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GRAPHITE INTERCALATION COMPOUNDS OF d-TRANSITION METAL FLUORIDES

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Among the graphite intercalation compounds (GIC) containing fluorinated species in appreciable amounts, only a few examples based on transition metal fluorides are available. The intercalation of such materials has been investigated, namely TiF_4, RuF_5 and OsF_5 for the 3d, 4d and 5d series, respectively.

TiF_4 is obtained free from traces of oxide fluoride by sublimation at 250°C under 1 bar fluorine pressure in a thick-walled nickel reactor. RuF_5 and OsF_5 are prepared in the same type of container by fluorination of the corresponding metal at about 200°C under 5 bar fluorine pressure.

The intercalation of TiF_4 in graphite takes place at 250°C under fluorine pressures of several bar. A second stage compound is obtained with a interlayer spacing $I_c \simeq 11.35$A = 4.65 + (2 x 3.35) Å. This value could be consistent with the presence of TiF_6 octahedra oriented with a three-fold axis perpendicular to the graphite layers. The compositions correspond to $C_{10-15}TiF_{5.3}$.

RuF_5 and OsF_5 intercalate at lower temperatures (70-150°C) by interaction of the gaseous pentafluoride with graphite. The resulting materials correspond essentially to first stage compounds with gallery spacing $I_c \simeq 8.42$ Å = 5.07 + 3.35Å. Precession photographs have shown, besides the graphite lattice, the presence of several hexagonal sublattices.

The in-plane electrical conductivities have been measured using the contactless method. The materials exhibit a metallic behavior. A strong variation of resistivity occurs for the RuF_5-GIC at about 120K, which is associated with a hysteresis. This behavior could be due to an order-disorder transition within the intercalated fluoride layers.