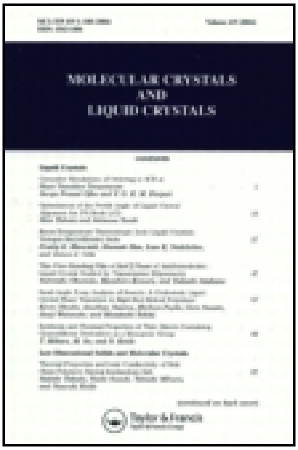

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Reduction of $CuCl_2$ Intercalated Graphite by Heavy Alkali Metal Vapour

Jean-François Marêché [a], Claire Hérold [a], Guy Furdin [a] & Nathalie Hubert [a]

[a] Laboratoire de Chimie du Solide Minéral, URA CNRS 158 B.P. 239, 54506, Vandoeuvre lès Nancy Cédex, France

Version of record first published: 23 Oct 2006.

To cite this article: Jean-François Marêché, Claire Hérold, Guy Furdin & Nathalie Hubert (1994): Reduction of $CuCl_2$ Intercalated Graphite by Heavy Alkali Metal Vapour, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 244:1, 275-280

To link to this article: http://dx.doi.org/10.1080/10587259408050117

Mol. Cryst. Liq. Cryst. 1994, Vol. 244, pp. 275–280
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

REDUCTION OF $CuCl_2$ INTERCALATED GRAPHITE BY HEAVY ALKALI METAL VAPOUR

JEAN-FRANÇOIS MARÊCHÉ, CLAIRE HÉROLD, GUY FURDIN AND NATHALIE HUBERT
Laboratoire de Chimie du Solide Minéral, URA CNRS 158
B.P. 239, 54506 Vandoeuvre lès Nancy Cédex, France.

Abstract Reduction of $CuCl_2$ intercalated graphite by heavy alkali metal vapour at low temperature gives several intercalated copper phases, depending on the reducing agent. These phases were studied by transmission electron microscopy.

INTRODUCTION

Reduction of copper chloride intercalated graphite has been studied by several authors. The early work of Gross[1] concerns the reduction by gaseous hydrogen, but even above 1000°C the reaction was not complete and a further reduction with potassium was necessary. The final product was a dispersion of three dimensional copper and CuCl crystallites in graphite. Vol'pin et al.[2] claimed that the use of aromatic anion radicals as reducing agents allows a smooth reduction of the intercalated halide without the metal escaping from the graphite layer. In a more recent paper[3], the existence of intercalated copper was indicated with an identity period of 560 - 580 pm for stage 1 and 930 - 960 pm for second stage. Braga et al.[4], reacting KC_8 with copper chloride dissolved in tetrahydrofuran obtained mixtures of stages 1 - 5 of intercalated copper. They suggested a sandwich thickness of 550 - 580 pm and that the copper atoms are located over the centers of the carbon hexagons (hexagonal unit cell a = 246 pm).

Small crystals of natural graphite are a good starting material for intercalation of transition metal halides and further reduction to intercalated transition metals by heavy alkali metal vapour at relatively low temperature[5]. We have, in this work, applied the same technique to the case of intercalated copper chloride.

EXPERIMENTAL

The starting material is constituted of single crystals of natural Madagascar graphite, 10 microns average diameter and 0.5 micron thick. These particles are obtained from bigger natural crystals by a process described elsewhere[6]. The starting material is outgassed in vacuum at 900°C prior to intercalation, which is done in the classical two bulb tube under a chlorine atmosphere (485°C, ten days). After reaction, some particles are pressed on a beryllium foil under inert atmosphere to allow examination of the X ray 001 reflexions. The remainder is transferred under an argon stream to a Pyrex glass reactor. Alkali metal is placed under argon in the same reactor and distilled beside the G.I.C. The evacuated and sealed reactor is placed in a furnace with a small temperature gradient to allow the vapour phase reaction. The reductions are carried out at 100°C for one week. After reaction the products have a red bronze color; as the reduction products occupy less than the total gallery volume, the remainder is filled with alkali metal (MC_8 phase). After reaction, the product is left overnight in an argon atmosphere containing 10 - 100 ppm oxygen to permit diffusion and slow oxidation of the excess alkali metal at the edges of the crystals. The particles are dispersed in alcohol, filtered through a Nuclepore filter covered with evaporated amorphous carbon. Another layer of carbon is further evaporated on the sample. A small part is cut off and placed on a microscope grid and the polymer membrane is dissolved with $CHCl_3$. So, the graphene layers are parallel to the grid plane, favouring the in-plane arrangement observation. Bright field magnification, electron microdiffraction and microanalysis where realized on a CM 20 Phillips microscope equipped with an Edax microanalysis accessory.

RESULTS

Bright field imaging shows that the carbon particles appear a little bit more distorted than those of products with other transition metal halides reduced in the same conditions[5], especially for potassium reduced compounds. However the general appearence of the sheets looks like that of reference (5), the size and number of clusters growing from cesium to potassium.

Products reduced by cesium

These products contain several phases: the graphite particle usually remains a single crystal, as can be seen on figure 1. Cesium chloride is present as microcrystals, part of them being oriented with respect to the graphite lattice. Copper is mostly present as a two dimensional lattice.

No trace of the starting intercalation compound remains, and no CuCl is visible: the reduction is complete. All the reflexions relative to CsCl appear. hk0 reflexions are however the most intense and 12 reinforcements can be seen. On the h00 rings, these spots are situated on the direction common to (100) or (110) spots of graphite, whereas those on the 110 and 220 rings of CsCl are rotated ± 15° with respect to the graphite

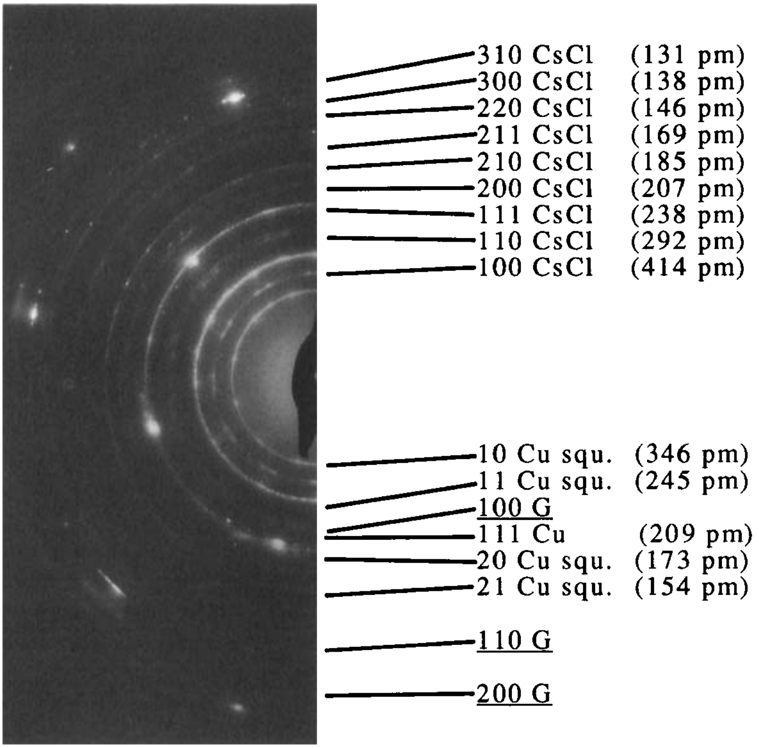

FIGURE 1 Electron diffraction diagram of $CuCl_2$ G.I.C. reduced by Cs

directions. These twelve spots, separated by 30° on their rings, can be explained by the existence of three domains rotated with respect to each other by 120°, due to the hexagonal symmetry of the planar graphene lattice. The cubic lattices of that CsCl crystallites have their basal planes parallel to the graphene sheets and the other faces oriented with respect to the in-plane graphite axes by 0° or ± 15°. The CsCl rings correspond to randomly distributed three dimensional microcrystals randomly distributed within the graphite matrix.

Weak reflexions are relative to a small quantity of clusters of three dimensional copper, randomly distributed. A series of weak rings on which are superimposed 12 arcs of strong intensity has been attributed to two dimensional copper. The first set of 12 spots starting from the center has been indexed as 10 reflexions of a square lattice, leading to an in-plane parameter of 346 pm. These spots are oriented ± 15° with respect to the (100) and (110) graphite spots. The second set of 12 spots is indexed as 11 being rotated ± 15° with respect to the 10 and are then collinear with the graphite lattice spots (100) or (110).

Products reduced by rubidium

These products also contain several phases, especially as regards their copper contents.

Rubidium chloride gives only hk0 reflexions, as can be seen on figure 2. There are 12 small arcs at 30° from each other. The 220 reflexions are in the direction of the (100) and (110) graphite spots; the 200 reflexions are rotated ± 15° with respect to the graphite directions. The lack of hkl reflexions shows that the cubic lattices of RbCl have their basal planes parallel to the graphene layers. As for CsCl, three domains also exist, the three axes also being oriented with respect to the graphite axes. There is a difference in rotation of 15° in the **a**,**b** plane of graphite between RbCl and CsCl lattices.

Copper is present only as two dimensional intercalated phases: the first is an hexagonal phase a = 645 pm. Its 10 reflexions can be seen as 6 spots on the direction of the (110) graphite spots.

The second copper phase is square, a = 555 pm. Its 10 reflexions are partly oriented ± 15° with respect to the (100) graphite spots. The reflexions of this phase are weak and probably involve only a small quantity of copper.

The third copper phase is the most abundant. The square lattice has a parameter

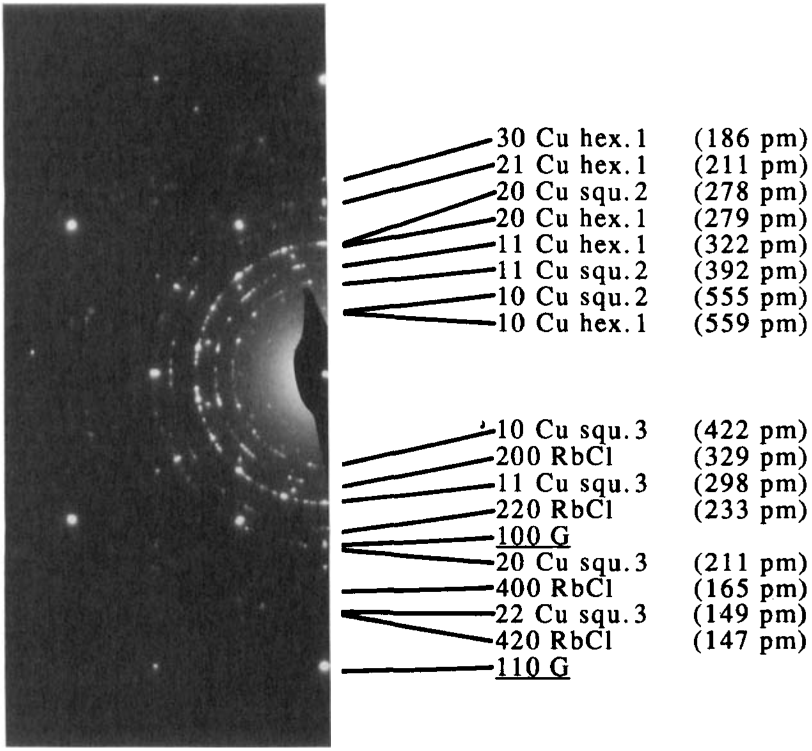

FIGURE 2 Electron diffraction diagram of $CuCl_2$ G.I.C. reduced by Rb

a = 422 pm and the 10 reflexions are in the directions of the (100) reflexions of graphite. As the parameter of this phase is close to twice the 100 reticular distance (212 pm) of graphite, a strong modulation occurs, and this creates numerous spots on the diagram. If the origin of the square lattice is placed sucessively to each spot of the graphite lattice, the diffraction spots of the square lattice will superimpose to some spots of the diagram and help to recognize them as the modulation pattern.

Products reduced by potassium

Here, the graphite lattice is more distorted than in the other products. No ordered phase is visible (figure 3). All KCl reflexions are present: the crystals are randomly dispersed. Metallic copper gives finely punctuated rings, but a significant part of the copper forms an unusual unoriented phase, which manifests itself by three rings (276, 252 and 230 pm). Russian authors[3] have often discussed the existence of "complexes of graphite and transition metals". It could be possible that a phase of this type is present. This coud be supported by the fact that if the products are heated to 700°C, all the copper escapes and forms big crystals, visible to the eye, outside the graphene layers.

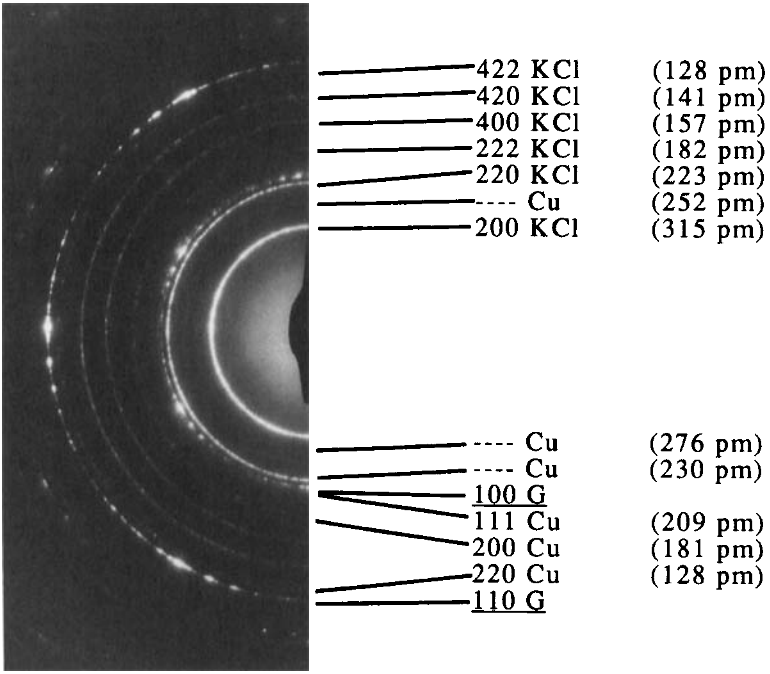

FIGURE 3 Electron diffraction diagram of CuCl2 G.I.C. reduced by K

DISCUSSION AND CONCLUSIONS

As in the case of the reduction of other intercalated transition metal halides, several two dimensional copper phases can exist. They are strongly dependent on the reducing agent. This is in agreement with the general behaviour of the intercalated halides, usually their reduction leads to three dimensional transition metals[7-10]. To obtain intercalated transition metals, the two dimensional intercalated halide must be reduced between the layers, so as to keep the strain of the graphene lattice on the transition metal atoms and to prevent them to gather to form three dimensional crystals. So, the experimental conditions seem to be, according to the literature and to our works, the following:

- the reducing agent must intercalate
- the reaction must be slow and the temperature must be as low as possible to reduce the mobilities.

Intercalated transition metals are difficult to obtain and even in the best case, we remain close to the limits of formation of these phases[11].

REFERENCES

1. R. Gross, Thesis (Nancy, France, 1962).
2. M.E. Vol'pin, Yu.N. Novikov, Yu.T. Struchkov and V.A. Semion, Izv. Akad. Nauk SSSR, Ser. Khim., 11, 2608 (1970).
3. M.E. Vol'pin, Yu.N. Novikov, N.D. Lapkina, V.I. Kasatochkin, Yu.T. Struchkov, M.E. Kazakov, R.A. Stukan, V.A. Povitskij, Yu.S. Karimov and A.V. Zvarikina, J. Am. Chem. Soc., 97, 3366 (1975).
4. D. Braga, A. Ripamonti, D. Savoia, C. Trombini, A. Umani-Ronchi, J. C. S. Dalton, 2026 (1979).
5. C. Hérold, J.F. Marêché and G. Furdin, Microsc. Microanal. Microstruct., 2, 589 (1991).
6. G. Furdin, J.F. Marêché and A. Hérold, French Pat. n° 91 12663, Int. Pat. n° PCT / EP 92 / 02317.
7. A. Messaoudi, R. Erre and F. Béguin, Carbon, 29 (4/5), 515 (1991).
8. G. N'Guessan and P. Touzain, Proc. Int. Coll. on Layered Compounds, (Pont à Mousson, France) D. Guérard and P. Lagrange Eds., 137 (1988).
9. G. Bewer, N. Wichmann and H.P Boehm, Mat. Sci. Eng., 31, 73 (1977).
10. D. Herein, T. Braun and R. Schlögl, This Book. and D. Herein, O. Timpe, R. Schlögl and A. Reller, Proc. Int. Carbon Conf. "Carbon 92", (Essen, Germany), 609 (1992).
11. A. Mabchour, G. Furdin and J.F. Marêché, C. R. Acad. Sci. Paris II, 312, 1293 (1991).