Mössbauer spectroscopic study of natural eosphorite, \[(\text{Mn,Fe})\text{AlPO}_4(\text{OH})_2\text{H}_2\text{O}\]

ANTOINE VAN ALBOOM\textsuperscript{1,2}, VALDIRENE GONZAGA DE RESENDE\textsuperscript{1}, GERALDO MAGELA DA COSTA\textsuperscript{3} and EDDY DE GRAVE\textsuperscript{1,*}

\textsuperscript{1}Department of Physics and Astronomy, University of Gent, B-9000 Gent, Belgium
\textsuperscript{2}Department of Industrial Technology and Construction, University of Gent, B-9000 Gent, Belgium
\textsuperscript{3}Chemistry Department, Federal University of Ouro Preto, 35400-000, Ouro Preto (MG), Brazil

ABSTRACT

A \(^{57}\text{Fe}\) Mössbauer spectroscopic study of natural eosphorite, \((\text{Mn,Fe}^{2+})\text{AlPO}_4(\text{OH})_2\text{H}_2\text{O}\), 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 \((360 \pm 20)\) K and the zero-Kelvin intrinsic isomer shift as \((1.480 \pm 0.005)\) mm/s. The variation of the quadrupole splitting with temperature is explained by the thermal population of the \(\text{Fe}^{2+}\) electronic states within the \(T_\text{g}\) 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 \(280 \pm 20\) and \(970 \pm 50\) cm\(^{-1}\), respectively, based on a point-charge calculation of the \(1D\) level scheme. This calculation confirms the sign of the \(V_{\text{as}}\) 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

INTRODUCTION

Eosphorite, ideally Mn\(^{2+}\)AlPO\(_4\)(OH)\(_2\)H\(_2\)O, has orthorhombic symmetry with space group \(B\text{bam}\) (Hanson 1960; Huminicki and Hawthorne 2002). The structure is depicted in Figure 1 and consists of alternating chains of Mn octahedra and Al octahedra that run parallel to the \(c\) axis. The strongly distorted Mn octahedra share opposite O1-O2 edges, while the more regular Al octahedra share opposite O3 corners occupied by H\(_2\)O groups. The two types of chains are linked to each other by sharing their O4 corners, thus forming parallel sheets that are held together by P cations in a tetrahedral O4 coordination. Based on single-crystal X-ray diffraction, Hoyos et al. (1993) concluded that the two aforementioned O4 sites are both occupied by OH groups. However, a more recent structure refinement using neutron diffraction data for a single-crystal of eosphorite has revealed that only one of the O4 sites is occupied by OH, while the other is occupied by H\(_2\)O (Gatta et al. 2013). Thus, the structure can be considered as being composed of chains of MnO\(_4\)(OH)\(_2\)H\(_2\)O\(_2\) and AlO\(_4\)(OH)\(_2\)H\(_2\)O\(_2\) octahedra. Eosphorite is isomorphous with childrenite, FeAlPO\(_4\)(OH)\(_2\)H\(_2\)O, and the two mentioned minerals form the end-members of a complete solid-solution series. It is generally accepted in the literature that only Fe\(^{2+}\) is present in the structure of iron-substituted eosphorite, (Mn,Fe)AlPO\(_4\)(OH)\(_2\)H\(_2\)O, and that these Fe\(^{2+}\) cations are found in the Mn octahedra.

Mössbauer spectra (MS) at room temperature (RT) of several iron-substituted eosphorites with different Fe/Mn ratios have