Ordre magnétique dans des spinelles à propriétés thermoélectriques

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Abstract

This thesis focuses on the study of spinel materials based on iron and chromium sulfides, such as $FeCr_2S_4$. The main objective is to investigate the effects of cationic substitutions of Fe by Cu and Cr by V on the structural and magnetic properties. ^{57}Fe Mössbauer spectroscopy was used as a local probe of the chemical and magnetic environment of iron. For the cubic spinel $FeCr_2S_4$, which is ferrimagnetic, iron is primarily located on tetrahedral sites in the form of Fe^{2+} ions. A quadrupole effect induced by spin-orbit coupling was observed at temperatures below the Curie temperature of 176 K, accompanied by a decrease in the mean hyperfine field below 80 K, indicating a transition to a helical magnetic state. The compound $Fe_{0.5}Cu_{0.5}Cr_2S_4$ exhibits a mixed valence of iron on tetrahedral sites, with a higher magnetic moment due to the presence of Fe^{3+} ions in addition to Fe^{2+} ions. Its transition temperature above room temperature (Tc = 330 K) makes it a promising candidate for magnetocaloric applications, although its maximum magnetic entropy variation and relative cooling power values under 5 T are lower than those of $FeCr_2S_4$. The antiferromagnetic behavior of the monoclinic spinel FeV_2S_4 is confirmed with a Néel temperature of 133 K. In this material, a cationic distribution of Fe^{2+} ions was quantified on the two sites intercalated between hexagonal compact sulfur layers, with a higher mean hyperfine field observed in the metal-deficient layers. The sample $FeVCrS_4$ predominantly exhibits a monoclinic structure with a minor cubic phase similar to $FeCr_2S_4$. Mössbauer analysis indicates that approximately 20% of iron ions belong to this cubic phase, which is responsible for the observed ferrimagnetic behavior. The magnetocaloric properties of $FeVCrS_4$ are inferior to those of the compound single-phase $FeCr_2S_4$, confirming that the latter remains the most promising compound for magnetocaloric applications