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CRYSTAL STRUCTURE, SPECTROSCOPIC AND MAGNETIC INVESTIGATION OF $CuWO_3F$

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The crystal structure of the copper-tungsten oxyfluoride $CuWO_3F_2$ has been determined from single crystal X-ray data. The symmetry is monoclinic ($P2_1/m$) with lattice parameters a = 5.223 Å, b = 9.599 Å, c = 3.670 Å and ß = 106.26° (Z=2). The structure has been fixed by the heavy atom method and refined by least square calculations down to R = 0.019. The lattice is built up of chains of trans-corner sharing WX_6 (X=O,F) octahedra along the c axis direction ; the Cu atoms being located between these chains in a (4+2) octahedral coordination. They also form chains of edge-sharing octahedra. Oxygen-fluorine ordering has been determined by several methods : Raman spectroscopy, electrostatic energy calculations and bond valence determinations. The structural formulation of the octahedra is $(WO_2F_2O_{2/2})^{2-}$.

Diffuse reflectance spectrum and ESR spectroscopy allowed us to confirm an ordered surrounding around the copper atoms.

The different values of Δ_1 ($^2B_{1g} \rightarrow {}^2B_{2g}$) = 11700 cm^{-1}, Δ_2($^2B_{1g} \rightarrow {}^2E_g$) = 13300 cm^{-1} ($g_\perp$ = 2.09 and $g_{//}$ = 2.48) lead to two covalency parameters in the copper elongated octahedra $k_{//}$ = 0.92, $k_\perp$ = 0.85 confirming that the two long bonds are Cu-F bonds. The four remaining bonds are two Cu-O and two Cu-F bonds.

The magnetic susceptibility curve was fitted by using a classical S = 1/2 Heisenberg antiferromagnetic chain and yields the exchange integral J/k = -5.7 K. The different magnetic exchange pathways are discussed.