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X-RAY DIFFRACTION FROM A TWO-DIMENSIONAL SOLID

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Résumé. — On décrit un montage simple ayant permis d'étudier la diffraction des rayons X par un solide bidimensionnel ; l'observation a porté sur la transition de phase solide congruent-solide non congruent de la monocouche de krypton adsorbé sur graphite à 80 K.

Abstract. — An arrangement to study the diffraction of X-rays by a two-dimensional solid is described ; spectra of the oriented and non-oriented solid monolayer of krypton adsorbed on graphite at 80 K are given.

Our aim is to demonstrate the potentialities of X-ray diffraction to study two-dimensional phases. In [1] the complexity and interest of their phase diagrams are shown, together with the difficulty of establishing the structure of these phases. Indeed low energy electrons do not propagate under pressures at which most of these transitions occur. Neutrons give interesting information, but they are scarce (limited number of experiments, poor statistics) ; resolution is poor ($\Delta\theta/\theta \simeq 10^{-2}$) ; contrast between adsorbate and substrate is weak : the best case is argon (scattering cross section 70 barns for its isotope 36) on graphite (5 barns).

To our knowledge a single tentative use of X-rays [2] has been made ; the apparatus did not operate below 147 K and only the liquid two-dimensional phase of xenon on graphite could be seen.

We present here some preliminary results with krypton on graphite ; they can be compared with adsorption isotherms [3], microcalorimetric measurements [4] and principally with structural studies by low energy electrons at low temperatures [5] and by neutrons [6, 7].

We use a classical powder diffractometer in the reflexion geometry :

- the generator (40 kV, 20 mA) has a copper anticathode ($\lambda = 1.5418 \text{ \AA}$),
- a bent monochromator out of a quartz monocrystal,
- an ω -2 θ goniometer,
- a proportional detector.

The diffraction plane is horizontal. 1/100 degree step-scanning is used in the most important angular domain. We choose the same substrate as used for neutron diffraction : an ex-foliated recompressed graphite (papyx from Carbone-Lorraine) which has numerous advantages over graphitized carbon like graphon ; it can be cut with a trimmer to get a plane reflecting surface which does not need to be supported by anything such as a beryllium sheet. The specific area is $20 \text{ m}^2/\text{g}$ (instead of $80 \text{ m}^2/\text{g}$ for graphon) but its preferential orientation [6, 8] largely overcomes this drawback. The sample is a hemicylinder with a vertical axis, 10 mm in diameter and 2 cm in height, held in a copper cylinder with a more than 180° opening having a mylar window. X-rays have to cross two similar windows (in the thermal shield and in the external wall of cryostat) but collimation is good enough to ensure the weakness of the signal due to diffusion by mylar. Preferential orientation of graphite optical c -axis is also vertical (in-plane geometry) ; this enhances the graphite $kh0$ lines and the diffraction by the adsorbed layer but eliminates most of the 002 line, the intensity of which will therefore be less disturbing. The cryostat uses liquid nitrogen flow ; a liquid nitrogen tank (with automatic refilling) was hung over it to increase autonomy without adding more weight to the goniometer table. Gas introduction is done through a glass apparatus developed by Y. Lahrer. As the dead volume is small (one half of the sample-holder cylinder and a pipe 15 cm long and 4 mm in diameter) the coverage can then be found from the quantity of gas introduced.

Figure 1 shows the diffraction spectra of graphite, bare (a) and covered with 0.75 (c) and 0.9 (b) monolayer (in the sense of [3]) at 80 K.

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FIG. 1. — Diffraction spectra of bare papyex (a), covered with 0.9 (b) and 0.75 (c) krypton monolayer at 80 K.

They show directly the evidence of an additional peak due to krypton. In neutron diffraction it was necessary to plot the difference between bare and covered spectra. This result emphasizes the power of X-ray diffraction which is due to

- the high cross section ratio between krypton and graphite (> 36),
- the good resolution ($\Delta\theta/\theta \simeq$ a few 10^{-3}); peak width is essentially due to grain size ($750 \times 300 \text{ \AA}$) and the distinction between the $\langle 002 \rangle$ line and $\langle 10 \rangle$ two-dimensional peak is plain,
- the weak background.

Note that the ratio between $\langle 002 \rangle$ and $\langle 110 \rangle$ intensities shows that cutting destroyed preferential orientation near the surface; this is somehow an advantage : 90 % of 002 line seems to come from this region and is not altered by the variation of X-ray absorption due to krypton, thus simplifying some interpretations.

After taking differences of spectra the additional peak has the characteristic shape of a 2-dimensional peak. The good resolution enables a direct analysis using table I in [9] :

- the half-width $\Delta\theta$ between the low angle half-maximum and the maximum gives the coherence length L of krypton domains :

$$L = 0.293 \lambda / \cos \theta \Delta(\theta) ;$$

— the position of its maximum gives Kr-Kr distance; a small displacement $0.52 \Delta(\theta)$ towards large angles due to the finite size L has to be taken into account; the precision is some 10^{-3} , i.e. better than any other method.

We found $L = 300 \text{ \AA}$, a value larger than obtained with neutrons ($130 \text{ \AA}$) for argon on grafoil as well as for krypton on papyex. The Kr-Kr distance is $4.26 \text{ \AA}$ for a 0.75 coverage and 4.065 for a 0.9 coverage. The first value is exactly that of the superstructure ($\sqrt{3} \times \sqrt{3}$) — 30° of the graphite surface. The second value means compression towards 3-dimensional krypton and a non-registered structure. In an observation by neutrons [7], this transition seemed to be partial but

- the statistics were rather poor,
- the neutron scattering sample had not been baked at 1500°C for one day as was done here; a difference which may also account for a larger coherence length L here.

The $\langle 20 \rangle$, $\langle 21 \rangle$ and $\langle 10 \rangle$ peaks are also present, but $\langle 11 \rangle$, $\langle 30 \rangle$ and $\langle 22 \rangle$ are under or near substrate lines.

Variations of the $\langle 002 \rangle$ line can also be observed and indicate a distance between krypton and carbon surface planes of about $3.35 \text{ \AA}$. Even a weak narrowing of this peak can be seen : the width in the difference spectrum is $2/3$ of the width of full $\langle 002 \rangle$ line according to the theory.

Variations of the 100 and 101 lines are characteristic of registry; we found persistence of some registry in the non-registered phase, which we attribute to static distortion waves due to the substrate [10].

We feel that X-ray diffraction allows a precise, rapid study with standard equipment of the structure of heavy atom monolayers adsorbed on a substrate composed of light atoms. We expect this method to develop further.

These experiments were done in the « Laboratoire de Rayons X of the C.N.R.S. » in Grenoble. They could not have succeeded without the very efficient help we were given. We are very grateful to the Director, Mr. Bertaut, who first recognized the interest of our project and the team which gave us quite exceptional hospitality : MM. de Bergevin, Brunel, Gremi, and Patrat. Discussions with MM. Croset and Thorel are also acknowledged.

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