Structural and Transport Studies for Ternary Graphite Intercalated Phases ($CoCl_2$, $AlCl_3$)

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Metal dihalide low-volatility is the major characteristic slowing down their intercalation into graphite (GICs: graphite intercalation compounds). An original synthesis using volatile heterocomplexes between metal dihalide ($CoCl_2$) and gaseous dimer Al_2Cl_6 increases strickingly $CoCl_2$ intercalation rate but entails cointercalation of significative amount of $AlCl_3$ in the compounds MGICs (mixture graphite intercalation compounds). Structural studies along *c*-axis, in plane and out the plane (3D stacking) display a similar behaviour as in the $CoCl_2$ containing binary compounds. Microstructural studies confirm the separation of $CoCl_2$ and $AlCl_3$ in distinct domains. Other ternary phases with alternate $CoCl_2$ and $AlCl_3$ layers and characterized by a similar $AlCl_3/CoCl_2$ ratio can be obtained using biintercalation method: (GBICs: graphite biintercalation compounds).

X-Ray diffraction shows that the biintercalation involves a complete lost of correlations in the successive $CoCl_2$ or graphite layers. Transport studies of ternary phases (MGICs and GBICs) display an anomalous behaviour as T is lowered below the magnetic ordering temperature T_c especially for in plane resistivity.

Introduction

The great number of studies dealing with metallic dihalides intercalated graphite is mainly explained by the large thermal stability of the different phases and by the good reproducibility of their structures. Moreover, their physical properties, especially magnetic [1], are closely related to those of the free reagent.

The main difficulty concerning the studies about these compounds comes from the low reactivity of the free halide versus graphite, requiring extremely long reaction times and generally high temperatures (5 weeks, T > 500 °C). Another synthetic method, already developed by Stumpp [2], relies on the existence of a gaseous heterocomplex phase which greatly improves the intercalation process. This method is especially suitable for the intercalation of low-volatile halides into graphite [3].

In our case, the increase of $CoCl_2$ reactivity relies on the formation, in the gaseous phase, of volatile cobalt chloride-aluminium chloride vapor complexes $CoAl_nCl_{3n+2}$ [4]. After reaction, it appears that the carrier gas (Al_2Cl_6 dimer) is consumed. Phases obtained using this method of synthesis, are ternary ones, containing the two halides ($CoCl_2$ and $AlCl_3$). The comparison between these ternary phases MGICs (mixture graphite intercalation compounds) and those obtained after intercalation of aluminium trichloride into a graphite preintercalated with cobalt dichloride (stage 2), leading to GBICs (graphite biintercalation compounds [5]) is determinant in understanding the specific properties of these materials. It is also the reason why binary compounds GICs (graphite intercalation compounds) prepared using the classical synthesis have been chosen as references, as they were widely studied previously [6].

Experimental

Intercalation via gaseous complexes

Chemical transport of $CoCl_2$ using gaseous Al_2Cl_6 dimers relies on the formation of gaseous complexes $CoAl_nCl_{3n+2}$ (n = 2, 3, 4), whose composition and existence domains are related to equilibrium conditions [7]. The action of gaseous complexes with graphite and an excess of chlorine gas (pCl_2 = 500 mm Hg at 25 °C) leads to an intercalation mechanism according to the following steps.

a) $CoCl_{2(s)} + Al_2Cl_{6(v)} \rightleftarrows CoAl_2Cl_{8(v)}$

b) $mC_{(s)} + CoAl_2Cl_{8(v)} \rightarrow CmCoCl_{2(s)} + Al_2Cl_{6(v)}$

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Temperatures (°C)		Elementary analysis	Stage	I_c (Å)	d_i (Å)
Tc	Th				
510	500	$C_{13.5}CoCl_2\ (AlCl_3)_{0.77}$	1	9.42	9.42
510	480	$C_{25.2}CoCl_2\ (AlCl_3)_{0.78}$	2	12.75	9.40
480	450	$C_{31.3}CoCl_2\ (AlCl_3)_{0.50}$	3	16.18	9.48
520	450	$C_{50.6}CoCl_2\ (AlCl_3)_{0.58}$	4	19.43	9.38

Table I. Experimental conditions and characteristics for compounds synthesized using a "*via* gaseous complexes" method.

In our case intercalation has been realized into Highly Oriented Pyrolytic Graphite (HOPG ≃ 50 mg), after *in-situ* chlorination of aluminium wires and within a two zone temperatures reactor (T_g and T_h which respectively represent graphite and halides temperatures).

Reaction temperatures and relative amounts of reagents have been chosen according to the following conditions:

- Gravimetric ratio limitation: $AlCl_3/CoCl_2$ (~25%); $60\% < AlCl_3/C < 120\%$.
- Temperature range: $Tg > 350$ °C.

The temperature must be higher than 350 °C in order to avoid the formation of binary phases graphite-$AlCl_3$. The conditions most favourable for the formation of $CoAl_2Cl_8$ gaseous complexes ($p_{complex}/p_{CoCl_2} > 10^2$) seem to be around 500 °C.

After a week of reaction compounds are obtained in which the stage index depends on the thermal gradient imposed on the system graphite-metal halide ($10\ °C < \Delta T < 70\ °C$).

Unambiguous analyses for carbon, cobalt and aluminium elements always indicate a lack of chlorine. That is the reason why reported analyses (Table I) have been established taking into account a metal/chlorine ratio equal to 2 for $CoCl_2$ and equal to 3 for $AlCl_3$. In these compounds, the Al/Co ratios ($0.5 < Al/Co < 0.78$) remain very much lower than that observed in gaseous complexes ($Al/Co \gg 2$). Enrichment of graphite with $CoCl_2$ as regards the gaseous phases is in good agreement with an exchange process entailing a partial release of the gaseous dimer Al_2Cl_6 as proposed in (b).

Stage index, fidelity and homogeneity were checked by $00l$ diffractograms using θ-2θ scans (MoK_α) taken in the reflection mode. The absence of $00l$ reflections splitting for greater reflection angles ($\theta > 20°$) is consistent with a pure phase (no mixture between graphite-$CoCl_2$ and graphite-$AlCl_3$). The *c*-axis correlation lengths determined by the FWHM (Full Width at Half Maximum) method [8], decrease (800 to 400 Å) as the stage index increases (s = 1 to 4), as observed in binary graphite-$CoCl_2$ compounds [9]. Finally, the interplanar distance after the cointercalation of $CoCl_2$ and $AlCl_3$ is practically the same (Table I) as observed for binary compounds intercalated with metallic chlorides ($d_i \sim 9.50$ Å). This typical value is explained by a three layer arrangement for the intercalated reagents.

Results

a) c-Axis charge density for the ternary compounds (MGICs and GBICs)

The *c*-axis charge density (Fourier transform using integrated X-Rays reflections) gives a direct representation of the layer arrangement perpendicular to the graphene sheets [8]. This method was applied without taking into account the absorption factor and the thermal motion and has given good results for binary compounds [9] as well as for biintercalation compounds like graphite-MCl_x–$AuCl_3$ with MCl_x = $CoCl_2$, $InCl_3$ [10]. For the ternary compound (MGIC stage 1), experimental and calculated *c*-axis charge densities are in good agreement with a chlorine-metal-chlorine *c*-axis sequence (Fig. 2a). The central metallic layer contains cobalt and aluminium atoms. Each mean chlorine layer is split into two neighbor planes (Δ = 0.07 Å) which are not equivalent (Table II).

The external plane is characterized by a chlorine to metal ratio very close to the stoichiometry of the

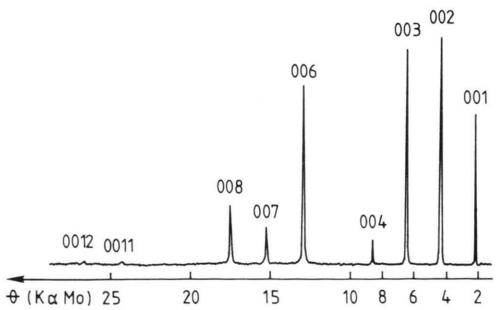

Fig. 1. X-ray $00l$ diffractogram for MGIC-($CoCl_2$, $AlCl_3$) (stage 1).

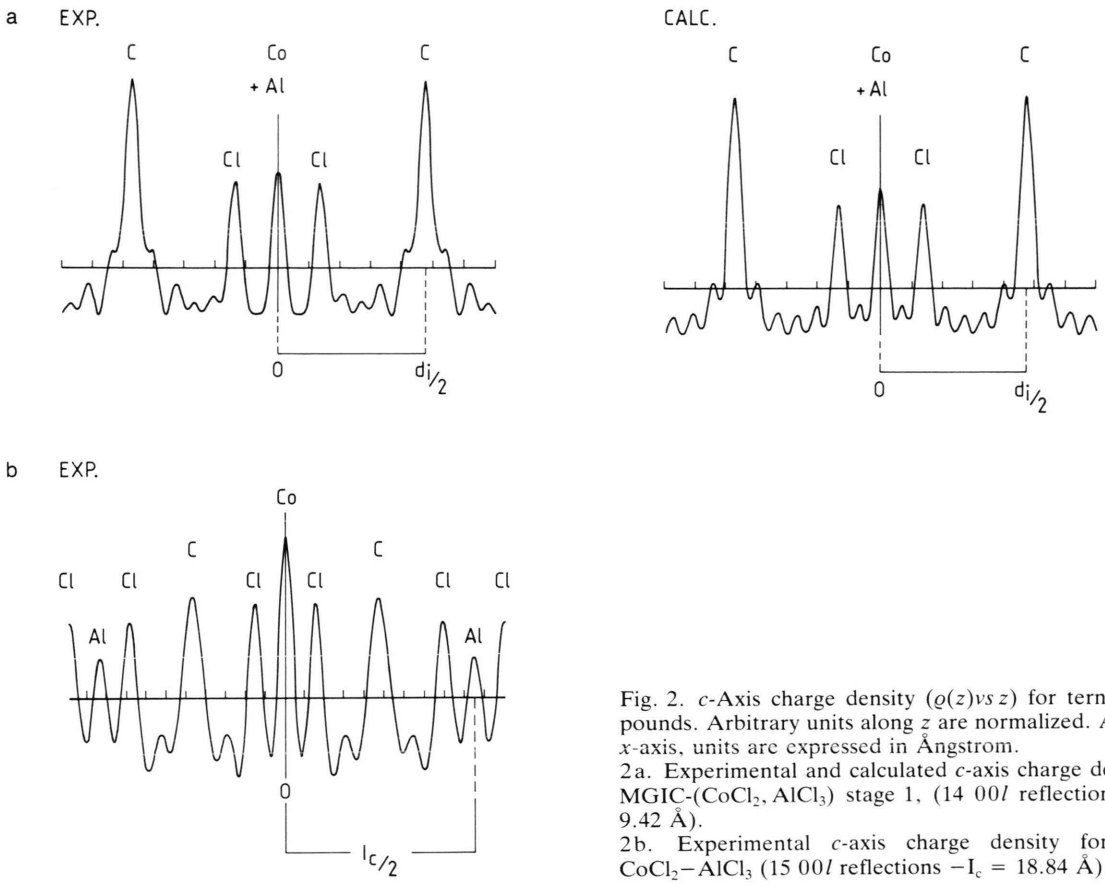

Fig. 2. *c*-Axis charge density ($\varrho(z)$*vs* z) for ternary compounds. Arbitrary units along z are normalized. Along the x-axis, units are expressed in Ångstrom.
2a. Experimental and calculated *c*-axis charge density for MGIC-($CoCl_2$, $AlCl_3$) stage 1, (14 00*l* reflections $-I_c$ = 9.42 Å).
2b. Experimental *c*-axis charge density for GBIC-$CoCl_2$–$AlCl_3$ (15 00*l* reflections $-I_c$ = 18.84 Å).

intercalated cobalt dihalide ($CoCl_2$) and corresponds to a layer metal-chlorine spacing equal to 1.39 Å, identical with the value determined in the binary graphite-$CoCl_2$ compound (stage 1). The internal plane is relative to aluminium chlorine atoms. Its location corresponds to the smallest Al–Cl interlayer distance d(Al–Cl) = 1.32 Å) ever observed in a saturated compound stage 1 GIC or GBIC.

Such a distribution for chlorine atoms in a split layers model approaches that existing for binary graphite-$GaCl_3$ compounds [11]. However, Fourier transform, whose resolution is limited by the number

Compounds		C	Co	Al	Cl	r [%]
GIC (stage 1)	z (Å)	4.69	0.00		1.38	7.4
	Stoichiometry	5.29	1.00		2.15	(11)
MGIC (stage 1)	z (Å)	4.71	0.00	0.00	1.32 1.39	17.0
	Stoichiometry	13.50	1.00	0.60	1.80 2.10	(14)
GBIC	z (Å)	4.68	0.00	9.42	1.39 7.95	14.0
	Stoichiometry	10.50	1.00	0.92	2.22 2.36	(15)

Table II. Crystallochemical values from 00*l* X-ray analysis (GIC, MGIC, GBIC). Layer position z (Å) is determined in comparison with a centrosymmetric origin (Co layer): r is the reliability factor and 00*l* X-ray number used for calculation is in parenthesis.

of $00l$-reflection taken into account ($n < 20$), does not allow to determine the splitting. Other ternary phases $C_{10.6}CoCl_{2.1}(AlCl_{3.3})_{0.9}$ obtained after biintercalation exhibit amounts of halides $AlCl_3$ and $CoCl_2$ relatively similar ($Al/Co \simeq 0.9$) and are characterized by an alternating layer sequence along the c-axis for the metallic halides $CoCl_2$ and $AlCl_3$ (Fig. 2b).

b) $hk0$ and hkl analysis for MGIC versus GBIC and GIC compounds

The *in-plane* order of MGIC-($CoCl_2$, $AlCl_3$) (stage 1, 2) has been determined using $hk0$ X-ray diffraction scan analysis. The diffractograms exhibit the superposition of two types of contributions (sharp Bragg peaks due to $CoCl_2$ lattice and diffusion scattering attributed to $AlCl_3$) in addition to those of the graphite lattice (Fig. 3). These scans are similar to the biintercalated HOPG-$CoCl_2$–$AlCl_3$ scans [9]. The crystallized phase attributed to an intercalated $CoCl_2$ lattice adopts a 2D hexagonal organization (a = 3.56 Å) comparable with that observed in binary graphite-$CoCl_2$ compounds. A disordered phase is typical of aluminium trichloride in a "semi liquid" state [12]. These results reveal cristallochemical heterogeneities in the intercalated layer [13]. The *in-plane* coherence length attributed to cobalt chloride and determined by the FWHM method seems to be smaller (L_{hk0} = 200 to 400 Å) than the values measured in binary graphite-$CoCl_2$ compounds (L_{hk0} = 400 to 600 Å) [9]. This effect increases with the amount of aluminium trichloride cointercalated in the layer (MGIC). The 3D stacking (stage 1) can be determined by the measurements of the integrated

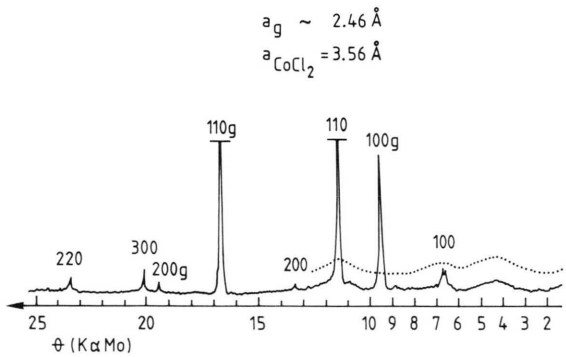

Fig. 3. X-ray $hk0$ diffractogram for MGIC-($CoCl_2$, $AlCl_3$) (stage 2). Dashed lines are diffusion effects observed in a binary graphite-$AlCl_3$ compound and reported in superposition.

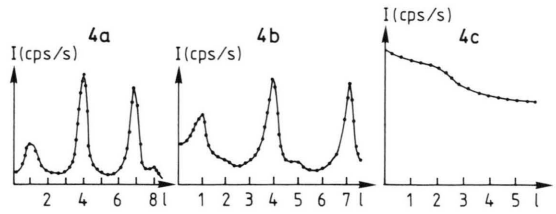

Fig. 4. Experimental $10l$ scans established for cobalt dichloride stacking.
4a. GIC-$CoCl_2$ (stage 1);
4b. MGIC-($CoCl_2$, $AlCl_3$) (stage 1);
4c. GBIC-$CoCl_2$–$AlCl_3$.

intensities along (10) rods for graphite and intercalant lattices [14]. For the GIC and MGIC compounds (stage 1), the experimental 10 l scan established for the $CoCl_2$ lattice agrees (Fig. 4a and 4b) with a lattice constant of $c = 3 \times I_c = 28.16$ Å, which leads to a $\alpha/\beta/\gamma$ stacking like that of pristine $CoCl_2$ [15].

Compared with the $CoCl_2$ stacking in binary graphite-$CoCl_2$ (stage 1), the $\alpha/\beta/\gamma$ sequence is more perturbated by faults (Fig. 4b). The loss of correlation between each $CoCl_2$ layer is complete in the graphite biintercalation compound HOPG-$CoCl_2$–$AlCl_3$ (Fig. 4c). This phenomenom was already observed in second stage compounds where successive $CoCl_2$ layers are separated by a free graphite interval (I_c = 12.75 Å), but is reinforced here by the increase of $CoCl_2$ layer spacing (I_c = 18.84 Å) and by the screening of an additional layer of aluminium trichloride.

As regards the MGIC graphite stacking, the 3D order displays a rhomboedric sequence A/B/C even more perturbated by faults (Fig. 5b) than observed in the binary compounds (Fig. 5a). Biintercalation involves a complete loss of the correlations between the intercalated layers and also between the graphite planes (Fig. 5c).

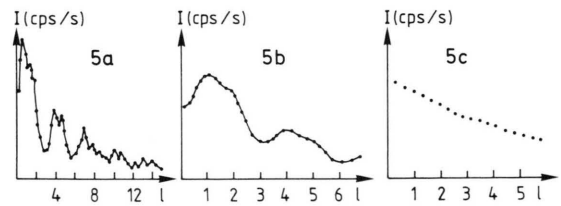

Fig. 5. Experimental $10l$ scans established for graphite stacking.
5a. GIC-$CoCl_2$ (stage 1);
5b. MGIC-($CoCl_2$, $AlCl_3$) (stage 1);
5c. GBIC-$CoCl_2$–$AlCl_3$.

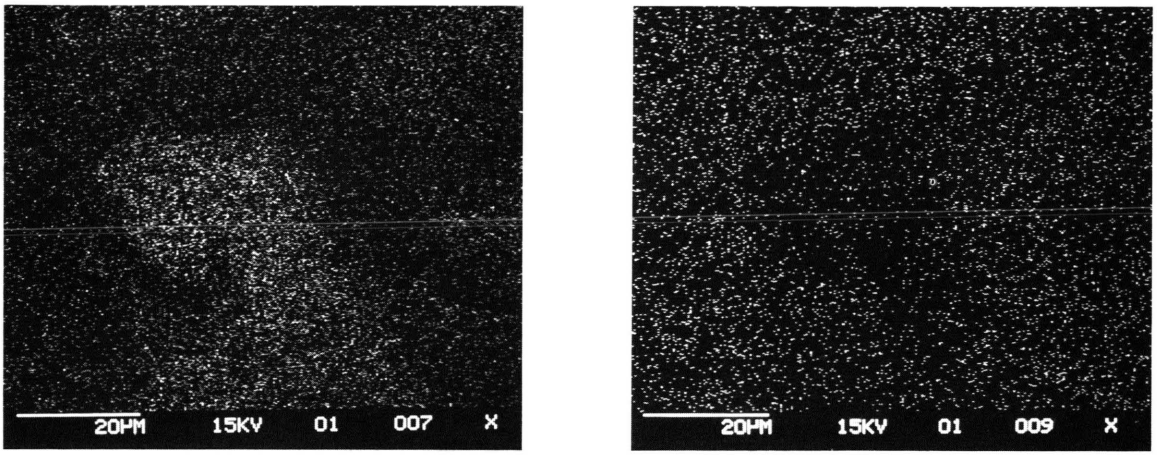

Fig. 6. X-ray mapping image for MGIC-($CoCl_2$, $AlCl_3$). 6a. Co localization; 6b. Al localization.

c) Specific 2D lattice orientation and segretation in MGIC

An analytical electron microscopy study is complicated by the presence of a very volatile species ($AlCl_3$) between the layers. The electron diffraction pattern for the MGIC-($CoCl_2$, $AlCl_3$) is consistent with results of the X-ray $hk0$ studies of the $CoCl_2$ lattice with $\delta(a_g, a_i) \simeq 0°$ for stage 1 and $\delta(a_g, a_i) \simeq 0°$ and 30° for stage 2.

On the other hand diffuse rings whose radii match the lattice constants of $AlCl_3$ have never been simultaneously observed. That behaviour suggests a separation of $CoCl_2$ and $AlCl_3$ into distinct domains. Confirmation was obtained by scanning electron microscopy associated with X-ray mapping image (Co–K_α, Al–K_α) (Fig. 6). The TEM dark field image of the $CoCl_2$ lattice (110 spots) displays needle shaped islands (200×50 Å) uniaxially oriented in good agreement with previous work [16].

d) Transport studies for MGIC, GBIC versus GIC

Electric resistivity measurements *versus* T have been carried out for the compounds GIC-$CoCl_2$ (stage 2), MGIC-($CoCl_2$, $AlCl_3$) (stage 2) and GBIC-$CoCl_2$–$AlCl_3$ especially chosen to have a similar configuration regarding the $CoCl_2$ layers: *i.e.* the magnetic layers are always screened by at least one non-magnetic one.

Basal plane resistivity measurements were carried out inductively, and *c*-axis measurements by the coaxial d.c. four probe method.

The general decrease for the *in-plane* resistivity *versus* T is similar to that observed for a non-magnetic acceptor GIC [17]. Moreover, an anomalous behaviour characterized by an abrupt increase of the *in-plane* resistivity occurs as T is lowered below the magnetic phase transition Tc (Fig. 7). The mag-

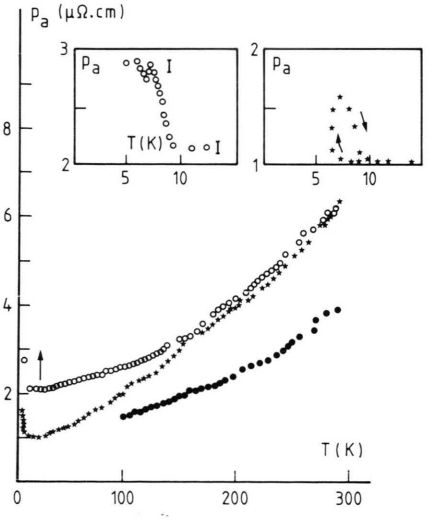

Fig. 7. Basal plane resistivity for $CoCl_2$ containing GIC (stage 2) and GBIC. Solid circles (•) for GIC, crosses (+) for MGIC and open circles (o) for GBIC. Inserts: left for GBIC, right for MGIC.

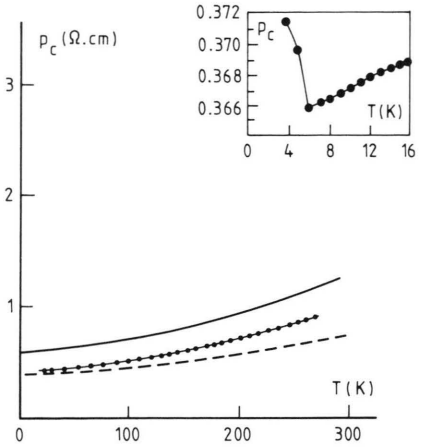

Fig. 8. *c*-Axis resistivity for $CoCl_2$ containing GIC (stage 2), MGIC (stage 2) and GBIC. Continuous line for GIC, dashed line for GBIC and solid circles for MGIC. Insert display behaviour at T < 16 K for MGIC-($CoCl_2$,$AlCl_3$).

nitude of this effect (20% of the total variation for MGIC and 15% for GBIC) is greater than the value of about 10% already reported for the binary compound graphite-$CoCl_2$ (stage 1) [18].

As regards *c*-axis resistivity, first measurements (Fig. 8) established that MGIC (stage 2) displays the same behaviour, but the magnitude of this increase remains very much weaker than that observed in ϱ_a (1% vs 20%).

Discussion

Assisted intercalation of cobalt dichloride always entails cointercalation of aluminium trichloride. This surprising result obtained at T = 500 °C suggests the existence of a reaction mechanism more complex than that suggested in (b). However existence of aluminium trichloride (Al/Co = 0.5 to 0.8) naturally induces a filling factor of $CoCl_2$ weaker (30 to 40%) than that observed with $CoCl_2$ containing binary compounds (≃70%). When the intercalated layer contains two halides ($CoCl_2$ and $AlCl_3$), the configuration of each Cl–M–Cl sequence is very close to that observed in the corresponding binary compounds.

In-plane structural studies clearly indicate that dihalides are demixed into distinct domains; this behaviour cannot be detected along the *c*-axis probably because of the small difference Δ between thickness as d_i of each intercalated layer. In our case,

$d_i(AlCl_3) = 9.50$ Å, $d_i(CoCl_2) = 9.42$ Å $\rightarrow \Delta = 0.08$ Å.

Presence of aluminium trichloride in the layer weakly perturbs the $CoCl_2$ 3D order ($\alpha/\beta/\gamma$ for MGIC stage 1). As regards transport studies, the most important characteristic is the great increase of the *in-plane* resistivity below Tc (MGIC stage 2 and GBIC).

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