

## Lattice dynamic of $^V\text{OH}$ stretching vibrations in tourmaline

The salient arguments supporting our theoretical modeling of OH stretching modes in chemically disordered tourmaline have previously been reported by Fuchs et al. (2022). Here, we further expose our strategy and assumptions:

1- Although the numerical calculations are performed in a Cartesian reference frame, a proper understanding of OH stretching modes is better achieved by considering the internal stretching coordinates, as usually done when discussing the properties of crystals with well defined molecular units (Califano et al., 1981).

2- The high frequency of the OH stretching modes ensures their decoupling from the other vibrational modes.

3- The vibrational properties of  $^V\text{OH}$  stretching modes in tourmaline can be understood by focusing on structural "clusters" containing three  $^V\text{OH}$  groups linked to a triplet of YZZ octahedral sites. In the ideal structure, the three  $^V\text{OH}$  groups and YZZ triplets are related to each other by a three fold rotation axis.

4- According to points 1, 2 and 3, and without any loss of generality, the real-space  $3N \times 3N$  matrix  $\mathbf{M}$  describing the  $^V\text{OH}$  stretching vibrational properties of a tourmaline fragment containing  $N$  clusters labelled  $i$  ( $i=1, \dots, N$ ) has the following form in the basis of local OH stretching coordinates:

$$\mathbf{M} = \begin{pmatrix} \omega_{1,1}^2 & f_{1,12} & f_{1,13} & & & & & & \\ f_{1,12} & \omega_{1,2}^2 & f_{1,23} & & \Delta_{12} & & \Delta_{13} & \cdot & \cdot & \cdot \\ f_{1,13} & f_{1,23} & \omega_{1,3}^2 & & & & & & & \\ & & & \omega_{2,1}^2 & f_{2,12} & f_{2,13} & & & & \\ & \Delta_{12} & & f_{2,12} & \omega_{2,2}^2 & f_{2,23} & & \Delta_{23} & & \\ & & & f_{2,13} & f_{2,23} & \omega_{2,3}^2 & & & & \\ & & & & & & \omega_{3,1}^2 & f_{3,12} & f_{3,13} & \\ & \Delta_{13} & & & & & f_{3,12} & \omega_{3,2}^2 & f_{3,23} & \\ & & & & \Delta_{23} & & f_{3,13} & f_{3,23} & \omega_{3,3}^2 & \\ & & & & & & & & & \cdot \\ & & & & & & & & & \cdot \\ & & & & & & & & & \cdot \end{pmatrix}$$

where each  $3 \times 3$  block on the diagonal describes the  $^V\text{OH}$  stretching vibrations of a single cluster. Diagonal elements are related to the stretching frequencies  $\omega_{i,j}$  of the uncoupled  $^V\text{OH}$  group  $j$  ( $j=1,2,3$ ) belonging to cluster  $i$ , whilst the  $f_{i,jk}$  terms describe the bilinear coupling between two OH groups  $j$  and  $k$  ( $j, k = 1,2,3$ ) belonging to the same cluster  $i$ . The out-of-diagonal  $3 \times 3$   $\Delta_{il}$  blocks describe the vibrational interactions between the  $^V\text{OH}$  groups belonging to different clusters.

5- As ascertained on pure dravite, the interaction between different clusters is weak enough to assume that the matrix  $\mathbf{M}$  is block diagonal ( $\Delta_{il}$  submatrix are  $3 \times 3$  nil matrix).

6- In **ideal tourmaline**, the 3-fold symmetry imposes that the stretching frequencies of the equivalent  $^V\text{OH}$  groups are equal to each other ( $\omega_{ij} = \omega_0$ ) and that the coupling coefficients are also equal to each other ( $f_{ijk} = f$ ). The zone-center dynamical matrix of the periodic system reduces to a 3x3 symmetric matrix whose diagonalization leads to a symmetric mode ( $A_1$  representation) with frequency  $\omega_0 + f/\omega_0$  and 2 degenerate modes (E representation) with frequency  $\omega_0 - f/2\omega_0$ . Due to the nearly parallel configuration of the  $^V\text{OH}$  dipoles, the  $A_1$  mode dominantly carries the IR and Raman spectroscopic activity. The splitting of the  $A_1$  and E modes is  $3f/2\omega_0$ , providing a measure of the coupling between the equivalent  $^V\text{OH}$  groups. In ideal dravite, this splitting is  $\sim 0.1 \text{ cm}^{-1}$ , indicating that the out-of-diagonal  $f$  terms are negligible with respect to the diagonal terms  $\omega_0^2$ . As a consequence, the matrix **M** is diagonal in both the local mode and the symmetry-adapted normal mode basis.

7- In **chemically disordered tourmaline**, the 3-fold symmetry is a property of the average crystal structure which is not ensured at the single cluster scale. Depending on the location of the substituting cation or vacancy, the YZZ-YZZ-YZZ cluster can display 3-fold, mirror or no symmetry element.

8- To determine the OH stretching modes in **chemically disordered tourmaline**, we build a series of 1x1x2 hexagonal supercell ( $> 320$  atoms) containing the chemically modified cluster embedded in a pure dravitic matrix. We compute and diagonalize the relevant 3x3 submatrix of the block diagonal matrix **M**, retrieving its three vibrational frequencies and related eigendisplacements. It is noteworthy that this calculation is performed in the Cartesian reference frame and fully considers the three, potentially interacting,  $^V\text{OH}$  groups of the defective cluster.

9- Depending on the local symmetry of the cluster, one, two or three spectroscopically dominant vibrational modes are obtained, arising from contributions of three, two or one  $^V\text{OH}$  group. The numerical results show that each mode can be ascribed to a specific YZZ occupancy because the  $^V\text{OH}$  groups with a different occupancy of their neighboring YZZ sites do not contribute to the same mode. This theoretical outcome of the ab initio calculation supports the traditional local interpretation of OH stretching bands in tourmaline.

## References

- Califano, S., Schettino, V., and Neto, N.: Lattice Dynamics of Molecular Crystals, Lecture Note in Chemistry, Springer, Berlin, ISBN: 978-3-540-10868-9, 1981.
- Fuchs, Y., Fourdrin, C., and Balan, E.: Theoretical OH stretching vibrations in dravite, Eur. J. Mineral., 34, 239–251, <https://doi.org/10.5194/ejm-34-239-2022>, 2022.