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An electrochemically reduced graphite-cobalt compound : synthesis and magnetic study

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Résumé. — Quand on l'utilise comme cathode dans une pile au lithium, le composé intercalaire du graphite CoCl_2 est réduit pendant la décharge. Cette réaction conduit à la formation d'un nouveau composé du cobalt qu'on a caractérisé par une analyse chimique et aux rayons X. Aux basses températures, ses propriétés magnétiques sont celles d'un verre de spin. La comparaison avec le composé intercalaire à deux dimensions CoCl_2 montre beaucoup de similitudes.

Abstract. — When it is used as a cathode material in a lithium primary battery, graphite intercalation compound with CoCl_2 is electrochemically reduced during the discharge process. This reaction leads to the formation of a new Co-graphite compound which is characterized by chemical and X-ray analysis. The magnetic properties exhibit a spin-glass behaviour at low temperature, due to the islandic character of the compound. Similarities with the 2-dimensional CoCl_2 compound are also found.

1. Introduction.

Though it is known that graphite reacts with most alkali, earth alkali and some rare earth metals to form the so-called graphite intercalation compounds (G.I.C.) [1], no evidence has been reported concerning direct intercalation of transition metals into graphite. One of the reasons could be the very high temperature needed for such a reaction to reach a sufficient metal vapour pressure. This could rather lead to metal-carbides formation than G.I.C.'s. Only indirect preparation methods have been described by many authors mostly consisting on a chemical [2-7] or electrochemical [8-10] reduction of the transition metal chloride-G.I.C. Bragga *et al.* [11] used KC_8 as reducing agent in a THF-metal chloride solution and could, according to them, reach first stage graphite-metal compounds. Stage s denotes the number of graphite layers between two successive metal layers. The other reduction preparations mostly lead to many phases mixtures including free metal, free graphite and more controverted graphite-metal G.I.C.

formation [12]. Graphite-iron compound remains the most studied compound. Touzain *et al.* [9] proposed a structural model and showed some magnetic and Mössbauer measurements for an electrochemically prepared iron-G.I.C.

This study deals with cobalt-G.I.C. preparation and magnetic properties. Many authors reported magnetic measurements on CoCl_2 -G.I.C. [13-16]. Very recently Elamy *et al.* [17] showed the field dependence of the in plane susceptibility for different intercalation stages. They compared their results to a two-dimensional planar XY model and obtained a good qualitative agreement with their susceptibility measurements.

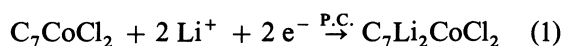
Concerning the reduced transition metals-G.I.C., magnetic properties, only few data have been reported especially on iron-G.I.C. [6, 9]. Recently, Inagaki *et al.* [18] presented the saturation magnetization measurements performed on a ternary Co-THF-graphite compound obtained by the Bragga *et al.* method [11]. Assuming that most magnetic properties are directly dependent on the sample preparation methods, the only significant comparisons we can give in this study concern the original CoCl_2 -G.I.C. before reduction as reported by Elamy *et al.* [17].

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2. Experimental results.

2.1 PREPARATION AND CHARACTERIZATIONS. — Original first stage CoCl_2 -G.I.C. was prepared by treating a natural celanese graphite/ CoCl_2 (molar ratio 4 : 1) mixture at 610 °C during 24 h in a quartz sealed tube containing chlorine under an estimated 3.5 atmospheres Cl_2 pressure at the reaction temperature. The compound was then washed with ethanol and dried under vacuum. X ray analysis gives a characteristic first stage diagram with $I_c = 9.5 \text{ \AA}$ as 001 periodic distance. Chemical analysis gives C_7CoCl_2 as average formula.

As reported in a previous publication [19], the use of this G.I.C. as positive electrode in a primary organic lithium battery leads to the electrochemical reduction during the discharge following the reaction



where P.C. denotes the propylene carbonate used as electrolyte solvent which intercalates during the reduction (Li^+ solvation).

P.C. is removed from the final reduced compound $\text{C}_7\text{Li}_2\text{CoCl}_2$, P.C. by washing it with acetonitrile and then with distilled water.

In table I we report the indexation of the Debye-Scherrer diffractogram performed on the final washed compound. One can note the presence of mixture of many phases attributed to Co-G.I.C. first and second stages, free graphite, α -cobalt and LiCl. As far as the Debye-Scherrer diffraction pattern can show, there is no evident presence in the reduced compound of any quantitative amount of the initial C_7CoCl_2 . The strongest 002 ray at 4.75 Å completely disappears after the electrochemical reduction and the successive washing operations. In the formula $\text{C}_{22}\text{CoLiCl}$, deduced from the chemical analysis,

Table I. — Indexation of the Debye-Scherrer diffractograms of the final compound.

Intensity	d_{mes}	Indexations				
		C-Co Stage I	C-Co Stage II	G	α -Co	LiCl
m (medium)	5.54	001	002	002		111
w (weak)	4.38					
S (strong)	3.35	002/100				
S	2.97					
w	2.8					200
v.w. (very weak)	2.7					
m	2.57		004			
m	2.29					
w	2.12				100	
m	2.02				002	
w	1.9	003 ?			101	220
m	1.82					
m	1.77		005			

we attributed the presence of chlorine to LiCl rather than to CoCl_2 , as shown in the indexation table I. We did not notice any free CoCl_2 precipitated as inclusion compound or outside the graphite layers (absence of the characteristic CoCl_2 diffraction rays). We used about 20 % more than 250 mAh needed to reduce 1 g of C_7CoCl_2 , so the reaction efficiency must be very close to 100 % even if we take into account the chlorine excess met in some samples composition as $\text{C}_7\text{CoCl}_{2.1}$ (Chemical analysis leads to the formula $\text{C}_{22}\text{Co}(\text{LiCl})$). That shows the cobalt impoverishment during the reduction reaction (CoCl_2 dissolves into P.C.) and the washing operations. α -Co and LiCl rays do not completely disappear even after a long-time-washing in a molar or fuming HCl solution and with distilled water. One can suppose their existence as inclusion compounds within the graphite structure [1].

The corresponding periodic distances for first and second stage are $I_{c1} = 5.53 \pm 0.05 \text{ \AA}$ and $I_{c2} = 8.9 \pm 0.1$. I_{c1} is lower than the value reported by Vol'pin *et al.* [5] (5.8 Å).

2.2 MAGNETIC PROPERTIES. — We have measured the magnetization of the sample as a function of magnetic field and temperature. The specimen was a powder ($m \cong 0.045 \text{ g}$) contained in a very pure copper sample holder in order to minimize the magnetic contribution of the container and to insure a good thermal contact. The measurements were made using a vibrating pick-up coil apparatus with a sensitivity of $3 \times 10^{-4} \text{ emu}$. The thermometer is a carbon resistor for $T \leq 30 \text{ K}$ and a 100 Ω platinum resistor for $T > 30 \text{ K}$. The temperature is known with a precision better than 20 mK over the whole range.

Figure 1 shows the magnetization measured at 4.2 K in an external maximum field of 10 T.

- i) In zero field a remanent magnetization exists.
- ii) In low fields ($H \lesssim 0.2 \text{ T}$) the magnetization increases rapidly and the $M(h)$ curve exhibits a strong curvature.
- iii) In high fields no saturation appears.

In figure 2 we have reported the magnetization $M(T)$ measured in different fields (50, 100, 200, 300, 1 690 Oe) as a function of temperature after cooling in zero field and heating in the field indicated above. All the five curves pass through a maximum at a temperature T_0 which is field dependent (Table II), the higher the field the lower T_0 . It should be also noticed that the maximum around T_0 becomes sharper when the field is decreased.

Above $T_c = 14.7 \text{ K}$, $M(T)$ obeys the following relation,

$$M(T) = \frac{C \cdot h}{T - T_c} + (M_0 + \chi_0 h). \quad (1)$$

For the highest field ($h = 0.169 \text{ T}$) this formula has been tested in the range 15 K-200 K.

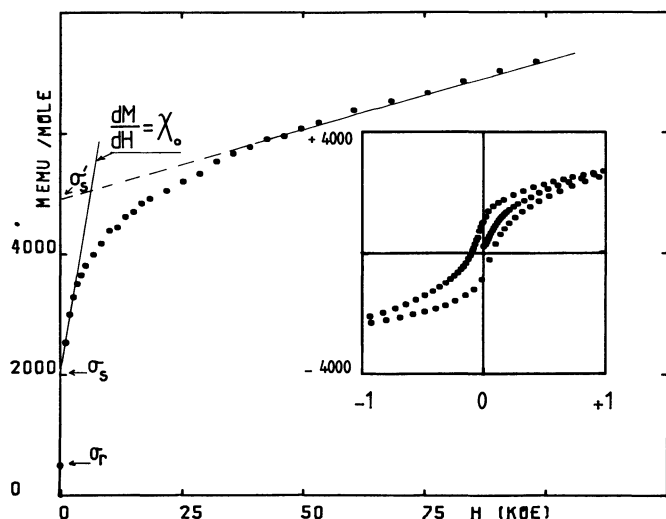


Fig. 1. — Magnetization $M(h)$ at 4.2 K up to 10 tesla. Insert shows a typical hysteresis loop obtained between -1 kOe and $+1$ kOe at 4.2 K. Also shown is the way of obtaining σ_s by extrapolating the curve with the slope χ_0 . Note that σ_s is not the remanent magnetization and χ_0 is not the initial susceptibility.

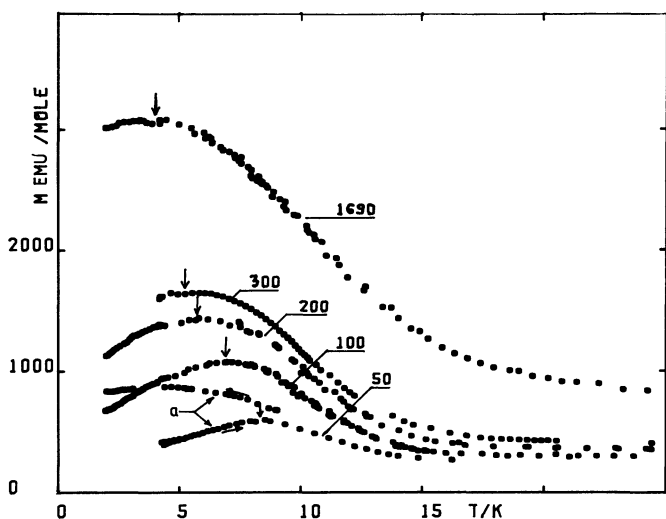


Fig. 2. — Magnetization $M(T)$ up to 30 K for different applied fields : 50 Oe, 100 Oe, 200 Oe, 300 Oe, 1 690 Oe. The curve (a) shows the thermal hysteresis observed when the sample is cooled under field. The arrows indicate the position of T_0 .

Table II. — Influence of the applied field on the temperature T_0 of the maximum M_{\max} of the magnetization.

Measuring field/Oe	T_0 /K	M_{\max} emu/mole
50	8.45	600
100	7.00	1 072
200	5.8	1 443
300	5.3	1 665
1 693	4.0	3 076

The first term is attributed to magnetic species whose Curie constant is $C = N_0 \mu_{\text{eff}}^2 / 3 k_B$ (k_B Boltzmann's constant, N_0 Avogadro's number, μ_{eff} effective moment), $C \cong 0.685$ uem/mole according to the formula $C_{22}\text{Co}$, LiCl for the compound. We find $\chi_0 = 0.465$ emu/mole and $M_0 = 254$ emu/mole. Attributing the term $\chi_0 \cdot h$ to the non magnetic atoms, or to the non saturated ones, one can deduce the saturation magnetization σ_s of the magnetic ones by extrapolation to zero of the magnetization $M(h)$ with the slope $\frac{dM}{dh} = \chi_0$ (see Fig. 1). One has $\sigma_s \cong 2\,000$ emu/mole. Note that σ_s , on the figure 1, is not the remanent magnetization which is much smaller and χ_0 is not the initial slope.

Writing the classical formulae $\mu_{\text{eff}}^2 = g^2 \mu_B^2 S(S+1)$, $\sigma_s = N_0 g S \mu_B$ where g is the gyromagnetic factor ($g = 2$), μ_B the Bohr magneton and S the spin of the magnetic species, we deduce,

$$C/\sigma_s = \frac{g\mu_B}{3k_B} (S+1) \quad \text{and} \quad S = 6.6.$$

This value which is much higher than the spin of bulk cobalt [20] ($S \cong 1$) proves that the magnetic properties are due to clusters of cobalt atoms. It is in fact an average value calculated over a number of clusters of various sizes. The temperature ($T = 4.2$ K) at which σ_s is obtained is not very low compared to T_c . If determined at $T \ll T_c$, σ_s would probably be higher. However the ratio C/σ_s would still lead to a high value of S .

It is worth noticing that the saturation magnetization σ_s deduced from the highest fields ($5\text{ T} \lesssim h \lesssim 10\text{ T}$) leads to an average moment per cobalt atom of $0.9 \mu_B$ less than the average moment of bulk cobalt. Thus we can have a simple picture of the compound : it is an assembly of clusters of cobalt atoms magnetically coupled of various sizes. When the magnetic field is increased one saturates clusters of decreasing sizes and finally in field greater than 10 T almost all the cobalt atoms are aligned in the external field. However it is clear from the magnetization curve that some mechanism prevents the complete alignment of the spins in high fields. This can be antiferromagnetic interaction, anisotropy, or spin canting [21].

The quantity M_0 in formula (1) may be attributed to a small amount of bulk cobalt. The concentration can be evaluated to approximately 2 at. % by comparing M_0 to the saturation magnetization of bulk cobalt. Another important feature is observed : if the sample is cooled below a given temperature T_0 under a constant field, a strong hysteresis appears (Fig. 2a). The field-cooled magnetization is higher than the zero field-cooled one. This behaviour is characteristic of the freezing of magnetic species below T_0 . This is observed in spin-glasses and in assemblies of superparamagnetic clusters [22]. This is also observed in ferromagnets near T_c . But, here,

the value of $M(T_0)/h$ is much lower than the inverse of the demagnetizing factor indicating that we are not in the case of a « good » ferromagnet.

The hysteresis loop (insert of Fig. 1) is narrow and shows a very low remanent magnetization compared to the saturation. Such magnetic properties have their origin in the existence of a long range antiferromagnetic interaction associated with some disorder. The disorder is due to the random distribution of Co-clusters. One generally admits that when the sample is cooled, the spin-glass state forms from the highest temperatures by freezing a large number of states separated by potential barriers becoming infinitely high when T approaches T_0 [23]. These states are non ergodic and the transitions from one state to another are time-dependent. The relaxation time τ depends on the temperature T and the barrier height $W(T)$. This effect is shown on figure 3 where we have plotted the ac-susceptibility χ_{ac} in a very low ac field (< 1 Oe) as a function of temperature at various frequencies. The temperature $T_0(\nu)$ of the maximum obeys the law,

$$\frac{1}{\nu} = \tau_0 \exp[E_a/k_B(T_0 - T_\infty)]. \quad (2)$$

This law, known as Volger-Fulcher's law is an empirical extension of the Arrhenius law and is generally admitted as the characteristic of spin-glasses rather than assembly of fine particles [22]. The values we find for τ_0 and T_∞ ($\tau_0 = 10^{-6}$ s, $T_\infty = 7.5$ K) are physical, T_∞ being the lower limit for the spin-glass transition.

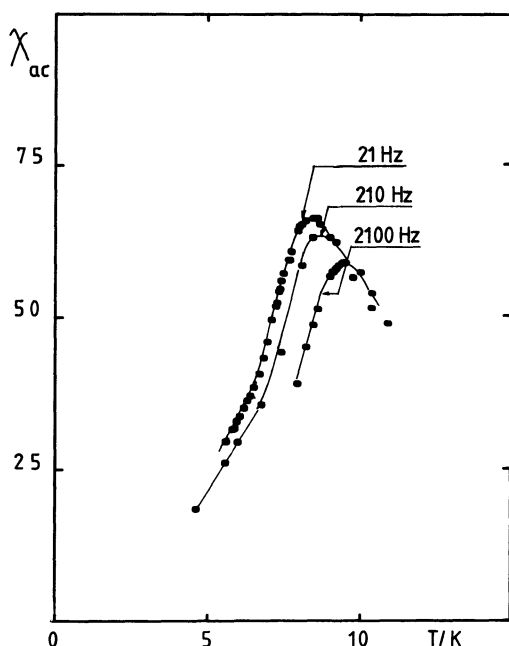


Fig. 3. — Effect of frequency on the susceptibility χ_{ac} (in arbitrary units).

The sensitivity to frequency, $\Delta T_0/T_0 \Delta \ln \nu$ is equal to 5×10^{-2} . This is of the same order of magnitude as in insulating spinelles [24] but an order of magnitude larger than in canonical spin-glasses CuMn or AgMn [22, 25]. This suggests a less cooperative freezing process in that case than in metallic spin-glasses [24]. A careful and extensive study of a wide variety of spin-glasses and glasses over several decades of temperatures show that the law $T_0(\nu)$ is a power law. No distinction between expression (2) and a power law is possible in a narrow range of temperatures.

It is interesting to compare our compound to other similar compounds. Among them, the CoCl_2 -G.I.C. has been extensively studied [17, 26, 27]. The magnetic susceptibility perpendicular to the c -axis shows a shoulder at T_{Cu} and a maximum at T_{Cl} . This structure can be resolved in two distinct peaks when the applied field is lowered. We have not observed such a behaviour, probably because our applied field (50 Oe) was too high. But the striking feature is that T_{Cu} , T_{Cl} and T_0 are exactly in the same range for CoCl_2 , G.I.C. and C_{22}Co , LiCl showing that in both cases the interactions are of the same order of magnitude. In CoCl_2 the islandic nature of the intercalent layers has been proved. Between T_{Cu} and T_{Cl} , the system is 2 dimensional and below T_{Cl} it becomes 3-dimensional. In the range $T_{Cl} \leq T \leq T_{Cu}$ a qualitative analysis following the Kosterlitz-Thouless [28] theory for XY systems is achieved although the experimental critical exponents do not agree with the theory. The main difference we have observed between CoCl_2 , G.I.C. and C_{22}Co , LiCl is the opposite variation of the temperature of the susceptibility maximum. In CoCl_2 , T_{Cl} increases with the field while in C_{22}Co , LiCl T_0 decreases showing that T_0 is not the onset of a ferromagnetic order.

We have found the empirical law $\frac{1}{T_0} = \frac{1}{T_M} + \alpha h^{1/2}$ up to $h = 1690$ Oe, with $T_M = 13.5$ K.

A more systematic study of the remanent magnetization vs. field, temperature and time would be necessary to get further informations on the spin-glass behaviour of the system. X-ray studies show that the final compound is a mixing of different stages. This leads to a distribution of the interplane Co-Co distances and to the formation of Co islands. Therefore, at this point of our study we think that C_{22}Co , LiCl is more likely an assembly of clusters having a spin-glass like behaviour than an homogeneous system exhibiting a phase transition.

3. Conclusion.

The new compound C_{22}Co , LiCl looks very much like a spin glass. The disorder which originates the spin-glass like behaviour than an homogeneous system character of the sample. Although the crystallographic structure and the chemical composition are quite diffe-

rent from those of the other compound C_7CoCl_2 [17, 26, 27] in its initial stages, many magnetic properties and characteristic temperatures are similar. It may be the indication that in both compounds the exchange interactions and thus the Co-Co distances are of the same order.

At the point of our investigation no conclusion can be drawn on the nature of this new spin-glass : is it two or three dimensional ? (independently of the well

established two-dimensional crystallographic structure). This cannot be decided on powdered samples.

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