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STRUCTURE AND MAGNETISM IN FLUOROMANGANATES(III) WITH JAHN-TELLER DISTORTED CHAINS

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The formation of linear chain structures with octahedral $[MnF_6]$ or $[Mn(H_2O)_2F_4]$ groups sharing trans vertices is favorized by the Jahn-Teller-effect of the d^4-high-spin configuration of Mn(III). Fluoromanganates(III) of this structure type are promising models for the study of one dimensional magnetic superexchange interactions.

The 'trans-chain' structures of two alkali fluoromanganates have been determined:

Na_2MnF_5: space group $P2_1/c$, Z = 4, a = 7.719, b = 5.236, c = 10.862 Å, β = 108.99°, R = 2.3% for 1679 reflections[1]. Strongly elongated $[MnF_6]$ octahedra ($Mn-F_{ax}$: 2.11, $Mn-F_{eq}$: 1.85 Å) are trans connected to form infinite kinked chains (Mn-F-Mn: 132.5°) and show ferrodistortiv order: as usual, all the elongated bonds point at the chain direction.

$KMnF_4 \cdot H_2O$: space group C2/c, Z = 8, a = 13.891, b = 6.212 c = 10.484 Å, β = 104.74°, R = 3.7% for 833 reflections, isotypical to $RbMnF_4 \cdot H_2O$ [2]. Elongated $[MnF_6]$ octahedra ($Mn-F_{ax}$: 2.14, $Mn-F_{eq}$: 1.84 Å) alternate in a trans-chain with $[Mn(H_2O)_2F_4]$ groups (Mn-O: 2.15, $Mn-F_{bridge}$: 1.92, $Mn-F_{term}$: 1.79 Å). The order of the distorted octahedra is antiferrodistortiv.

The structural relationships within two families of octahedral trans-chain compounds - deriving either from a tetragonal or a pseudohexagonal rod packing model - can be described via group-subgroup relations between the space groups.

The temperature dependence of the magnetic susceptibilities of these two compounds as well as of the related linear chain compounds $SrMnF_5 \cdot H_2O$ and $BaMnF_5 \cdot H_2O$[3] or $(NH_4)_2MnF_5$[4] can be interpreted on the basis of theoretical calculations performed for short-range antiferromagnetic interactions within the trans-chains.

The antiferromagnetic coupling even in the case of the antiferrodistortively ordered chain of $KMnF_4 \cdot H_2O$, where the σ- and π-interactions are antagonistic, suggests the dominance of π-interactions at the low bridge angle of 137.7°.

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