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NEW STRUCTURAL AND MAGNETIC ASPECTS IN FLUORIDE SOLID STATE CHEMISTRY

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Hydrothermal synthesis provides an interesting way to obtain, as single crystals, metastable or low temperature forms of fluorinated compounds. The behaviour of iron trifluoride FeF_3 has been studied under 2 kbar, in a temperature range 250-460°C, using various media : H_2O, HF 49 % or aqueous solutions of NH_4HF_2. When H_2O is used, the increase of the temperature successively leads to FeF_3, $3H_2O$, $(H_2O)_{0.33}FeF_3$* and Fe_2F_5, $2H_2O$*. The dehydration of $(H_2O)_{0.33}FeF_3$ at 120°C leads to a new form of FeF_3, with hexagonal bronze structure. With HF 49 %, rhomboedral FeF_3* is obtained at temperatures up to 400°C. Above, $Fe^{III} \rightarrow Fe^{II}$ reduction due to H_2 diffusion through Pt occurs and the new compound $Fe^{II}Fe_2^{III}F_8$, $2H_2O$* appears. In NH_4HF_2 medium, $NH_4Fe^{II}Fe^{III}F_6$* is formed at 450°C. Compounds with an asterisk have been submitted to single crystal X ray determination. Their common structural feature is the existence of hexagonal tungsten bronze (HTB) layers. They are stacked in $(H_2O)_{0.33}FeF_3$, shifted in $Fe^{II}Fe_2^{III}F_8$, 2 H_2O and connected by supplementary $(FeF_6)^{3-}$ octahedra in Fe_2F_5, $2H_2O$ and $NH_4Fe^{II}Fe^{III}F_6$ to ensure in each case a three dimensional network. In the HTB layers, the iron sublattice can be described by the juxtaposition of triangular and hexagonal cycles : in the odd membered rings, all the antiferromagnetic superexchange interactions cannot be satisfied, and magnetic frustration must occur. Its different manifestations characterized by the orientation of the spins have been determined by neutron diffraction below the magnetic ordering temperature of each compound. The frustration is minimized by a Yaffet-Kittel configuration in HTB FeF_3, by an orthogonalization of Fe^{2+} and Fe^{3+} spins in $NH_4Fe_2F_6$ or with an idle spin behaviour of Fe^{2+} in Fe_3F_8, $2H_2O$.

Frustration is maximum in the speromagnetic amorphous FeF_3. The study of its recrystallization using Mössbauer spectroscopy shows that frustration decreases when the various forms of FeF_3 successively appear.