

## Mössbauer spectroscopic study of natural eosphorite, [(Mn,Fe)AlPO<sub>4</sub>(OH)<sub>2</sub>H<sub>2</sub>O]

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### ABSTRACT

A <sup>57</sup>Fe Mössbauer spectroscopic study of natural eosphorite, (Mn,Fe<sup>2+</sup>)AlPO<sub>4</sub>(OH)<sub>2</sub>H<sub>2</sub>O, is reported. The Mössbauer spectra were collected at temperatures between 295 and 4.2 K. At temperatures exceeding 30 K, the Mössbauer spectra consist of a somewhat broadened quadrupole doublet with a splitting of 1.73 mm/s at 295 K. From the spectrum recorded at 250 K in an external magnetic field of 60 kOe, it is derived that the sign of the principal component of the electric field gradient (EFG) is negative and that the EFG's asymmetry parameter is large (~0.5). From these findings, it is concluded that the octahedral coordination of the ferrous cations exhibits in first order a trigonal compression with a further lowering from axial symmetry due to an additional distortion. The spectrum collected at 4.2 K shows the existence of magnetic ordering. It was analyzed in terms of the full hyperfine interaction Hamiltonian, yielding a magnetic hyperfine field value of 146 kOe and EFG characteristics that are fully in line with those obtained from the external-field spectrum. In the temperature range from 10 to 30 K, the spectra indicate the occurrence of relaxation effects. They could be satisfactorily described in terms of the Blume-Tjon (BT) model for electronic relaxation, assuming a superposition of a slow- and a fast-relaxation component. The observed temperature dependence of the isomer shift is adequately described by the Debye model for the lattice vibrations. The characteristic Mössbauer temperature was found as (360 ± 20) K and the zero-Kelvin intrinsic isomer shift as (1.480 ± 0.005) mm/s. The variation of the quadrupole splitting with temperature is explained by the thermal population of the Fe<sup>2+</sup> electronic states within the T<sub>2g</sub> orbital triplet, which is split by the trigonal crystal field in a singlet ground state and an upper doublet state, the latter being further split into two orbital singlets by an additional distortion. The energies of these latter excited states with respect to the ground state are calculated to be 280 ± 20 and 970 ± 50 cm<sup>-1</sup>, respectively, based on a point-charge calculation of the <sup>5</sup>D level scheme. This calculation confirms the sign of the V<sub>zz</sub> component of the electric field gradient being negative as it is determined from the external magnetic field measurement and from the magnetic spectrum acquired at 4.2 K. Iron phosphates are widely spread minerals in the Earth's crust and are expected to occur in soils and rocks on Mars as well. Mössbauer spectroscopy as complementary source of information to the results of other analytical techniques, could therefore be useful to identify and characterize the environmental Fe-bearing phosphates.

**Keywords:** Eosphorite, Mössbauer spectroscopy, hyperfine parameters, temperature variation