Anomalous magnetic behavior in electrodeposited chromium thin films

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Metallic chromium exhibit three different magnetic phases: paramagnetic phase (P) above the Néel temperature (T_N = 311 K), transversal antiferromagnetic phase characterized by a spin density wave with transversal polarization (AF_1) and spin-flip temperature (T_{SF} = 123.5 K) and longitudinal antiferromagnetic phase characterized by a spin density wave with longitudinal polarization (AF_2) bellow T_{SF}. Although metallic chromium has been extensively investigated in the last 40 years[1], several doubts concerning its magnetism remain unexplained. The preparation of thin electrodeposited films of chromium was not investigated considering its magnetic properties. Therefore, in this paper we show the magnetic properties of chromium thin films prepared electrochemically.

Thin films of chromium were prepared from a 2.5 M CrO_3 in 0.026 M H_2SO_4 aqueous solution on copper sheet (A=1.0 cm^2). As reference and counter electrodes were used a SCE electrode and two Pt plates (A = 1.0 cm^2 each). The samples were prepared at constant potential at E = -1.7 V for different times. This procedure were carried out in a potentiostat mod.283 (EG&G PARC) with the M270 software. The magnetic measurements were carried out using a MPMS5-5 SQUID magnetometer (Quantum Design).

The magnetic behaviour obtained for the electrodeposited chromium thin films are presented in Figures 1 and 2. Figure 1 presents the magnetization, M, as function of the magnetic field, H, for the sample prepared in this work. The insert in this figure show the ~~It is presented also as an insert, the~~ MxH curve for bulk chromium single crystal sample. As can be seen in this Figure, there are important differences between the electrodeposited and bulk samples. The expected behaviour for chromium is a linear behaviour up to 120 kOe[1] that one observed in the insert. Nevertheless, the electrodeposited sample prepared in this work have a different behaviour, showing a typical superparamagnetic behaviour..

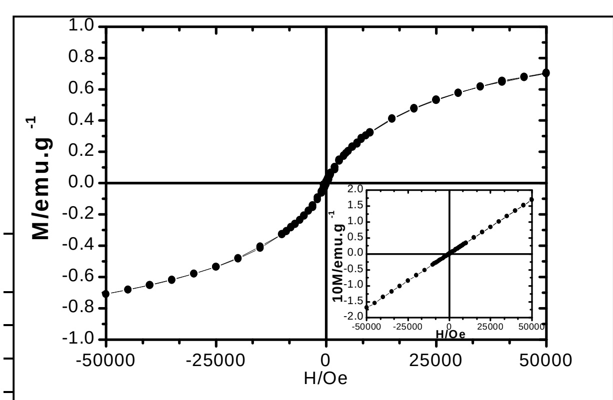

Figure 1: MxH curve for the electrodeposited sample and a bulk single crystal sample (insert). T = 1.8 K.

Figure 2 presents the magnetization as function of the temperature for the electrodeposited and bulk chromium single crystal samples (insert). In this case also there is an important difference between the magnetic behaviour of the samples. As observed in Figure 1, the magnetic behaviour of the bulk sample is that one expected for chromium. Otherwise the observed behaviour for the thin electrodeposited films was theoretically predicted for chromium powder [2,3]. In this case, each particle behaves like as a ferromagnetic particle non interagent and independent leading to a surface ferromagnetism[2,3]. Our electrodeposited thin films have a granular nature. The possibility of contamination can be ruled out by chemical analysis, using absorption spectroscopy and XPS. From the results obtained using XPS coupled with ion beam, in order to investigate the sample composition at different depth, it was detected the presence of Cr^{3+} related to chromium oxide and chromium hydroxide. Therefore, one proposition to explain our results is that the granular structure of the electrodeposited film are associated with a surface ferromagnetism due to the non interacting nature of each grain. This non interacting nature could be related with the presence of oxide or hydroxide on the surface of each grain. This behaviour, macroscopically leads to a superparamagnetic behaviour which is well characterized in Figures 1 and 2. The tendency of saturarion (Figure 1) and the irreversibility of the ZFC and FC curves are both signature of superparamagnetism. Finally, the magnetization value, one order higher than the expect one (Figure 2) is also a mark of superparamagnetism behaviour.

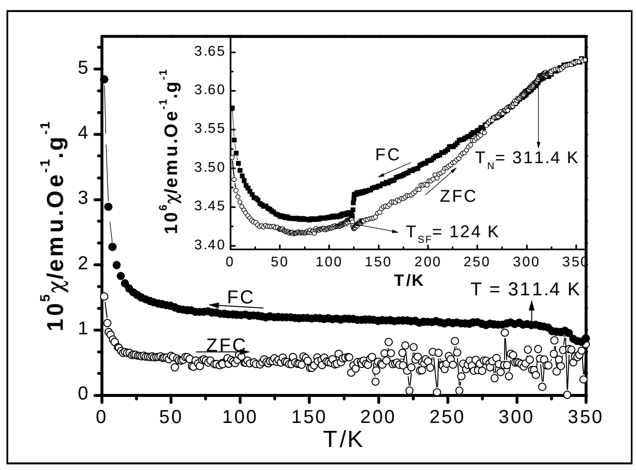

Figure 2: MxT for the electrodeposited sample and bulk monocrystalline sample (insert). H = 1000 Oe.

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