ 6 apfu and Fe²⁺ = 0 apfu, with symmetrical or almost symmetrical intensities of both branches;
2) spectra of schorls with Al ≥ 6 apfu and Fe²⁺ > 0 apfu, revealing more distinct asymmetry of intensities of both branches;
3) spectra of Fe²⁺- and Fe³⁺-tourmalines with a deficit of aluminium in their structure, i.e. those with Al < 6 apfu and Fe³⁺ > 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 - Krazcka 1994, 1996), and a spectrum of Fe-eeibaite as well (Pieczka - Krazcka 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 crystalchemical formulae of the tourmalines are in question as follows:

(S35) - Al-schorl from Strzegom (Poland)
(Na0.12K0.021Ca0.01Fe0.77Al0.67Si0.22)Fe²⁺0.13(Al0.59

Mg0.005Fe³⁺0.07Zn0.007Al0.007Si0.01Al0.004)
Al0.008Fe³⁺0.01Si0.001(OH)0.007(O2·OH1.166Bu0.45Fe0.36)

(35)
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 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<sup>2+</sup> and Fe<sup>3+</sup> ions, i.e. the ligands of the 1st coordination shell. This reasoning is supported by the fact that the 1st coordination shell of the Fe<sup>3+</sup> ion in Y octahedron is strongly differentiated in its anis 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)<sup>-</sup>, but O(1) also F<sup>-</sup>, and if the substitution of the deprotonation type takes place, at least one of the two possible (OH)<sup>-</sup> sites is occupied by oxygen. The authors dealing with Mössbauer investigations of minerals with 1 single possible variant of the 1st coordination shell around Fe<sup>2+</sup> or Fe<sup>3+</sup> ions (e.g. spinels - Bancroft et al., 1983) pointed to a significant effect of varying cations in the 1nd 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 1st and 2nd 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<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Al<sup>3+</sup> and Ti<sup>4+</sup>. These ions can be arranged into 21 variants in which at least one Fe<sup>2+</sup> ion occupies the triad of Y octahedra, and also 21 variants with at least one Fe<sup>3+</sup>, respectively. Since the amount of Fe<sup>3+</sup> in the group of tourmalines studied in this work is rather low (3.4 % of the total Fe for the samples S35, S49, S5 and about 14 % for the sample N3), the analysis of crystallochemical differentiation around this ion has been omitted. When Fe<sup>2+</sup> occurs as a central ion, the O(3) site is occupied by (OH)<sup>-</sup>, and the variability within the 1st coordination shell results from substitution of (OH<sup>-</sup>, F<sup>-</sup>, O<sup>2-</sup>) 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<sup>2+</sup>/4O(OH)<sub>3</sub>(OH,F,O)<sub>1</sub> / (Y,Y) central / 1st coordination shell / variable components in ion 
1nd coordination shell

For any estimation on the content of Fe<sup>2+</sup> ions to the total iron content on the 1st coordination shell of every group of iron in the tourmaline structure, it is necessary to calculate probabilities of occurring different variants of the 1st and 1nd 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<sup>2+</sup> ions within the 1nd coordination shell. The mentioned 21 possible variants of the structure of the Y octahedra triad, out of which at least one contains Fe<sup>2+</sup>, may be subdivided into 4 groups taking into account crystallochemical criteria (valency, effective ionic radius, electronegativity):

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<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
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<tbody>
<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;3+&lt;/sup&gt;Al&lt;sup&gt;3+&lt;/sup&gt;</td>
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<td>Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MgFe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MgAl&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MgAl&lt;sup&gt;3+&lt;/sup&gt;</td>
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<td>Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MnFe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MnAl&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MnAl&lt;sup&gt;3+&lt;/sup&gt;</td>
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<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MgMn</td>
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<td>Fe&lt;sup&gt;2+&lt;/sup&gt;MgMn</td>
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</table>

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<sup>2+</sup> 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<sup>2+</sup> ion in a more complicated way. If the structure of these ionic arrangements is expressed in the most generalized manner:

I) Fe<sup>2+</sup>R<sup>2+</sup>R<sup>2+</sup> 
II) Fe<sup>2+</sup>R<sup>2+</sup>R<sup>3+</sup> 
III) Fe<sup>2+</sup>R<sup>3+</sup>(Al,Ti) 
IV) Fe<sup>2+</sup>(Fe<sup>3+</sup>,Al,Ti)(Fe<sup>3+</sup>,Al,Ti)

and all possible variants of the 1st coordination sphere are considered, it is possible to calculate maximum 12 different combinations of ion groups, representing simultaneously changes within the 1st and 1nd coordination shell of the closest neighbours of Fe<sup>2+</sup> ions. They are as follows:

1) Fe<sup>2+</sup>4O2(OH) R<sup>2+</sup>R<sup>2+</sup> 
2) Fe<sup>2+</sup>4O(OH)F R<sup>2+</sup>R<sup>2+</sup> 
3) Fe<sup>2+</sup>5O(OH) R<sup>2+</sup>R<sup>2+</sup> 
4) Fe<sup>2+</sup>4O2(OH) R<sup>2+</sup>R<sup>3+</sup> 
5) Fe<sup>2+</sup>4O(OH)F R<sup>2+</sup>R<sup>3+</sup> 
6) Fe<sup>2+</sup>5O(OH) R<sup>2+</sup>R<sup>3+</sup> 
7) Fe<sup>2+</sup>4O2(OH) R<sup>2+</sup>(Al,Ti) 
8) Fe<sup>2+</sup>4O(OH)F R<sup>2+</sup>(Al,Ti) 
9) Fe<sup>2+</sup>5O(OH) R<sup>2+</sup>(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 Γ 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 1st and 2nd 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
schorls (Fig. 2 A D) are presented in Table 1. These results, likewise those partly presented earlier (Peezka - 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 neighborhood structure of Fe$^{2+}$ ions, there may be noticed a gradual differentiation of ligands of the 1st coordination shell from (OH,F)$^{-}$ toward O$^{2-}$, and also of cations of the IIId coordi- nation 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 that the triad of Y octahedra share common ligands - O(1) and O(2), while the bond lengths of Y-O changes from about 2.08-2.04 Å for variants of the nearest neighbourhood of Fe$^{2+}$ ions corresponding to doublets I and II, up to about 2.00-1.96 Å for variants of the nearest neighbourhood of Fe$^{2+}$ ions corresponding to doublets IV and V. Although the classical Y octahedron is built of four oxygens, OH$^{-}$ = O(3) and (OH,F)$^{-}$ = O(4), still the O(1) site in naturally occurring tourmalines is filled with oxygen in some percent to about 20 % of Y octahedra. The 1st coordination sphere of the Y ions changes distinctly in such a case [4O - (OH,F)$^{-}$ - 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$^{2+}$-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 Izeria Mts (Poland), Överhogdal (Sweden) and Erzgebirge (Germany)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\chi^2$</th>
<th>MISFIT</th>
<th>IS mm/s</th>
<th>QS mm/s</th>
<th>$\Gamma$ mm/s</th>
<th>A %</th>
<th>$A_{\text{calc}}$ %</th>
<th>Interpretation</th>
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<tbody>
<tr>
<td>S35</td>
<td>1.088</td>
<td>0.010</td>
<td>1.08</td>
<td>2.54</td>
<td>0.24</td>
<td>27</td>
<td>31</td>
<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$(Fe$^{3+}$)</td>
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<td>1.08</td>
<td>2.37</td>
<td>0.25</td>
<td>23</td>
<td>20</td>
<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$R$^{2+}$</td>
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<td>1.08</td>
<td>2.11</td>
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<td>23</td>
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<td>1.08</td>
<td>1.68</td>
<td>0.41</td>
<td>17</td>
<td>15</td>
<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Ti</td>
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<td>1.08</td>
<td>1.17</td>
<td>0.34</td>
<td>6</td>
<td>11</td>
<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$(Fe$^{3+}$,Al,Ti)</td>
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<td>0.35</td>
<td>0.46</td>
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<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Ai</td>
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<tr>
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<td>0.000</td>
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<td>2.47</td>
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<td>30</td>
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<td>2.17</td>
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<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$R$^{2+}$</td>
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<td>1.09</td>
<td>1.86</td>
<td>0.34</td>
<td>11</td>
<td>9</td>
<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Fe$^{3+}$,Al,Ti</td>
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<td>1.08</td>
<td>1.53</td>
<td>0.34</td>
<td>12</td>
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<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Ti</td>
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<td>1.13</td>
<td>0.34</td>
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<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Ti</td>
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<td>0.36</td>
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<td>0.76</td>
<td>1.30</td>
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<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Al</td>
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<tr>
<td>N3</td>
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<td>0.003</td>
<td>1.08</td>
<td>2.48</td>
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<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$(Fe$^{3+}$,Fe$^{3+}$)</td>
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<td></td>
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<td>1.08</td>
<td>2.21</td>
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<td>1.86</td>
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<td></td>
<td>1.07</td>
<td>1.51</td>
<td>0.27</td>
<td>9</td>
<td>13</td>
<td>Y-oct: Fe$^{2+}$(OH,F)R$^{2+}$Fe$^{3+}$,Al,Ti</td>
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IS = isomeric shift against α-Fe, QS = quadrupole splitting, $\Gamma$ = half width at half maximum, A = quadrupole abundance, $A_{\text{calc}}$ = 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 doublets 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 tournaminals based on disordering of Fe²⁺ and Al³⁺ ions between Y and Z octahedra, the spectra of practically all tournaminals (also elbaites), not only schochris, 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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- (in prep.): Statistical interpretation of structural parameters of tournaminals: the unit cell parameters in Al-rich tournaminals.


Mössbauerovská spektre skorylů chudých Fe³⁺: reinterpreace na základě uspořádaného strukturového modelu

Mössbauerovská spektra tournamínů jsou obvykle interpretovány za předpokladu uspořádaného rozšiřování oktaedrických kationů, především Fe²⁺ a Al³⁺ mezi strukturální pozicemi Y a Z (Herborn et al., 1973, Korovalkin et al., 1979, Ferrow et al., 1988). Na základě krystalochimie, jako je to v případě Fe-štírů, nemají takové předpoklady žádné základy. Statistická analýza vztahu mezi vzdálenostmi dělek vzniklých v oktaedrických pozicích Y a Z u tournamínů s Al > 6 aput ukázala výrazný případ substituce iontů sousedních pozic kationů (v závěrech oktaedrů v pozici Y) na stejnou velikost obou strukturálních pozic. Proto má uspořádanost oktaedrických iontů mnohem menší význam nebo zcela chybí. Tento článek prezentuje možnost krystalochimické interpretace kvadrupolového rozšiřování dvojic ve spektrech tournamínů s nízkým obsahem Fe³⁺. Navrhovaná interpretace je založena na analýze frekvence výskytu Fe²⁺ v určité skupině iontů v I.a II. koordinátní slupce. Pokud se Fe³⁺ vyškakuje jako centrální ion v Y oktaedru, pozici O(K) je obsazena (OH) a rozdíly v I. koordinátní slupce jsou výsledkem substituce (OH, F, O²⁻) v pozici O(V). Ve II. koordinátní slupce je randaživá ionty omezena na kationy ve dvou zbývajících Y oktaedrech. Skupiny iontů, které se mohou vyskytovat v oktaedrech, mohou být uspořádané do příp. skupin různých variant, které souvisí s krystalochimickou podobností v každé skupině. Výsledky jsou charakterizovány dobrým souhlasem spektroscopytických a chemických dat, např. příspěvku kvadrupolového rozšiřování dvojic Fe²⁺ iontů na celé spektru a vyslovených podílů Fe²⁺ ve specifických skupinách iontů I. a II. koordinátní slupky ve vzduchu k Fe³⁺. Přítomnost minimálního dvojic kvadrupolového stření v měření všech spektram tournamínů může být úplně vysvětlena na základě krystalochimických vlastností, bez přeskočení některých uspořádaných oktaedrických iontů.