MAGNETIC PROPERTIES OF THE SPINEL COMPOUND $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$.

Résumé

Les propriétés magnétiques du composé spinelle $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ ont été étudiées par des mesures magnétiques. Les mesures en champs statique (DC) montrent l'établissement d'un ordre ferromagnétique-réentrant spin-glass. La frustration géométrique est introduite à travers les interactions antiferromagnétiques dues à la substitution de Cr magnétique aux atomes Zr, dans le sous réseau B. La magnétisation mesuré après un refroidissement sous champ magnétique (FC) et refroidissement sans champ magnétique (ZFC) sont irréversible à T≤ T_f, la température de Curie moyenne, le moment effectif et le domaine de température dont lequel la susceptibilité peux être linéaire sont établies.

<u>*Mots clés*</u>: $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$, comportement verre de spin et mesures DC.

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Abstract

The magnetic properties of the spinel compound $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ have been studied using, magnetic measurements. These measurements (DC) reveal that $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$, orders ferromagnetically-re-entrant spin-glass. The geometrical spin frustration is introduced through antiferromagnetic interactions due to the substitution of magnetic Cr for Zr atom, on the B sites forming a network of linked tetrahedral. The magnetization in field-cooled (FC) and zero-field-cooled (ZFC) are observed with irreversibility in T≤ T_f, the overage Curie temperature, the effective magnetic moment and the temperature range, for which magnetic susceptibility can be regarded as linear are given.

<u>Keywords</u>: $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$, Spin glass behaviour and DC measurements.

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<u>ملخص</u>

تمت دراستها بواسطة قياسات مغناطيسية $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ الخواص المغناطيسية للمركب القياسات في وجود حقل مغناطيسي مستمر تبين ظهور ترتيب فيرومغناطيسي داخلي-سبين الزجاج. الفروستراسيو الهندسية عرفت من خلال الانتيفيرومغناطيسية الراجع الى انغراس ذرات الكروم المغناطيسية الى ذرات الزركونيوم في الموظع الرباعي لتحت الشبكة - ب. نلاحظ انعكاس المغنطة في وجود الحقل مغناطيسي و غيابه. العزم المغناطيسي و مجال درجات الحرارة التي من اجلها السماحية المغناطيسية خطية تم تحديدهم

<u>الكلمات المفتاحيــــة</u> : $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ ، سبين الزجاج و القياسات DC

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Introduction

The cubic spinel structure is one of the most frequently encountered structure types among transition metal compounds of stoichiometry AB_2X_4. The spinel structure is described by space group Fd3m with tetrahedrally coordinated A sites and octahedrally coordinated B sites as shown in Figure 1.
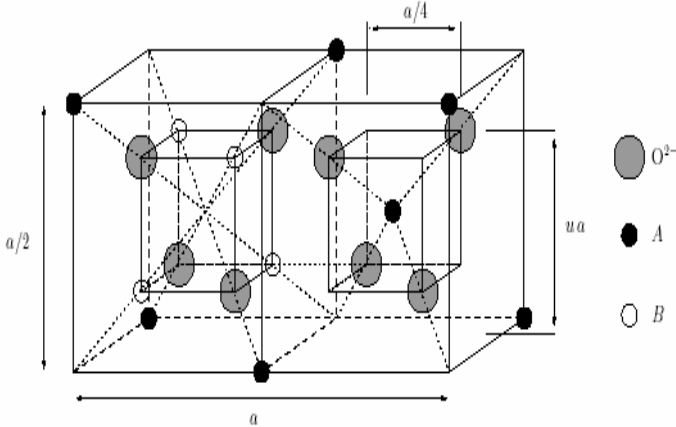

Figure 1: spinel structure

It is well known that the B-site ions from a pyrochlore lattice with inherent strong frustration for the nearest-neighbor antiferromagnetic interactions. Geometric frustration denotes inability of a system to satisfy all pairwise interaction [1]. The spin-glass states arises from an underlying frustration in the magnetic interactions between localized magnetic moments which are trying to order magnetically and exists below a certain freezing temperature T_f. The frustration may be due to completing ferromagnetic and antiferromagnetic exchange interactions or from purely topological effects when the interactions are predominately antiferromagnetic. In principle, both magnetic metals and insulators (or semiconductors) can exhibit spin-glass behavior, and several examples have been found of both classes of materials. In the pseudo-binary systems $CuCrS_2$- MS_2 (M = Ti, Zr, Sn), spinel phases CuCrMS have been observed. Their homogeneity is wide: for y = 1, the Cu ions fully occupy the tetrahedral A sites, whereas magnetic Cr^{3+} and diamagnetic M^{4+} ions are distributed on the octahedral B sites. X-ray diffraction did not show any ordering to occur between Cr^{3+} and M^{4+} remain located on the B sites. For y > 1, the non-stoichiometry mechanism has not yet been elucidated. It has been showed that susceptibility measurements, performed from 10-300K, showed the nature of the M metal and on the stoichiometry. The systematic studies relating to $M^I_y M^{III}_y M^{IV}_{2-y} X_4$ series (M^I = Cu, M^{III} = In, Y,…, M^{IV} = Zr, Sn, Ti, X = S, Se), having the spinel structure, were initially concerned compounds families, where the octahedral sites accommodated couples of elements, not carrying a magnetic moment;

then, it was interesting to bring the chromium, in order to introduce magnetic couplings [2]. The great flexibility of substitution which characterizes this type of system, encouraged us to bring on the B sites: chromium (trivalent element), and zirconium (tetravalent element). The difference in size of the concerned elements, combined with the differences in electronegativity, would not fail to influence the magnetic properties; via the orbital covering of the surplus spinels samples obtained $Cu_yCr_yZr_{2-y}Se_4$ [3,4]. The magnetic properties of the spinels structures are related to the nature of the metal cations of the structure, and to their distribution on the two types of octahedral and tetrahedral sites: by magnetic order or magnetic dilution [5]. The spinel $Cu_{1.30}Cr_{1.30}Zr_{1.70}Se_4$ presents the crystallographic characteristic to have CrIII and ZrIV to share the octahedral B sites: 16d of Fd3m space group [6], with an occupancy rate function of the composition.
In this communication we report a study, on the magnetic properties of $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$, using magnetic measurements.

2. Experimental

The present sample is obtained by heating, according to the stoichiometric ratio, a mixture of high purity powders of the elements, and sealed into evacuated quartz ; this method leads to a better homogeneity than a starting mixture y $(CuCrSe_2)$ + (2-y) $ZrSe_2$. A progressive rise by stages until 900°C with an agitation for 500°C of the tubes vacuum lefted, it is necessary to be followed with 900°C of a crushing of the obtained powders pouting again in tubes under vacuums carried 5 days at 950°C, and followed of an open furnace stop. A single cubic spinel phase is obtained the lattice parameter is 10.6076 (2) Å for y = 1.30 (value obtained through high-angle reflexions [6]). The DC-magnetic investigations were performed with a Quantum Design MPMS-5 SQUID magnetometer in a temperature range 2-300 K. For the zero-field cooled (ZFC) experiments the sample was cooled down to 2 K and a constant field was applied during the warm up scan. Corrections of the data taken were made for the nacelle contribution $\chi_{corrected} = (\chi_{mesured} - \chi_{nacelle}) / H_0. m_{sample}$.

3. Results and discussion

The magnetic properties of the $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ phase is interpreted from those of the chalcogenide $M^{II}Cr_2X_4$ (M^{II} = Cu, Fe, Zn, Cd, Hg, ½ (Cu + In) et X = Se, S), which have spinel structures, and were the subject of a lot of studies [7, 8, 9, 10, 11]. The important issue in the chalcogenide spinels is the valence states of the elements. The question on the valency of Cu in CuM_2X_4 (M = transition metal element; X = S, Se, Te) has been a longstanding problem. Goodenough said that the Cu state corresponds to the divalent one, while Lotgering et al claimed it is monovalent and $CuCr_2S_4$ should be written as $Cu^+(Cr^{3+}Cr^{4+})S_4^{-2}$ [12,13,14]. Several experiments give different results. Core-level X-ray photoemission spectroscopy (XPS), X-ray emission spectroscopy, and

the Cu K-edge X-ray absorption spectroscopy (XAS) measurements on CuM_2X_4 (M = V, Cr, Rh, Ir, X = S, Se) suggested that the Cu ions are monovalent [15, 16, 17, 18]. Cu^+ $(Cr^{3+}Cr^{4+})$ S_4^{-2} has for the magnetic contributions: Cr^{3+} $(3d^34s^0)$ ion with $3\mu_B$, Cr^{4+} $(3d^24s^0)$ ion with $2\mu_B$, the Cr moments being parallel to each other. So for $CuCr_2S_4$ the magnetic moment is $5\mu_B$ per formula. Then the ferromagnetic ground state of $CuCr_2S_4$ can be explained in terms of the double exchange interaction between Cr^{3+} and Cr^{4+} ions. But NMR, neutron diffraction, and magnetic studies suggested that experimental results [19, 20, 21, 22], could be interpreted with Cu^{2+} ions, $Cu^{2+}Cr_2^{3+}Se_4^{2-}$ with two Cr^{3+} ions, with three spin up electrons in 3d $(3d^34s^0)$, and Cu^{2+} $(3d^94s^0)$ ion having a $1\mu_B$ moment in the opposite direction. So, the formula unit of $CuCr_2S_4$ has for magnetic moment: $5\mu B$ [23]. In the ideal $CuCr_2S_4$ spinel structure, the Cu^{2+} ions are localized on the Td sites (A), and Cr^{3+} on Oh (B) sites. The ferromagnetic character prevails when A sites are occupied by copper. No systematic investigations of the magnetic properties of $CuCrZrSe_4$ have been reported in the literature. The $CuCrZrSe_4$ formulation is deriving from $CuCr_2Se_4$, substituting Cr by Zr. The magnetic properties of $CuCr_2Se_4$ samples corresponding to the $CuCr_2X_4$ (X = S, Se) formulation militate in favour of CrXCr positive interactions, which means that the superexchange via X anion overrides the direct exchange Cr-Cr. Moreover, the mixed valence model of $CuCr_2Se_4$ should have similar electronic states and physical properties as those of $CuCr_2S_4$, since Se is just below S in the periodic table as discussed above.
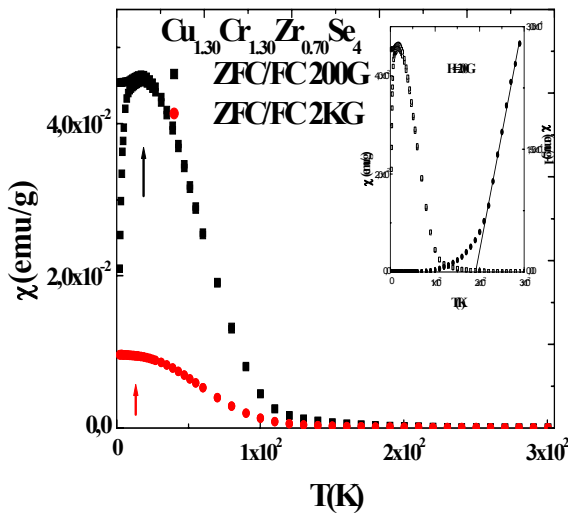
cooled from 300 to 5 K in zero magnetic fields and the field is turned on just before the measurement starts, whereas in an FC measurement the field is switched on when the compound is paramagnetic before being cooled. The susceptibility χ_{DC} is fitted using a modified Curie-Weiss law $\chi_{DC} = C / (T-\theta) + \chi_0$, where χ_0 is the temperature-independent term, C is the Curie constant with a value of 1.55 K emu mol-fu^{-1} and θ is the Weiss temperature. The χ^{-1} shows a straight line as in inset of Figure 2, positive average Curie temperature $<\theta_p> = 172.8$ K indicates ferromagnetic couplings between the Cr ions, and gives respectively for H = 200 G, and 2 KG an effective magnetic moment corresponding to $\mu_{eff} = 3.83\mu_B$, and $3.46\mu_B$/Cr-atom.

It is interesting to compare the $CuCrZrSe_4$ and $CuCrZrS_4$ magnetic properties. If the Cu ions are in a divalent state (S = 1/2), their moments being antiparallel to Cr spins lead to ferrimagnetic couplings. But the magnetic measurements show that all the Cr ions possess a localized magnetic moment (S = 3/2), while Cu, Zr and Se ions have no magnetic ones. These experimental results indicate strongly that the Cu ion valence state is Cu^+ and that Zr is tetravalent (Zr^{4+}), the both being non-magnetic; this is in agreement with our results. In addition, an irreversibility between the ZFC and FC branches appears below T = 5 K. The ZFC and FC curves exhibit a maxima around 12 K. At low temperatures, the magnetization of $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ is strongly dependent of its cooling history. Figure 3 shows the ZFC and FC susceptibilities between 5 and 24 K, and the difference between FC and ZFC magnetization, above 5 K, at 200 G and 2 KG: they decrease when the external magnetic field is increasing; this behaviour corresponds to a re-entrant spin glass one from the ferromagnetic state.
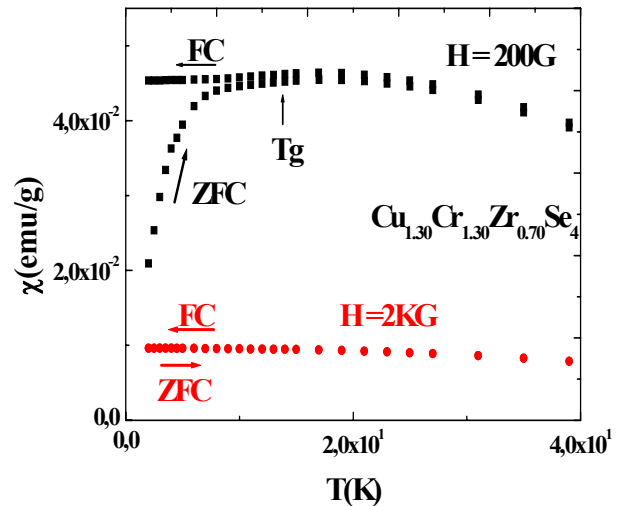

Figure2: Temperature dependence of the susceptibility of $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ in zero DC (ZFC) and in DC field H = 200 G, and 2 KG (FC). The inset shows the inverse magnetic susceptibility. The straight line is the Curie-Weiss law.

Figure 3: As for Figure 2 but for temperature between 5 and 24 K.

Figure 2 shows the temperature dependence of ZFC and FC susceptibility of $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ in an applied fields H = 200 G, and 2 KG. For ZFC the compound is

It is found near the phase boundary between the spin glass phase and the ferromagnetic phase: as the temperature decreases from higher temperatures, magnetizations increase, then stops at a lower temperature. At the end,

the spin glass state is obtained. The field dependence of the magnetization of $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ is presented on Figure 4 for selected temperatures. Below T = 5 K, the magnetization exhibits a narrow hysterisis phenomena without any saturation up to 25000 G. This excludes a ferromagnetic ordering for $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ at low temperature.
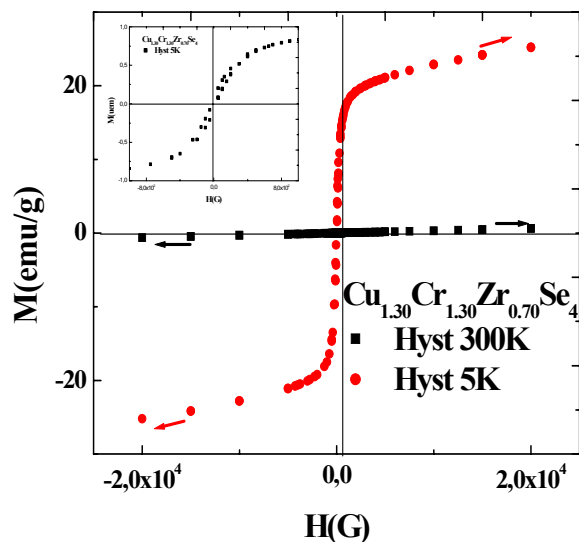

Figure 4: Field dependence of magnetization of CuCrZrSe$_4$. The inset shows the field dependence of its magnetization measured at T = 5 K.

Re-entrant spin-glass transition is initially the phenomenon, at first it was considered as a phase transition which is characterized by ferromagnetic clusters. Because at low temperatures the spin glass phase is composed of ferromagnetic clusters. In the ferromagnetic phase, although the spin arrangement is considerably modulated, a ferromagnetic spin correlation extends over the lattice. The breakdown of ferromagnetism and the re-entrant transition to the spin-glass phase in CuCrZrSe$_4$ takes place in the dilute ferromagnetic system based on the ferromagnet CuCr$_2$Se$_4$ particularly it originates from the random weak links of disordered clusters resulting from dilution and geometrical frustration. The long-range ferromagnetic order is depressed for the diluted system. This re-entrant behaviour may be found only in restricted Zr concentration region around the freezing temperature T_f = 5 K. In general, spin-glass freezing originates from the frustration of the magnetic interaction in the system. The Cr^{3+} anions in CuCrZrSe$_4$ have a tetrahedral network with each Cr^{3+} anions. When the interaction between Cr^{3+} anions is antiferromagnetic, the tetrahedral network causes strong geometrical frustration in the system. This is similar to behaviour in the pyrochlore crystal structure.

CONCLUSION

In conclusion, the spinel compound $Cu_{1.30}Cr_{1.30}Zr_{0.70}Se_4$ has been studied with magnetization measurements. CuCrZrSe$_4$ was obtained by substituting half of Cr by Zr in a known chalcogenide spinel CuCr$_2$Se$_4$. On the other hand, the experimental results clearly indicate that CuCrZrSe$_4$ exhibits a ferromagnetic transition in which the positive average Curie temperature $<\theta_p>$ = 172.8 K. In addition a successive magnetic transition suggesting re-entrant spin glass observed at the temperature T_f = 5 K

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