

A Magnetic and Mössbauer Spectral Study of Several Na-Mn-Fe-bearing Alluaudites

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The crystal structure of alluaudite was reported in 1971 by Moore who found that the mineral was monoclinic with the C2/c space group and the stoichiometry, $X(2)X(1)M(1)M(2)_2(PO_4)_3$, with four formula units per unit cell. The actual composition of alluaudite minerals may vary between $Na_2MnFe_2(PO_4)_3$ and $GNaMnFe_2(PO_4)_3$, where the first composition is mixed valent with equal amounts of iron(II) and iron(III) and the second contains only iron(III). In the second composition G represents a lattice vacancy. The Mössbauer spectra of four alluaudites, synthetic $Na_2Mn_2Fe(PO_4)_3$, synthetic and natural $NaMnFe_2(PO_4)_3$, and synthetic $Na_2MnFe_2(PO_4)_3$, have been measured between 4.2 and 295 K. The resulting spectra have been analyzed in terms of a binomial distribution of iron(II) and manganese(II) on the M(2) site for the first compound and iron(II) and iron(III) on the M(2) site for the remaining three compounds. The results indicate that alluaudite often, unexpectedly, contains iron(II) randomly distributed on the M(2) site. Further, alluaudites are structurally unaffected by the presence of manganese(II) on the M(2) site. Iron(II) on the distorted six-coordinate M(2) site exhibits a crystal field splitting of ca. 500 cm^{-1} . All of the alluaudites studied are paramagnetic above ca. 35 K and have M(2) sites which are antiferromagnetically ordered below ca. 35 K. The M(2) magnetic exchange seems to be mostly unaffected by the presence of manganese(II) on the M(1) site. The Mössbauer spectra clearly indicate that the iron(III) on the M(2) sites is magnetically ordered at higher temperatures than is the iron(II) on the M(2) sites.