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Intercalation into Graphite of Sulphur or Selenium with Potassium

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Intercalation into graphite of sulphur or selenium with potassium

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New first stage ternary graphite-potassium-chalcogen compounds were synthesized. They are very rich in alkali metal : their chemical formulas are close to KC_3A_x (A = sulphur or selenium). We studied their structural arrangement by X-ray diffraction. We calculated the charge transfers and measured the electrical resistivities.

Keywords: intercalation, graphite, potassium, sulphur, selenium, charge transfer, electrical resistivity

INTRODUCTION

Intercalation into graphite of pure potassium leads to a binary phase with only one intercalated layer in each interlayer interval. In the presence of elements more electronegative than potassium, intercalation into graphite of this metal allows the formation of poly-layered sheets. These elements are unable by themselves to intercalate into graphite. Oxygen added to potassium reacts with graphite to form a compound with a chemical formula close to $KC_4O_{0.07}$ [1]. It contains two potassium layers surrounding a central oxygen plane. Oxygen

provides the cohesion between the potassium planes. More recently, we synthesized another phase in which the potassium concentration is higher. Its chemical formula is close to $KC_{3.2}O_{0.5}$ [2].

We showed that sulphur or selenium, which are also chalcogen elements, are able to intercalate into graphite with potassium, in spite of their smaller electronegativity (≈ 2.5 for sulphur and selenium on the Pauling scale instead of 3.5 for oxygen). Thus, we observed several new ternary phases [3].

EXPERIMENTAL CONDITIONS

These phases are prepared by immersing pyrographite (HOPG) in liquid potassium containing small amounts of sulphur or selenium (< 1% atomic). The reaction is carried out in a sealed stainless steel tube. The temperature is increased to 350°C- 450°C. The reaction time ranges from one hour to three days for the graphite-potassium-sulphur system and from three to six days for the graphite-potassium-selenium system.

GRAPHITE-POTASSIUM-SULPHUR COMPOUNDS

In the case of the graphite-potassium-sulphur system, we mainly obtained two first stage ternary compounds, one of which is described here. This purple phase has a repeat distance I_c of 875 pm. The experimental dilation along the **c**-axis reaches 175 %. This value is slightly higher than that calculated, which is 160 %. This phase presents a great stability towards air and water.

The experimental **c**-axis electronic density is established from the Fourier transform of the *00l* structure factors. This profile is compared to the profile given by an unidimensional model (figure 1). The best fit between both profiles is obtained for a model containing in each graphitic interval two potassium planes surrounding a median sulphur layer, with a chemical formula close to $KC_3S_{0.25}$. The distance between each potassium plane and the adjacent graphitic sheet is 280 pm.

An X-ray *hk0* diffraction pattern presents two main reflections on both sides of the graphite 100 reflection. They can be indexed as 100 and 200 reflections of a 2D-hexagonal unit cell, with the parameter a = 429,83 pm (figure 2a). This

cell, commensurate with that of graphite ($a = \sqrt{3}\ a_G$), is characteristic of the dense arrangement of Li-planes in LiC_6, which is a binary phase containing single-layer sheets. In the ternary compound, the superposition of two potassium layers in each intercalated sheet justifies the chemical formula $KC_3S_{0.25}$ (or $K_2C_6S_{0.5}$), which is proposed in the previous 1D structural model.

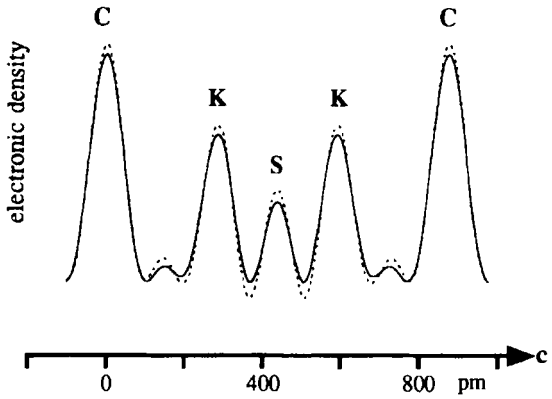

FIGURE 1 : 1D Fourier transform of $KC_3S_{0.25}$ (or $K_2C_6S_{0.5}$)
(solid line : experimental ; dashed line : model)

Moreover, a rotating crystal diffractogram confirms these results and shows that the compound is also organized in the third space direction, with the c parameter equal to the repeat distance 875 pm. The stacking of the graphene planes is AAA and in each intercalated stack, the position of the potassium atoms creates octahedral sites which are occupied statiscally, one out of two, by sulphur atoms. This new phase crystallizes in the centered hemiedry of the hexagonal system with a space group $P\bar{3}m(1)$.

However, a superstructure sometimes appears. Another sample, which resembled the previous one, was also studied by the rotating crystal method ; at small angles, one observes, the presence of supplementary reflections with very weak intensities. This result leads thus to an extension of the parameters of the 3D-hexagonal unit cell, with a = 744,64 pm and c = 1750 pm. The

space group becomes $P\bar{3}(1)c$ (figure 2b). The observed superstructure is certainly due to the presence of sulphur atoms, because the structure factors of the supplementary reflections depend only on the diffusion factor of sulphur. The occupation of the octahedral sites by sulphur atoms is no more statistical.

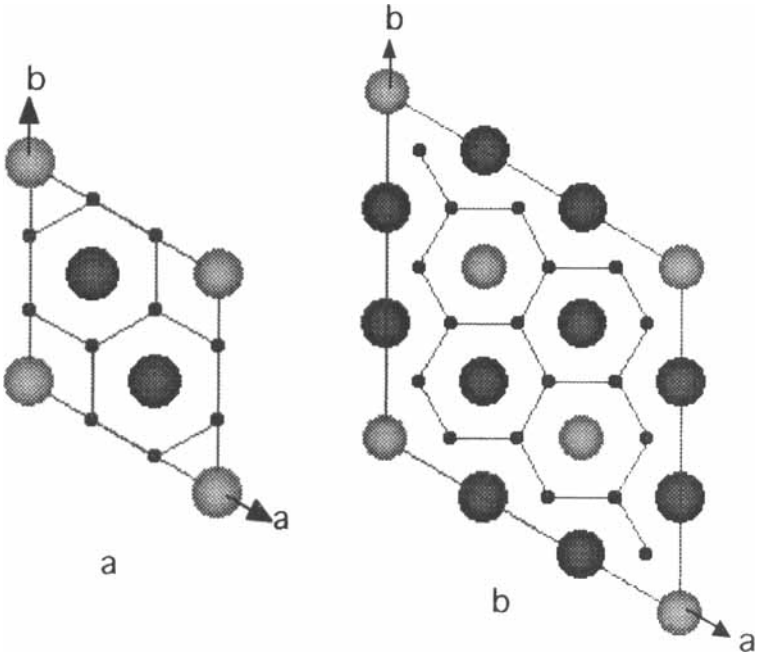

FIGURE 2 : a : 2D projection of the 3D unit cell (a = 429,83 pm) of $KC_3S_{0.25}$
b : 2D projection of the 3D unit cell (a = 744,64 pm) of $KC_3S_{0.25}$
(small dark balls : carbon; grey balls : sulphur and black balls : potassium)

GRAPHITE-POTASSIUM-SELENIUM COMPOUNDS

In the case of the graphite-potassium-selenium system, several ternary first stage phases were observed. They are distinguished on the one hand by their repeat distance and on the other hand by their different *00l* reflection intensities. We present here one phase, which has quite the same *00l* intensities reflections as the ternary graphite-potassium-sulphur compound just presented. This purple phase, obtained at 400°C during three days, exbihits a repeat distance of 871 pm. It is also stable towards air and water.

The intercalated sheet contain two superposed potassium layers surrounding a central selenium plane (figure 3). The formula is close to $KC_3Se_{0.1}$ from crystallographic data.

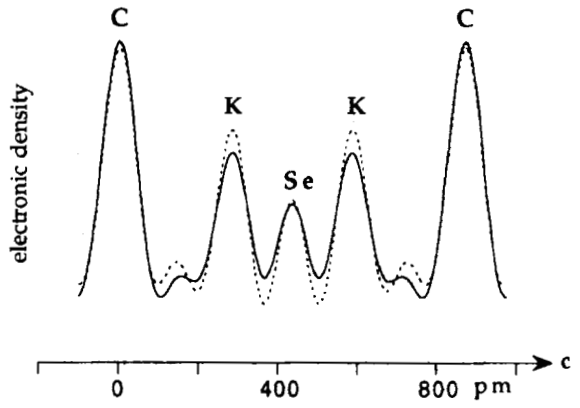

FIGURE 3 : 1D Fourier transform of $KC_3Se_{0.1}$ (or $K_2C_6Se_{0.2}$)
(solid line : experimental ; dashed line : model)

The 3D arrangement corresponds to a centered hemiedry of the hexagonal system (space group $P\bar{3}(1)c$). This structure is similar to the second structure proposed for $KC_3S_{0.25}$. The parameters are a = 743,9 pm and c = 2Ic = 1742 pm.

CHARGE TRANSFER AND ELECTRICAL RESISTIVITY

We calculated the charge transfers and measured the electrical resistivities of $KC_3S_{0.25}$ and $KC_3Se_{0.1}$. The results are given respectively in Table I and Table II.

One observes a greater temperature variation of resistivity for $KC_3S_{0.25}$ than for $KC_3Se_{0.1}$, probably due to fewer defects and the anisotropies are quite weak for graphite intercalation compounds, but much higher than for KC_8.

TABLE I : charge transfers fc of $KC_3S_{0.25}$ and $KC_3Se_{0.1}$

(fc_1 : calculated from Pietronero and Strässler equation [4] ; fc_2 : calculated from chemical formula, considering a total ionization of potassium and sulphur atoms)

	fc_1 (e^-/C)	fc_2 (e^-/C)
$KC_3S_{0.25}$	0.066	0.166
$KC_3Se_{0.1}$	0.057	0.266

The charge transfer fc_1 is very similar for both phases. The difference between fc_1 and fc_2 for each phase shows that the atoms are not entirely ionized.

TABLE II : electrical resistivities of $KC_3S_{0.25}$ and $KC_3Se_{0.1}$
(ρ_a : electrical resistivity measured perpendicular to the c-axis ; ρ_c : electrical resistivity measured along the c-axis)

	ρ_a ($\mu\Omega$.cm)			ρ_c (Ω.cm)		$A = \frac{\rho_c}{\rho_a}$	
	285 K	4.2 K	$\frac{\rho_a (285\ K)}{\rho_a (4.2\ K)}$	285 K	4.2 K	285 K	4.2 K
$KC_3S_{0.25}$	≈ 20	≈ 2.6	≈ 7.7	0.079	0.0096	≈4000	≈3300
$KC_3Se_{0.1}$	≈ 20	≈ 7	≈ 2.85	0.08	0.021	≈4000	≈3000

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