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Claire Hérold^a, Frédérique Goutfer-Wurmser^a, Jean-François Maréché^a & Philippe Lagrange^a

^a Laboratoire de Chimie du Solide Minéral (URA CNRS 158) Université Henri Poincaré Nancy I, B.P. 239, 54506, Vandoeuvre-lès-Nancy Cedex, FRANCE

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New graphite intercalation compounds : the potassium pnictographitides

CLAIRE HÉROLD, FRÉDÉRIQUE GOUTFER-WURMSER,
JEAN-FRANÇOIS MARÊCHÉ and PHILIPPE LAGRANGE
Laboratoire de Chimie du Solide Minéral (URA CNRS 158)
Université Henri Poincaré Nancy I
B.P. 239 - 54506 Vandoeuvre-lès-Nancy Cedex - FRANCE

New first stage ternary compounds associating potassium and phosphorous were synthesized in liquid potassium containing a few atomic percent of red phosphorous. The structural arrangement of these alkali metal rich phases was studied by X-Ray diffraction. Electrical measurements parallel and perpendicular to the c-axis were carried out between room temperature and 4.2 K.

Keywords: graphite, intercalation, potassium, phosphorous, electrical resistivity, charge transfer

INTRODUCTION

Potassium intercalates easily into graphite leading to graphite intercalation compounds containing mono-layered sheets. The first stage phase is the well known KC_8 compound, prepared for the first time in 1926 [1].

Fifteen years ago, a new family of compounds was born : the ternary compounds containing at the same time an alkali metal and a fairly electronegative element as mercury, thallium, arsenic, antimony, bismuth (electronegativities around 2 in the Pauling's scale) [2]. These compounds are prepared by intercalation of an alloy containing at least 20 atomic percent of

the less electropositive element. Due to the presence in the interlayer space of two elements whose electronegativities are quite different, the intercalated sheets are systematically poly-layered, with an alternating of positive and negative charges along the *c*-axis. The chemical formulas of the first stage phases show generally a *C/K* ratio close to 4, as in the KHgC_4 compound. These compounds are two times richer in alkali metal than the binary ones, but contain a large amount of the fairly electronegative element.

More recently, alkali metals were intercalated into graphite associated with strongly electronegative elements (electronegativities higher than 2.5) [3]. In this case the reagent is the molten alkali metal containing approximately one atomic percent of the second element. The compounds contain also poly-layered sheets, two alkali metal planes surrounding a central layer constituted of the most electronegative element, as in the previous case. But, although the enrichment of the electronegative element during the intercalation is significant, this second element amount remains small in the intercalated compounds ; the typical example is the graphite-potassium-oxygen phase whose chemical formula is $\text{KC}_{3.8}\text{O}_{0.07}$.

Considering these observations, the route for intercalating phosphorous is not easy to choose ; its electronegativity is 2.1. Consequently, should it be considered as the other elements of the same column, intercalated as alloys, or is it comparable to sulphur or selenium, added to potassium in very small amounts to obtain their intercalation ?

We considered that this element is sufficiently electronegative to be intercalated by the second route and we describe in this paper the new ternary compounds containing potassium and phosphorous, obtained by the intercalation of potassium with small amounts of added phosphorous.

SAMPLE PREPARATION AND CHARACTERIZATION

HOPG platelets of $2 \times 10 \times 0.2 \text{ mm}^3$ are used. Pyrographite samples are immersed in liquid potassium containing one atomic percent of red phosphorous. The reaction is carried out in a stainless steel reactor, which is filled up in a glove box under a pure argon atmosphere. The reaction duration

ranges from 2 to 5 days, and the temperature reaches 390°C. When the reaction is finished, the reactor is opened in the glove box and the sample is placed in a Lindemann capillary tube for X-Ray examination.

The intercalation reaction gives blue color samples, whose weight uptake is close to 110%. The thickness increase, in the *c*-axis direction, ranges from 160 to 180%. Several phases were obtained with repeat distances ranging from 850 pm to 900 pm. The samples dilation and the repeat distance values allow us to determine that the different phases all belong to the first stage. One phase of which interplanar distance is 886 pm was isolated. Moreover, these new compounds present a very good stability towards air and water.

From now on, the paper will deal with the structural arrangement and the electrical properties of the isolated phase.

X-RAY DIFFRACTION

1D structural arrangement

00l X-Ray diffraction pattern registered with the presence in the Lindemann capillary tube of diamond as internal standard allows to determine precisely the interplanar distance of the isolated phase, which is 886 pm. *00l* diffractogram of this phase is shown in Fig. 1.

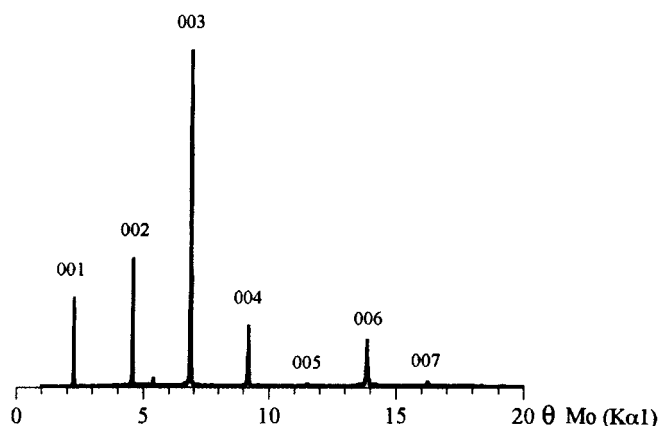


FIGURE 1 *00l* X-Ray diffraction pattern of the graphite-potassium-phosphorous compound (repeat distance of 886 pm).

The experimental c-axis electronic density profile is obtained by the Fourier transform of the $00l$ structure factors. It is compared on Fig. 2 with a unidimensional model. In the latter, each intercalated sheet is constituted by two potassium planes, situated at 290 pm from the nearest graphene layer, surrounding a central phosphorous plane. The proposed chemical formula is $\text{KC}_{3.2}\text{P}_{0.3}$.

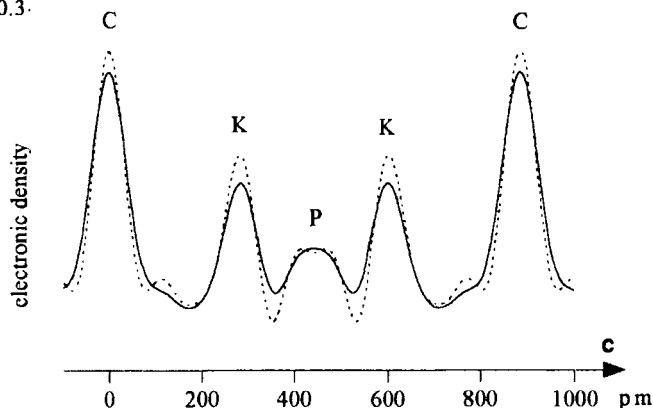


FIGURE 2 Electronic density profiles of the $\text{KC}_{3.2}\text{P}_{0.3}$ compound (solid line : experience ; dashed line : model).

2D and 3D structural arrangements

The rotating crystal method applied to the previous phase confirms the repeat distance of 886 pm and shows that the compound is organized in the 3D space. However, although the sample presents only one interplanar distance, one can observe two 2D arrangements. Indeed, some reflections can be indexed in a hexagonal lattice with a unit cell parameter of 430 pm, which is commensurate with that of graphite. Concerning the 3D arrangement, the c parameter is one time the repeat distance. Consequently, $c = I_c = 886$ pm. The other reflections belong to another hexagonal unit cell with a parameter of 500 pm, that is not commensurate with the graphitic one. The presence of both 2D unit cells corresponding to only one interplanar distance, leading to two 3D arrangements, explains the fact that the correspondence between both calculated and experimental electronic density profiles is not excellent. Indeed, the experimental profile is the superimposition of two structural arrangements, probably very close but not exactly identical.

CHARGE TRANSFER

Intercalation leads to an increase in the in-plane carbon-carbon distances. So, we consider that the intercalated sheets give electrons to the carbon layers and we apply the Pietronero-Strässler's relationship [4] to evaluate the charge transfer f_c which reaches $0.046 \text{ e}^-/\text{C}$. This value can be compared to that deduced from the chemical formula $\text{KC}_{3.2}\text{P}_{0.3}$, supposing the potassium fully ionized and the phosphorous at the -III oxidation state, that is $0.031 \text{ e}^-/\text{C}$. On the contrary, the charge transfers deduced from the chemical formulas are usually much higher than those calculated from physical parameters.

ELECTRICAL MEASUREMENTS

Electrical resistivity measurements were carried out parallel and perpendicular to the *c*-axis, between room temperature and 4.2 K (Fig. 3). Due to the difficulties to synthesize samples from HOPG discs, electrical measurements were done on rectangular platelets (same samples used for X-Ray diffraction studies) coated with silver paint, using standard four points methods. This is the reason of the approximate accuracy of *a*-axis resistivity and anisotropy values. Room temperature resistivity values are of the same order of magnitude than that of the first stage potassium-oxygen compounds [5]. However, their decrease with temperature is less pronounced. Perpendicular to the *c*-axis, the RRR value is around 2. This could be due to a much higher number of defects than in potassium-oxygen products. First stage ternary compounds containing two superimposed potassium layers in each intercalated sheet have very small RRR values compared to that of the first stage binary compound KC_8 , whose intercalated sheets are only mono-layered. The electrical resistivity anisotropy ρ_c/ρ_a is close to 25000, quite temperature independent.

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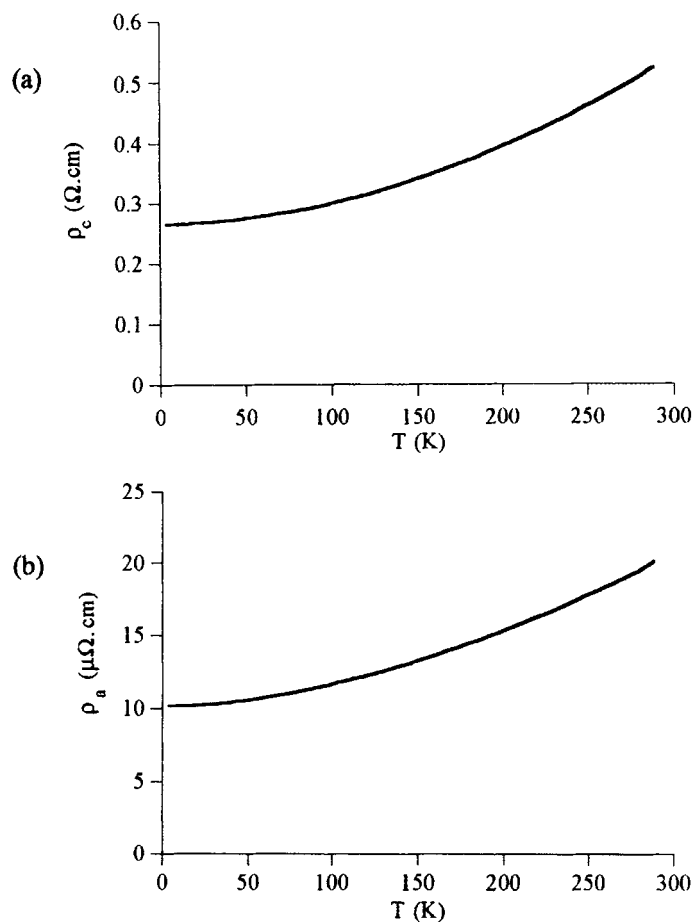


FIGURE 3 Electrical resistivities between room temperature and 4.2 K
(a) ρ_c parallel to the c-axis (b) ρ_a perpendicular to the c-axis.

References

- [1] K. Fredenhagen and G. Cadenbach, *Z. Anorg. allg. chem.*, **158**, 249 (1926).
- [2] P. Lagrange, *Chemical Physics of Intercalation II* (P. Bernier et al., Plenum Press, New York, 1993), p. 303.
- [3] C. Hérold, A. Hérold and P. Lagrange, *J. Phys. Chem. Solids*, **57**, 655 (1996).
- [4] L. Pietronero and S. Strässler, *Phys. Rev. Lett.*, **47**, 593 (1993).
- [5] C. Hérold, M. El Gadi, J.F. Marêché and P. Lagrange, *Mol. Cryst. Liq. Cryst.*, **244**, 41 (1994).