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X-ray photographic study of the phase transitions in KC_{24} single crystals

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Résumé. — On présente une étude photographique, par diffraction des RX entre 300 K et 10 K, de l'ordre planaire du potassium dans des monocristaux du composé KC_{24}. Dans la phase désordonnée haute température, on observe une modulation du halo diffus qui indique l'existence de fortes interactions au troisième voisin qui augmentent lorsque la température diminue. A 124 K $\pm$ 2 K, l'ordre à longue distance s'établit et nos résultats confirment les études précédentes. Nous avons mis en évidence pour la première fois des modifications importantes des clichés de diffraction à environ 90 K. Celles-ci révèlent un changement de l'ordre planaire des atomes de potassium.

Abstract. — An X-ray photographic study of the temperature dependence of the in-plane ordering of potassium in stage 2 KC_{24} single crystals was performed between 300 K and 10 K. In the disordered high temperature phase, one observes a modulation of the diffuse halo reflecting strong third-nearest neighbour correlations which develop as T is reduced. At 124 K $\pm$ 2 K long range ordering occurs and our diffraction data confirm previous studies. The present work shows, for the first time, that the diffraction patterns change drastically at about 90 K, thus revealing a change in the in-plane potassium order at low temperature.

1. Introduction.

X-ray structural studies [1-4] of stage 2 potassium intercalated graphite (KC_{24}) have confirmed the existence of two structural phase transitions at $T_U \simeq 123$ K and $T_L \simeq 98$ K. These transitions have also been detected by means of in-plane resistivity measurements [5]. According to these different authors, the upper transition is described as an order-disorder transition. At room temperature, the diffraction patterns obtained from highly oriented pyrolitic samples (HOPG)

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exhibit diffuse l-independent (l = Miller index in the direction perpendicular to the layers) scattering which reveals that only short range order correlation exists within the alkali layers while the different layers remain uncorrelated in the sample. A detailed study of this disordered state is not yet available. Some papers agree with a 2D closed-packed liquid-like structure where the alkali atoms are unregistered with the graphite lattice [6-8], while others suggest a planar lattice gas model where the potassium ions are restricted to occupy sites over the carbon hexagons centres [9, 10]. At T_U, the diffraction patterns of single crystals show Bragg reflections ($hk.0$) which are related to a long range order in the alkali layer plane while smooth modulations ($hk.1$) traduce interlayer correlations. The alkali planar lattice is hexagonal, incommensurate with the graphite host and rotated with respect to it. The stacking sequence is of the $\alpha\beta\gamma$ type. In addition, one can observe satellites which are distributed on circles about each of the six graphite (10.0) reflections. These satellites have been interpreted as strain induced modulations that reveal the interaction which exists between the graphite host and the alkali intercalant. Again, several interpretations have been proposed to decide which one of the graphite or the intercalant is modulated by the other [4, 7, 11]. Below T_U, the 3D coupling improves until T_L. At T_L, there is a second structural transition which is considered to involve a change in the stacking of the potassium layers ($\alpha\beta\gamma/\alpha'\ \beta'\ \gamma'$).

In the present paper we report the results of an X-ray diffuse scattering study of KC_{24} as a function of temperature between 300 K and 10 K. The experiments were performed on single crystals as is required for a proper analysis of the phase transitions. The data have been obtained by use of a photographic method which gives information mainly about the in-plane structural features. This study is the first one to provide a general overview of the phase transitions in KC_{24} in a broad temperature range. Important new features are observed in the high and low temperature regions, while previous results on the intermediate region, between T_U and T_L, are confirmed. This semi-quantitative study demonstrates that the behaviour of KC_{24} differs from that of higher stage potassium compounds and also from other alkali metal-intercalated graphite. This should initiate more detailed studies.

2. Experiments.

In the experiments we used single crystals of high quality [12] with typical dimensions $6 \times 1.5 \times 0.5$ mm. The samples were prepared by the two-bulb method and inserted in a Lindman glass tube under inert atmosphere. We performed X-ray diffraction stationary exposures with the CuK_α radiation. A doubly bent graphite monochromator focused the direct beam on the photographic film. The sample was attached with conductive paint to the cold finger of a displex cryocooler that allows the temperature to be varied continuously from room temperature to about 10 K with a stability of 0.5 K. Around the sample, a beryllium cylinder (R = 40 mm) was used as vacuum chamber and film holder. As the **c** axis was kept in the incident beam direction and was normal to the chamber axis, the reciprocal lattice ($hk.0$) positions can be obtained. The wave vector resolution Δq was typically 0.02 $Å^{-1}$ at q's of the order of 2 $Å^{-1}$.

With this photographic method one obtains a projected image of the intersection of the reciprocal space with the Ewald sphere. The patterns are therefore distorted and the correct location of the reciprocal lattice features has to be calculated using simple geometrical relations. Quantitative data were extracted from the photographs by means of microdensitometric readings.

3. Results.

X-ray diffraction photographs were taken at the following temperatures : 300, 200, 140, 130, 120, 110, 100, 90, 80, 50 and 10 K. Figure 1 displays a selection of these photographs showing the basic features of the structural changes occurring in that temperature range.

At room temperature, one can observe, on figure 1a, the alkali contribution as a ring-like diffuse scattering about the fundamental (000) reflection. The ring's intensity is not isotropic but shows six maxima oriented in the six graphite reciprocal { 10.0 } directions. The wave vector of the maximum is $q(hk.0) = 1.25 \pm 0.005$ Å^{-1}. This halo is repeated about each of the six graphite reciprocal lattice spots (10.0).

At 200 K (Fig. 1b) all the diffuse scattering concentrates in the maxima.

Then, at 140 K, each maximum splits into a pair of diffuse spots which are rotated by an angle $\pm\ \theta$ with respect to the graphite { 10.0 } direction. Thus the alkali diffraction pattern now consists of rings constituted by six pairs of broad diffuse spots around the (000) reflection and each of the six graphite (10.0) reflections. This diagram exhibits an apparent translational symmetry whose vector is equal to the unit vector of the graphite reciprocal lattice. The hexagonal symmetry of the pattern is associated with the symmetry operations of the graphite matrix and is a general feature of graphite intercalation compounds. The diffuse spots can be considered as primary reflections coming from some short range ordering in the alkali layer which is not specified for the moment. They will be labelled K(10) for those centred around the (000) reflection and K(10) × C(10) for the others (Fig. 2). These latter reflections are presumably due to a graphite induced modulation and will be referred below as modulation satellites. The wave vector of the K(10) spots is 1.26 ± 0.005 Å^{-1}. The intensity of the K(10) × C(10) spots is about three times weaker than that of the K(10) spots.

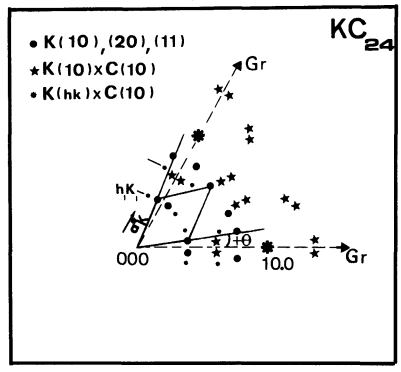

Fig. 2. — Schematic drawing of the 100 K photograph. Primary reflections are indexed as K(*hk*) while modulation satellites are labelled K(*hk*) × C(10).

On further cooling, the general features of the diffraction pattern do not change until 120 K (see Fig. 1c). However, in the range 140-120 K, the intensity of the diffuse spots slowly increases and their profiles sharpen (see Figs. 3 and 4), while the intensity ratio of the K(10) × C(10) types of spots do not appreciably vary. The θ angle also increases from $5.6° \pm 0.05°$ (140 K) to $7.5° \pm 0.02°$ (110 K) (Fig. 5). Although no data were taken in the 200-140 K temperature range, the splitting of the high-temperature single maximum is certainly detectable above 140 K [13]. From 140 to 120 K, the K(10)'s wave vector value remains constant and equal to 1.26 ± 0.005 Å^{-1}.

Then at 110 K, the diffraction pattern exhibits new well resolved reflections which can be divided into two sets for clarity. The first set corresponds to higher order reflections with respect to the primary K(10) ones (see Figs. 1d and 2). They reveal a marked improvement of the long range order and they allow to define two triangular lattices rotated by $\pm\ 7.5°$ from the graphite { 10.0 } direction and with a parameter $a_K = 5.74$ Å which is incommensurate with the graphite parameter $a_G = 2.46$ Å. Assuming primitive triangular lattices (one K atom per unit cell) the

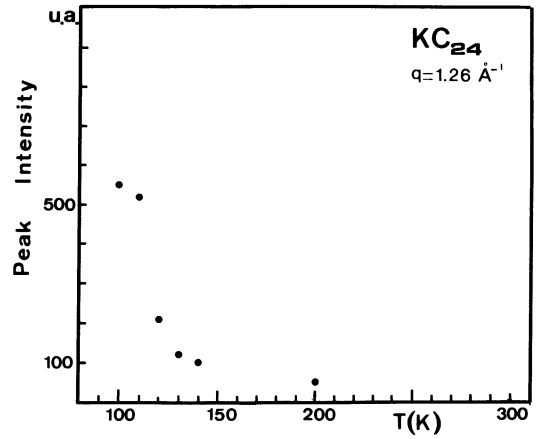

Fig. 3. — Temperature dependence of the K(10) peak intensity obtained from microdensitometer readings of the photographs, at $q = 1.26$ Å^{-1}.

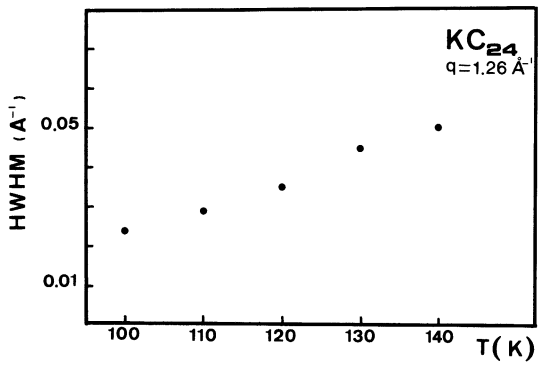

Fig. 4. — Temperature dependence of the K(10) width (HWHM) at $q = 1.26$ Å^{-1}.

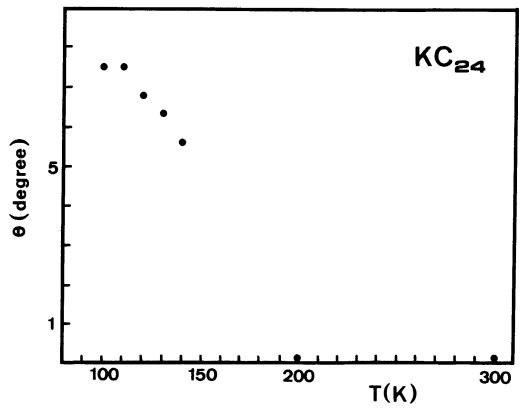

Fig. 5. — The rotation angle θ *versus* temperature. θ is the angle between the graphite { 10.0 } direction and the K(10) wave vector direction.

potassium concentration is easily derived from the a_K^2/a_G^2 ratio. In the present case, the composition of our crystal is found to be $C_{10.9\pm0.05}$ K.

The second set corresponds to higher order satellites of the K(10) × C(10) first order modulation satellites. In table I are reported the wave vector values of one reflection of each type and the complete pattern can be deduced using symmetry operations. Intensities visually estimated from the films are also given. The general geometrical features of the reciprocal lattice and in particular the wave vector values are in fair agreement with the results of Mori *et al.* [4] and Dicenzo [11]. However, the agreement with previous HOPG scans (see Fig. 2a in [4]) is not satisfactory, especially for the two first peaks for which the relative intensities are inverted compared with our photographs.

Table I. — *Indexing of the diffraction patterns based on Fig.* 1 *and Fig.* 2 *with the corresponding wave vector values q(hk.0) and observed intensities* I_0.

(*hk*.0)	*q*(*hk*.0) Å^{-1}	I_0
K(10)	1.26	Very strong
K($\bar{2}$1) × C(10)	1.27	Weak
K(0$\bar{1}$) × C(01)	1.75	Medium
K(11)	2.17	Medium
K($\bar{1}$1) × C(10)	2.42	Strong
K(20)	2.45	Weak
K(1$\bar{1}$) × C(01)	2.77	Medium

The phase transition at T_U is clearly second order as shown by the temperature dependence of the K(10) peak intensity (Fig. 3) and the transition temperature is estimated to be 124 ± 2 K. The peak width behaviour is less affected by the transition although a slight sharpening may be present between 120 and 130 K (Fig. 4). This effect should be studied in more detail.

Between T_U and 100 K no drastic change was noticeable in the (*hk*.0) plane. Then, at 90 K, a new complex diffraction pattern is observed which has not been reported before. It involves a great number of Bragg reflections (Fig. 1e). This pattern gets more intense and well resolved as the temperature decreases down to 10 K (Fig. 1f). This new set of reflections cannot be explained by a simple change in the stacking sequence as was proposed earlier [1-3]. Since no change in the overall geometry if the diffraction pattern was observed when the **c** axis of the crystal was tilted with respect to the direct X-ray beam, we consider that photograph 1f corresponds to the (*hk*.0) reflections of the new low temperature ordering. Therefore we are dealing with a new complex 2D structure, probably incommensurate and modulated by the graphite potential. The analysis of this structure is in progress and will require further photographic and diffractometer studies. The transition at T_L appears as involving a transition between two different types of 2D long range potassium orderings. The temperature range of T_L (90-100 K) is consistent with earlier studies [2-4].

4. Discussion.

From room temperature to 200 K, an orientational order exists in the disordered potassium layers as revealed by the modulation of the diffuse halo reflecting the six-fold symmetry of the graphite host. (Fig. 1a, b). It is noteworthy that the intensity maxima are centred on the six graphite { 10.0 } reciprocal directions. This is in contrast with the observations reported for

other alkali metal graphite compounds where the corresponding intensity maxima have always been found to be centred on the { 11.0 } directions. This is the case of C_S C_{24} [14-16] and of higher stage potassium graphite [17].

In the present study, the particular location of the maxima in the high temperature disordered phase reflects pronounced correlations between K atoms in the graphite { 10.0 } real space direction. Associating this with previous results showing that the K atoms are partly (60 %) or totally registered with respect to the graphite sites [9, 18], one can suggest that third nearest-neighbour correlations are dominant, indicating a strong tendency to form 2 × 2 arrangements.

In this respect, it is interesting to compare the experimental radial intensity scans $I(q)$ in the $\{ 10.0 \}_G$ direction (Fig. 6) with those calculated by Winokur, Rose and Clarke [14] for randomly decorated triangular lattices. Taking only into account the position ($q = 1.25$ Å^{-1}), the width ($\Delta q \simeq 0.3$-0.4 Å^{-1}) and the shape of the first maximum together with the concentration $C_{10.9}$ K, our results seem to be compatible with a model where 2 × 2 (third nearest-neighbours) correlations are enhanced (see table I, packing rules (a) and (b) in ref. [14]). However a better description of the 2D potassium arrangement would require quantitative comparisons of the experimental diffraction patterns with Fourier transforms of such models as we plan to do. Once more we would like to emphasize the particular behaviour of KC_{24} compound with temperature. This specificity is clearly related with the high concentration of alkali metal, namely KC_{11}, for a stage two.

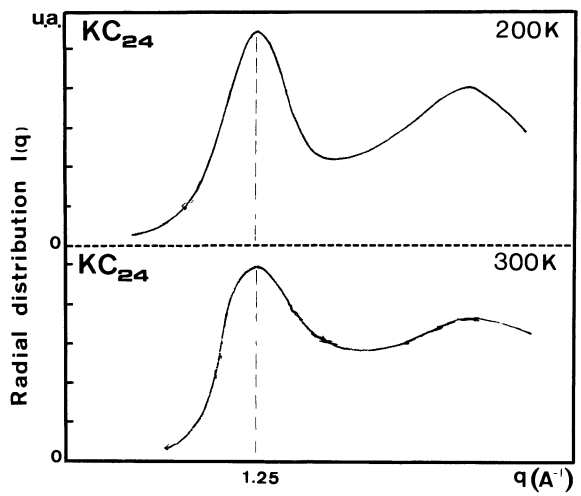

Fig. 6. — Densitometric readings in the radial graphite { 10.0 } direction at room temperature and 200 K. The diffusion provided by the Lindman glass tube has been subtracted.

At low temperature (< 100 K) the 2D structural order has still to be analysed. Considering the high complexity of the (*hk*.0) reciprocal lattice observed in the present study, the problem of the interlayer correlations should also be reinvestigated since previous studies on HOPG samples [1, 2] were not sensitive to the changes which occur in the 2D ordering at T_L.

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