

[s11.m1.p15] Determination of the environment of Fe³⁺ using the fourth order Spin-Hamiltonian constants, its power and limits. J.-M. Gaije*, Y. Dusausoy**, S.S. Hafner*** and H. Rager***. *Centre de Recherche sur la Matière Divisée. Université d'Orléans-CNRS Rue de Chartres - BP 6759 -45067 Orléans Cedex 2 France. **LCM³B, Université de Nancy I, B.P.239 54600 Vandoeuvre -les Nancy, Cedex France. ***Institute of Mineralogie, University of Marburg, Hans Meerwein Strasse, 3550 Marburg, Germany.
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Many years ago, it has been established that it was possible to locate Fe³⁺ using the fourth order constants of the Spin-Hamiltonian (H4) describing the spectra.

Afterwards, the original method was improved in order to obtain some characteristics on the short range environment of Fe³⁺. The norm N of H4 depends on the nature and on the number of ligands, N being smaller for tetrahedral environments than for octahedral ones. It was expected that it could be possible to obtain some relations between N and the mean Fe-X distance, but at this time the situation is not clear.

There are two kinds of limitation of this method.

-First, the constants of H4 must be determined, this is possible only if the transition lines are not too broad. Then only diamagnetic well ordered single crystals containing low concentrations of paramagnetic impurities can be investigated. On another hand, enough transitions sensitive to the crystal field must be observed. It is impossible to calculate the constants of H4 if the zero field splitting is so large that only transitions inside the Kramers' doublets can exist. Recently, we studied Fe³⁺ substituted for Mg²⁺ at M1 position in forsterite for which the constant B₂² is equal to 0.1845 cm⁻¹. This value is near from the upper value of applicability of the method at Q band frequency. We can then consider that to use this method the ratio B₂²/hν must be less than 0.16.

-The second limitation concerns the crystal structure itself. If there are similar polyhedra having the same orientations, from H4 it may be impossible to distinguish them. One example of this limitation was observed in the case of Fe³⁺ in kyanite, in which 4 Al-O₆ octahedra having similar orientations are present and we were not able to assign the different EPR spectra to a given substitution of Al by Fe.

[s11.m1.p16] Structure of Triclinic Na-rich Birnessite. B. Lanson, V.A. Drits, Q. Feng*, A. Manceau. *Environmental Geochemistry Group - LGIT, University of Grenoble - CNRS, BP53, 38041 Grenoble cedex 9, France* & **Research Laboratory of Hydrothermal Chemistry, Kochi University, Japan.*
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The structure of synthetic Na-rich birnessite (NaBi) was studied by powder X-ray diffraction (XRD). It is shown that NaBi has a one-layer triclinic structure with sub-cell parameters a = 5.174 Å, b = 2.848 Å, c = 7.334 Å, α = 90.53°, β = 103.20°, γ = 90.07°, and a P $\bar{1}$ space group. A structural model has been refined from the simulation of the experimental XRD profile.

According to this model, NaBi consists of almost vacancy-free manganese octahedral layers whose negative charge arises from the substitution of Mn³⁺ for Mn⁴⁺. The departure from the hexagonal symmetry of layers results from the Jahn-Teller distortion of Mn³⁺ octahedra, which are systematically elongated along the a axis.

For each interlayer species (Na and H₂O) two split sites have been determined. This splitting is consistent with the modulated structure of NaBi, which arises from the periodic displacement of interlayer species along the b axis with a periodicity λ = 6b (Drits et al.¹)

[1] Drits V.A. "Structure of Synthetic Monoclinic Na-Rich Birnessite an Hexagonal Birnessite: I. Results from X-rays Diffraction and Selected Area Electron Diffraction.", *American Mineralogist*, (1997), 82: 946-961.