MIXED VALENCE IRON AND CHROMIUM FLUORIDES. BRONZES AND RELATED COMPOUNDS. CHEMISTRY, STRUCTURE AND MAGNETISM.

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ABSTRACT. A review is given of the chemistry and structure of 3d transition metal (II,III) fluorinated bronzes and related compounds with a special emphasis on A\textsubscript{x}FeF\textsubscript{3} (A = K and NH\textsubscript{4}) compounds for which neutron diffraction and Mössbauer spectroscopy have been used to characterize their cationic order/disorder and the corresponding magnetic behaviour. Substitutions on the cationic sublattice show that the simultaneous presence of M(II) and M(III) favours the cationic ordering.

1. Introduction

The existence and the study of the so-called tungsten bronzes results from the pioneering work of A. Magnéli at the very beginning of the fifties [1]. It corresponds to a crystal chemistry approach that is illustrated by the following example. Let us consider the ReO\textsubscript{3} type and the ABO\textsubscript{3} perovskite structures (Fig. 1). They are both built up from a three dimensional network of corner sharing ReO\textsubscript{6} (or BO\textsubscript{6}) octahedra. The only difference consists in the occupancy or not of the cubooctahedral vacancy in the middle of the cell. Suppose now that the same metal M (obviously with two different oxidation states, for instance (V) and (VI) if A is a monovalent cation) occupies the center of the octahedra. One can imagine that, between these two limits, phases can occur, which correspond to a partial occupancy of the cubooctahedral sites, and therefore to the formulation A\textsubscript{x}M(V\textsubscript{I}M(VI)\textsubscript{\textfrac{1}{x}}O\textsubscript{3}. The x value can be discrete and can correspond to a definite compound. On the other extreme, x can take all the values comprised between two finite limits and define a range of compositions of a non-stoichiometric compound. The latter case happens in the Magnéli’s bronzes in which tungsten is the concerned metal and A an alkali metal. They are the first examples of non stoichiometry due to insertion. For instance, three potassium bronzes K\textsubscript{x}W(V\textsubscript{I}W(VI)\textsubscript{\textfrac{1}{x}}O\textsubscript{3 exist, corresponding to the composition ranges 0.18 < x < 0.33 (α phase), 0.40 < x < 0.60 (β phase) and 0.95 < x < 1 (γ phase).

Fig.1. Perspective view of the ReO\textsubscript{3} (left) and ABO\textsubscript{3} perovskite (right) structures.
This example immediately shows the problems arising from this progressive insertion of A ions in the host matrix. From the structural point of view, the crystal structure adopted in each phase will depend on the shape and the size of the vacancy of the initial host matrix, the nature, the size and the amount of the inserted ion, and the problem of an eventual cationic ordering between the two cations of the same metal at two different oxidation states for special values of x. From the physical point of view, the presence of $M^{n+}$ and $M^{(n-1)+}$, ordered or disordered, will induce electric, optical and magnetic properties correlated to the structural characteristics of the corresponding phases. The color, particularly, strongly depends on the value of x and therefore on the ratio $M^{(n+1)+}/M^{n+}$ (red or blue tungsten or molybdenum oxygenated bronzes); the same bronzes exhibit also a metallic behaviour, and at low temperatures superconductivity.

In 1965, R. de Pape [2], using the fact that $O^{2-}$ and $F^{-}$ are isoelectronic and that the compounds $FeF_{3}$ and $KFeF_{3}$ adopt the $ReO_{3}$ and the perovskite structures respectively, synthetized the first fluorinated bronzes $K_{x}FeF_{3}$ isotypic with the Magnéli’s bronzes $K_{x}WO_{3}$ and found three domains with $0.18 < x < 0.25$ ($\alpha$ phase), $0.40 < x < 0.60$ ($\beta$ phase) and $0.95 < x < 1$ ($\gamma$ phase). At variance with the oxides bronzes, they are insulators owing to the small extention of the orbitals of the ion $F^{-}$. A lot of studies were then undertaken [3-16] to synthetize other fluorinated bronzes varying either the nature of the inserted ion and/or the nature of the 3d transition metal element. Actually, the $A_{x}MF_{3}$ mixed valence compounds are known for $A = Li, Na, K, Rb, Cs$ and $NH_{4}$ and $M = V, Cr$ and $Fe$, and except in a few cases, only characterized structurally by isotypy with Magnéli’s bronzes, and magnetically by macroscopic measurements. This paper will be presented in two parts: the first will concern the non stoichiometric fluorinated bronzes of iron, chromium and vanadium, with a particular emphasis on the problem of cationic order and its magnetic consequences; the second part will be devoted to mixed valence stoichiometric compounds of iron and the influence of the structural topology on curious magnetic properties such as ‘idle spin’ behaviour.

2. The $A_{x}MF_{3}$ compounds and the fluorinated bronzes

2.1 CHEMISTRY

All the compounds of the ternary systems were synthesized by solid state reaction between the elementary fluorides, by heating the mixtures in gold or platinum tubes in the range of temperature 700-850°C for one or two days. Table I summarizes the results obtained for the mixed valence compounds with the different alkali metals, the limits of x being determined from X-ray diffraction. It clearly shows that, whatever the system, the $\alpha$ and $\gamma$ phases exist when A is at least K. For lighter A atoms, either a definite compound appears (Li) or a very small amount of A is inserted in the host matrix (Na). In the medium range of composition the nature of the phase strongly depends on the size of A and on the nature of M (Jahn-Teller ion or not). Indeed, Fe and V exhibit the same sequence of phases, whatever the nature of the A ion. On the contrary, when M is chromium, the divalent ion $Cr^{2+}$, with a $d^{4}$ configuration correlated to the Jahn-Teller effect, induces a new phase without any similarity with the iron or vanadium phases. Note finally that it is very difficult to synthetize the non stoichiometric compounds for the highest values of x.

The phase diagram (Fig.2) has been established only for the system $KF - FeF_{2} - FeF_{3}$ [16] by DTA measurements. It first confirms the room temperature composition ranges. In the $FeF_{3}$-rich zone ($x < 0.25$), one observes first the phase transition rhombohedral - cubic of $FeF_{3}$ at 410°C. In the range $0.08 < x < 0.25$, two reversible invariants are observed at 814 and 952°C, unexplained up to now. As the thermal effect is maximum for $x = 0.125$, one could conclude either the formation