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## Imaging of $\text{MnPS}_3$ lamellar material and of $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})$ ( $x = 0.2$ ) intercalated compound by Atomic Force Microscopy

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**Résumé.** — Cet article décrit l'observation de la surface du matériau lamellaire isolant  $\text{MnPS}_3$  et du composé d'intercalation  $\text{Mn}_{1-x}\text{PS}_3(\text{K}^+)_{2x}$  ( $x = 0.2$ ) par Microscopie à Force Atomique (AFM). Dans les deux cas, les surfaces sont observées avec une résolution atomique. Curieusement, les images AFM d'un cristal de  $\text{MnPS}_3$  révèlent trois types de surfaces. Comme attendu, nous avons observé le plan des atomes de soufre situés en surface; la distance mesurée entre deux atomes (3.5 Å) étant en parfait accord avec les données cristallographiques du matériau. Mais de plus, nous avons mesuré une autre périodicité (6.5 Å) qui apparaît également sur la surface du composé intercalé avec des ions potassium. Nous tentons d'expliquer ce phénomène par une modification structurale située à l'intérieur des feuillets de  $\text{MnPS}_3$ . Selon toute vraisemblance, il est possible que la présence d'espèces insérées dans l'espace interlamellaire soit la cause de cette perturbation. Dans le cas du composé  $\text{MnPS}_3$  pur, l'insertion spontanée et réversible de molécules d'eau pourrait expliquer les modifications structurales observées en surface.

**Abstract.** — The surface of the insulating  $\text{MnPS}_3$  layered material and the related intercalation compound  $\text{Mn}_{1-x}\text{PS}_3(\text{K}^+)_{2x}$  ( $x = 0.2$ ) were observed by Atomic Force Microscopy (AFM) with an atomic resolution. Unexpectedly, pure  $\text{MnPS}_3$  surface displays three types of images. The sulfur atom plane is naturally observed, with a S-S distance (3.5 Å) in good agreement with the crystallographic structure. Moreover, we measured an other periodic spacing (6.5 Å) which also appears on the images of the potassium intercalate surface. This feature is discussed in terms of structural modifications inside a  $\text{MnPS}_3$  sheet. The presence of guest species in the interlamellar space could explain this modification. In the case of pure  $\text{MnPS}_3$ , water molecules could be reversibly inserted between the layers, thus disturbing the slab structure.

### 1. Introduction.

As shown by Highly Ordered Pyrolytic Graphite (HOPG) and mica used as calibration standards in STM [1-5] and AFM [6-9] respectively, lamellar compounds are very convenient for the study of surfaces by near-field microscopies [10-15]. After cleavage, their surfaces are indeed without

impurities and perfectly planar on the atomic scale. The possibility of intercalating atomic or molecular species into the interlayer space results in composite materials with physical properties that are often different from those of the host lattice. However, several problems occur for the determination of the structure of these intercalated compounds, and we think that near-field microscopies could contribute to clear up these difficulties. Up to now, only a few intercalated compounds of graphite have been studied by STM [16-20], but their air-sensitivity makes the study of their surfaces rather difficult.

Within layered materials, the insulating hexathiohypodiphosphate  $MPS_3$  compounds [21-24] ( $M = Mn, Fe, Cd, Ni$  in the +II oxidation state) offer several advantages: they are available as monocrystalline flat platelets and are able to intercalate a great variety of cationic molecular species [25-29]. Moreover, the resulting intercalation products are perfectly air stable over very long periods [27]. Each sheet of  $MPS_3$  consists of sandwiches of layers of closed packed sulfur atoms enclosing layers of phosphorus and metal [21] (Fig. 1).  $MPS_3$  slabs have also been described as coordination compounds made of  $M^{2+}$  cations coordinated to  $P_2S_6^{4-}$  bridging ligands [27-28]. This last feature is important to understand the unusual intercalation process which takes place in these materials. A large range of  $M_{1-x}PS_3(G_{2x})$  ( $G$  monocation) can actually be synthesized via a unique cation exchange process in which the electrical charge of the entering cationic guest species is counterbalanced by the loss of part of the intralayer  $M^{2+}$  cations [26-27]. The resulting materials contain intralamellar metallic vacancies and have physical properties that are very different from those of the pure host lattice [29-33].

Here we present an AFM study of the surface of pure  $MnPS_3$  crystals and of the potassium intercalate  $Mn_{1-x}PS_3(K^+)_{2x}(H_2O)(x = 0.2)$ .

## 2. Material and methods.

Pure  $MnPS_3$  was synthesized as previously described [21]. Monocrystalline platelets (approx.  $4 \times 4 \times 0.05 \text{ mm}^3$ ) were grown from the vapor phase, by heating stoichiometric mixtures of the elements at 750-780 °C in quartz ampoules sealed under vacuum. Intercalation of potassium ions was carried out by soaking  $MnPS_3$  platelets into an excess of  $\approx 2M$  aqueous solution of KCl for about 30 minutes [25,27]. The intercalated samples were then rinsed with water and air dried. The samples were finally glued on the sample holder and cleaved prior to examination.

Imaging the sample surface was carried out using a commercial Nanoscope II AFM equipment from Digital Instruments (Santa Barbara California U.S.A.) equipped with a 100  $\mu\text{m}$ -long  $Si_3N_4$  cantilever with a spring force constant of 0.58 N/m. The force intensity used was about  $2 \times 10^{-8}$  N. The surface of the crystals was scanned (10 to 20 lines/sec) using the height mode, where the force and hence the distance between the tip and the surface is kept constant. All images ( $400 \times 400$  pixels) were obtained in the air at room temperature using slight high and low pass filtering during data acquisition.

## 3. Results.

**3.1 PURE  $MnPS_3$ .** — The AFM images of a pure  $MnPS_3$  crystal after cleavage unexpectedly showed three types of atomic arrangements noted A, B and C. Figure 2a reveals an hexagonal pattern of spots separated by 3.5 Å (Type A). This distance fits very well with the sulfur-sulfur crystallographic distance [21] suggesting that this image is a layer of sulfur atoms of the  $MnPS_3$  sheets. This hexagonal pattern as well as the 3.5 Å period is also found on the 2D Fast Fourier Transform (2D-FFT) of figure 2a (Fig. 2b). A second type of surface, recorded on the same

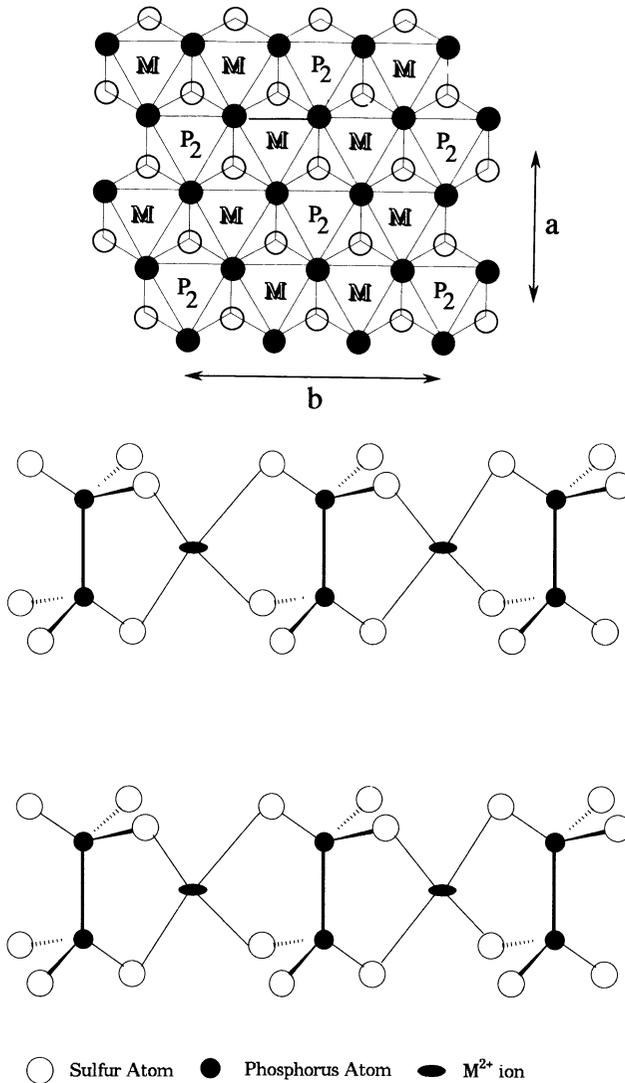


Fig. 1. — a) Schematic top view of a single  $\text{MPS}_3$  slab. The sulfur atoms describe octahedra which share edges to generate the layer. The  $\text{M}^{2+}$  ions and the  $\text{P}_2$  pairs (perpendicular to the plane of the figure) are located inside the sulfur octahedra. The  $a$  and  $b$  axis of the monoclinic unit cell are shown ( $a = 6.077 \text{ \AA}$  and  $b = 10.524 \text{ \AA}$  for the  $\text{MnPS}_3$  material [21]). b) Layer stacking in a perspective view. Each third  $(\text{P}_2\text{S}_6)^{4-}$  unit coordinated to each  $\text{M}^{2+}$  ion was omitted for clarity.

sample in a different area, is shown in figure 2c (Type B). As previously, an ordered hexagonal pattern of the protrusions is observed, but the periodic spacing is this time around  $6.5 \text{ \AA}$ . Scanning always the same sample of  $\text{MnPS}_3$ , a third type of surface on which both previous distances were simultaneously measured was imaged (Type C). The crude image is not really different from figure 2a (Fig. 2d), but its 2D Fast Fourier Transform (2D-FFT) (Fig. 2e) displays twelve spots grouped in two hexagons, the inner one being rotated by  $30^\circ$  with respect to the external one. The outer peaks correspond to the  $3.5 \text{ \AA}$  period, and the inner peaks to the  $6.5 \text{ \AA}$  period. Figure 2f shows

the filtered image of this surface obtained by performing the inverse Fourier transform from the twelve bright spots on the 2D-FFT. The superimposition of two hexagonal arrangements is then observed (see the bottom left corner of Fig. 2f). Two protruding points are separated by  $\approx 6.5 \text{ \AA}$  whereas the distance between two “lower” points is  $\approx 3.5 \text{ \AA}$ .

**3.2  $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(\text{H}_2\text{O})(x=0.2)$  INTERCALATE.** — Figure 3a shows an unfiltered AFM image of the  $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}(x=0.2)$  intercalate surface. Despite a noisy scan, the resolution on the atomic scale is preserved and an ordered atomic arrangement appears. The 2D-FFT of this image (Fig. 3b) displays twelve peaks drawing two imbricated hexagons as previously observed in pure  $\text{MnPS}_3$  (Fig. 2e). The autocorrelation of figure 3a (Fig. 3c) clearly reveals spots at different heights in the real space. The distance is  $\approx 6.5 \text{ \AA}$  between two protruded spots and  $\approx 3.5 \text{ \AA}$  between two “lower” points. Unexpectedly, these periods measured on the potassium intercalate surface fit very well with those found on the pure  $\text{MnPS}_3$  surface.

However, the contrast between the protruding and the lower spots is more apparent in the images of intercalate than in those of pure  $\text{MnPS}_3$ . Other potassium intercalated samples display a slightly different atomic arrangement. Thus, figure 3d shows a superimposition of two atomic planes. An ordered hexagonal disposition of atoms can be observed on the upper plane, whereas on the lower plane, the atoms form a pair and seem to be “bound” to an upper atom.

#### 4. Discussion.

Interpretation of the present AFM images raises a number of issues which need to be clarified. Except for figure 2a which reveals an expected image of a sulfur atom layer of the  $\text{MnPS}_3$  sheets, the understanding of the other images is not simple. The protruding spots observed at the surface of the potassium intercalation compound might tentatively represent potassium cations ordered on the top of a layer of sulfur atoms. However, this hypothesis can be convincingly ruled out, since a pyridinium ( $\text{C}_5\text{H}_5\text{N}^+$ ) intercalate sample which does not contain any potassium cations displays an identical image (unpublished observation). The periodic spacing close to  $6.5 \text{ \AA}$  measured on pure  $\text{MnPS}_3$  surface as well as on intercalate surface could be assigned to the distance between phosphorus atoms of two P-P pairs (within the estimated error of  $\leq 10\%$  due to the drift and other uncertainties of the AFM) (Fig. 1). However, as these atoms constitute a lower lying layer, it is most unlikely that they represent the protruded spots observed in figures 2f, 3c and 3d. Therefore, we think that all spots seen in these figures represent sulfur atoms. Some of them protrude with a period of  $6.5 \text{ \AA}$  which is also a distance found in the lattice (a parameter of the unit cell). The images shown in figures 2f, 3c and 3d suggest that structural modifications occurred within the  $\text{MnPS}_3$  sheet. The precise nature of these modifications is not clear yet and two explanatory hypothesis may be proposed.

At first, cations intercalation in the interlamellar space is counterbalanced by a removal of  $\text{Mn}^{2+}$  intralayer ions, leading to intralayer  $\text{Mn}^{2+}$  vacancies [27]. In this case, the six sulfur atoms surrounding each vacancy are destabilized and, in a first approach, we thought that a dilatation of the octahedra formed by these sulfur atoms could result in the superimposition of two atomic planes observed in figures 2f, 3c and 3d. However, due to the amount of vacancies ( $\approx$  one fifth of the  $\text{Mn}^{2+}$  cations,  $x = 0.2$ ), it is difficult at present to find a model accounting for the observed images (Figs. 2f and 3c) which would imply that one sulfur atom out of three sticks out. Moreover, such protruding atoms separated by  $6.5 \text{ \AA}$  can be seen in some areas at the surface of pure  $\text{MnPS}_3$  (Fig. 2f), whereas the pure material should not contain any manganese vacancies. Therefore, this first assumption seems rather unlikely.

As a second possibility, we suggest that the intralayer  $(\text{P}_2\text{S}_6)^{4-}$  entities undergo a rotation

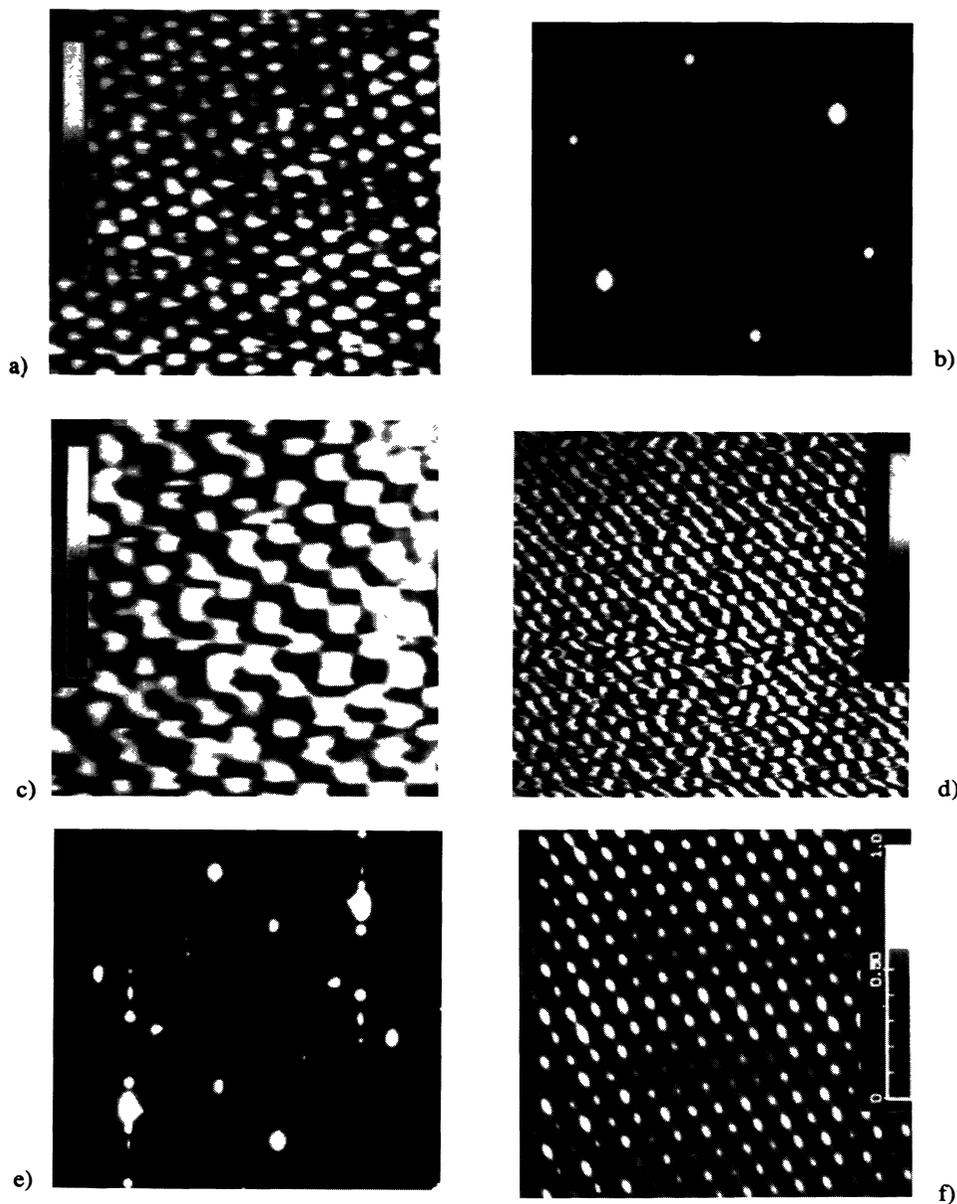


Fig. 2. — a) Unfiltered AFM image of a pure  $\text{MnPS}_3$  area ( $6 \times 6 \text{ nm}^2$ ) (Type A). The distance between spots is close to  $3.5 \text{ \AA}$ . b) 2D-FFT of figure 2a: six peaks describe one hexagon corresponding to a  $3.5 \text{ \AA}$  period. c) Unfiltered AFM image of pure  $\text{MnPS}_3$  area ( $6 \times 6 \text{ nm}^2$ ) (Type B). The periodic spacing is  $\approx 6.5 \text{ \AA}$ . d) Crude AFM image of a pure  $\text{MnPS}_3$  area ( $8 \times 8 \text{ nm}^2$ ) (Type C). e) 2D Fast Fourier Transform (2D-FFT) of figure 2d: twelve peaks draw two hexagons rotated with respect to each other; the other peaks are assumed to arise from noise or instrumental effects. f) Filtered image ( $6 \times 6 \text{ nm}^2$ ) of figure 2d obtained by performing the inverse Fourier transform: a superimposition of two hexagonal arrangements of spots can be seen in the bottom left corner of the image.

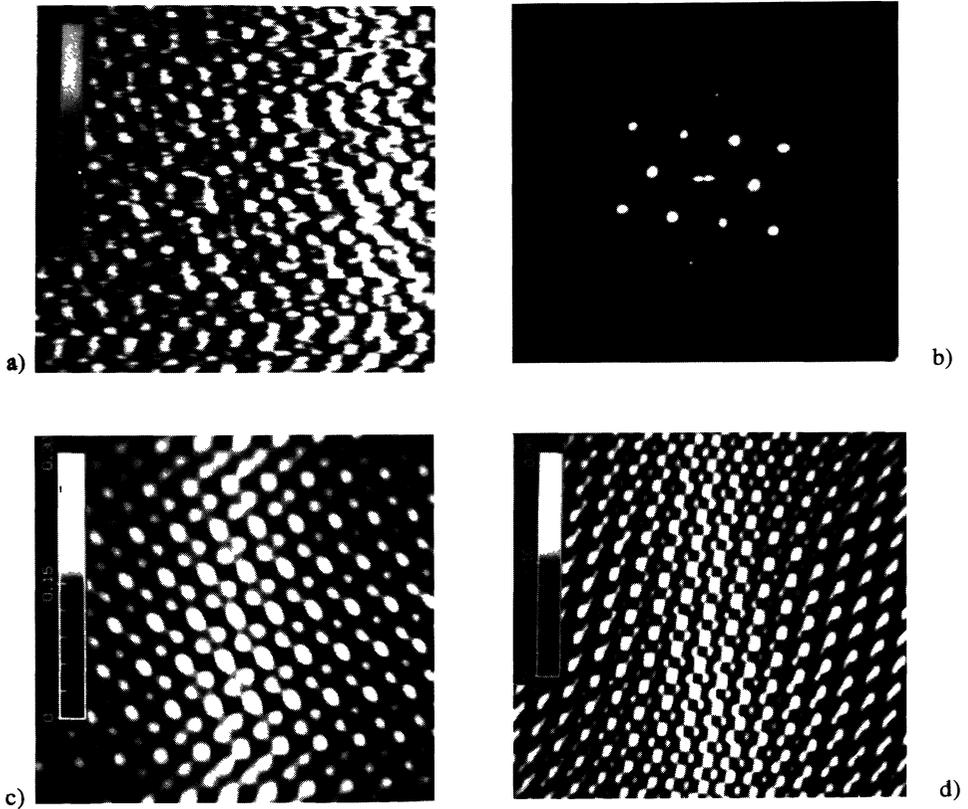


Fig. 3. — a) Crude AFM image of a  $8 \times 8 \text{ nm}^2$  area at the surface of a potassium intercalate  $\text{Mn}_{1-x}\text{PS}_3\text{K}_{2x}$  ( $x=0.2$ ) crystal. b) 2D-FFT of figure 3a: twelve peaks describe two hexagons rotated with respect to each other. c) Autocorrelation filter image of figure 3a: superimposition of two hexagonal arrangements, the inner one being rotated by  $30^\circ$  with respect to the outer one. d) Autocorrelation image of a surface of another potassium intercalate sample: the atomic disposition is slightly different from that observed in figure 3c.

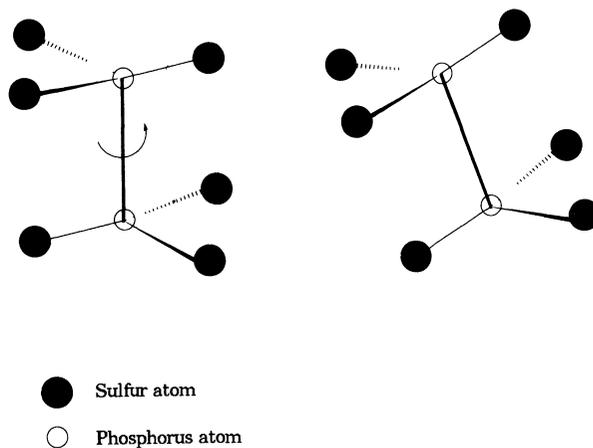


Fig. 4. — Schematic representation of the  $(\text{P}_2\text{S}_6)^{4-}$  entity rotation. After this rotation, all the upper sulfur atoms are not in the same plane.

around the P-P axis because of the presence of the intercalated species (Fig. 4) [23]. So, the three upper sulfur atoms would not stay in the same plane. Two of those would be coplanar and the third would be in a different plane. This structural feature clearly appears in the figure 3d. The similarity between pure  $\text{MnPS}_3$  surface (Fig. 2f) and potassium intercalate surface (Fig. 3c) could be due to the intercalation of  $\text{H}_2\text{O}$  molecules in the interlamellar space of the pure  $\text{MnPS}_3$  compound. These molecules could contribute to the slight rotation of the  $(\text{P}_2\text{S}_6)^{4-}$  entities. Moreover, we have often observed changes on the pure  $\text{MnPS}_3$  surface: on the same scanned area, the spot arrangement is always hexagonal but, upon scanning the distance between spots was alternatively 3.5 Å and 6.5 Å. Depending on the humidity, the amount of  $\text{H}_2\text{O}$  molecules in the interlamellar spacing of  $\text{MnPS}_3$  would vary, thus reversibly disturbing the structure of slabs. Up to now, the precise nature of the interaction between the host lattice and the guest species which causes this rotation still remains unknown.

This work shows that the surface of  $\text{MnPS}_3$  crystals can be studied by AFM with atomic resolution. As a main striking result, this atomic resolution is preserved even after intercalation has occurred, although this process is known to cause many defects. Unexpected structural features seen on the pure  $\text{MnPS}_3$  surface make the images more difficult to interpret than expected from previous AFM or STM studies on the layered dichalcogenides [10,13,34]. As already carried out for other lamellar compounds [14,35,36], calculations of the total electron density distribution is now necessary to analyse these first observations. By comparison with pure  $\text{MnPS}_3$ , the observations of other  $\text{MPS}_3$  material (with  $\text{M} = \text{Fe}, \text{Ni}$  or  $\text{Cd}$ ) surfaces will be considered. Further studies are in progress using a technically improved equipment. Scanning  $\text{MnPS}_3$  crystal surface in a liquid containing cationic species should lead to a better understanding of the intercalation process.

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