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PREPARATION AND CHARACTERIZATION

X-RAY AND ELECTRON MICROSCOPY STUDIES OF SINGLE-LAYER TaS_2 AND NbS_2

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Single-molecular-layer suspensions and various restacked forms of the metallic layered compounds TaS_2 and NbS_2 were prepared using the intercalation of hydrogen and water. It was found that the intercalation of water separates the layers by at least 10 nm and single-layer X-ray diffraction patterns with only (*hk*.0) lines are observed for this system. Single layers in suspension are readily made from the water-intercalated material. Restacked films obtained from dried suspensions appear to have a random layer stacking sequence. Electron microscopy shows evidence of single layers up to 200 nm in lateral size in the suspension. The charge density wave superlattice diffraction pattern which is observed in bulk crystalline TaS_2 below 75 K is not observed in thin platelets obtained from TaS_2 suspensions.

1. INTRODUCTION

For a long time there has been an interest in two-dimensional atomic and electronic systems. Dimensionality effects including localization and the quantum Hall effect[1,2], for example, are of considerable current interest. The layered transition metal dichalcogenides, well known for their pseudo-two-dimensional structure, appear to be ideal materials for two-dimensional studies when they are dispersed into a single-molecular-layer form. By such a form we mean an ordered layer of tantalum atoms sandwiched between two layers of sulphur atoms which are chemically bonded to the tantalum. Such single molecular layers of TaS_2 form the basic building blocks of the layered compounds. Murphy and Hull[3] have shown that hydrogen can be electrointercalated into TaS_2 and that a high degree of exfoliation can be obtained by subsequent intercalation of water. Agitation of this system in a high speed blender produces a dispersion and Murphy and Hull[3] have presented evidence that this dispersion consists of single TaS_2 layers, basing their conclusion on dye adsorption studies and that, when a dispersion (with a surfactant) is ultracentrifuged, X-ray patterns indicate that the surfactant is observed between each layer. The work presented here is part of a study being carried out on single-molecular-layer suspensions and thin films obtained by the restacking of macro-

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scopic layers. Thin films thus obtained cannot be grown by conventional crystal growing techniques and studies on such systems should help in the understanding of the effects of interlayer interactions and periodicity on the properties of layered compounds.

2. EXPERIMENTAL DETAILS

2.1. Preparation of single layers

The starting materials were single crystals of 2H-TaS_2 and 2H-NbS_2 which were grown from high purity elements by vapour phase transport with iodine as the transport agent. Following Murphy and Hull[3], single layers were obtained by the intercalation of hydrogen and water into these single crystals with subsequent ultrasonic dispersion. Hydrogen ions were intercalated electrolytically with a 1 M H_2SO_4 solution as electrolyte and with the crystal as the cathode and a platinum sheet as the anode. For a crystal of 2–4 mg, typically 4 mm × 5 mm × 0.02 mm in size, a constant current of 50–80 μA was usually used. The potential between the electrodes was around 1.65 V at the beginning of hydrogen intercalation and increased gradually to around 2 V a few hours later. The electrolysis was terminated using a sharp increase in current of about 50–80 mA (the potential increased correspondingly to about 3 V) for a fraction of a second and violent bubbling was observed at both electrodes. The crystal was then taken out of the acid and put into deionized water where a considerable expansion (by a factor of approximately 30) could be observed. The surface of the water-expanded crystal became silvery while the inside part was dark brown. The effects on the crystal of the sharp increase in hydrogen intercalation current are not entirely clear; however, we have found that the water expansion proceeds more quickly and uniformly in crystals that have been subjected to such treatment.

To make single-layer suspensions, the inside part of the expanded crystal was put into a test-tube with deionized water and was broken up into a uniform suspension by placing it in an ultrasonic cleaner for a few seconds. (It was found that the inner brown region of the expanded crystal was more readily dispersed than the outer crystal region.) A coloured suspension was obtained from the ultrasonic treatment and the results presented below indicate that such suspensions consist of freely floating single layers.

Concentrated single-layer suspensions of both TaS_2 and NbS_2 (about 1 mg cm^{-3}) are dark brown for a 1 cm path length. It was observed that single layers of TaS_2 in suspension tend to flocculate in about 1 h and the suspension usually became clear after about 1 day as the floccules settled to the bottom of the test-tube. The NbS_2 single-layer suspensions were observed to be much more stable with regard to flocculation. Dilute NbS_2 single-layer suspensions can last for more than 1 week without serious flocculation. As noted by Murphy and Hull[3], a slight odour of hydrogen sulphide emanates from fresh TaS_2 water suspensions which becomes quite strong after a few days. However, for NbS_2 suspensions, no such odour was smelt even after 1 week.

The experimental work described here is mainly concerned with TaS_2, but similar results were also obtained for NbS_2.

2.2. X-ray powder pattern of TaS_2 layers

X-ray powder diffraction patterns were obtained using nickel-filtered Cu Kα radiation in a Debye–Scherrer camera 57.3 mm in diameter on a Philips 1 kW X-ray machine. The X-ray examination was carried out immediately after the crystals were water expanded, using the inside part of the "expanded crystal" which was mounted at the end of a thin wall (approximately 10 μm) glass capillary (about 0.2 mm in diameter). A short exposure of about 20 min was used. For longer exposures (about 34 min) deintercalation of water was observed.

When a water-expanded TaS_2 crystal was allowed to dry, it reverted to the original thickness. Uniform thin films can be obtained by allowing the suspension to dry on glass. X-ray powder photography was also performed on these materials.

2.3. Electron microscopy of TaS_2 layers

The specimens for the electron microscopy work were prepared by spreading a small drop of dilute single-layer TaS_2 water suspension over a carbon support film on a copper grid. They were then examined in a Philips 300 electron microscope at an accelerating voltage of 100 kV. Cold blades in the microscope were cooled with liquid nitrogen to limit contamination of the sample.

Crystal thicknesses were measured from the image contrast defined as $\ln(I_0/I)$ where I and I_0 are the intensities of the electron microscopic images with and without the presence of the crystal in the electron beam respectively. Electrons collected by a Faraday cage were transmitted to a Keithley 600A electrometer and read directly with a PDP8 computer. The readings were taken in quick succession in order to minimize the effects due to contamination and beam fluctuations. The contrast measurements were reproducible to within $\pm 2\%$. The absolute value of the thickness was obtained by using a graph of contrast *versus* thickness which was obtained from a series of contrast measurements of thinly cleaved bulk 2H-TaS_2 samples with thicknesses in the range 20–60 nm. These thickness values were determined by measuring the optical density for the mercury green line (wavelength, 546.1 nm).

Electron diffraction patterns were taken from thin platelets obtained from TaS_2 suspensions at 25 K [4].

3. RESULTS AND DISCUSSION

The X-ray powder photograph results for TaS_2 are shown in Fig. 1, where Fig 1(a) is the X-ray pattern of the original 2H-TaS_2 crystal, Fig. 1(b) is that of the water-expanded TaS_2 crystal, Fig. 1(c) shows the water-expanded TaS_2 crystal with some partially deintercalated regions, Fig. 1(d) shows the powder pattern when the water-expanded crystal is totally dried or deintercalated of water, and Fig. 1(e) shows the powder pattern of layers obtained from a dried single-layer water suspension. The indices of some main diffraction lines for Figs. 1(a), 1(b) and 1(d) are shown in Fig. 2. For clarity, some very very weak lines and the doublets in the high angle region are not shown. The heights of the lines in Fig. 2 indicate the relative diffraction intensity qualitatively.

From Figs. 1(b) and 2(b) we can see that the water-expanded crystal gave no $(00.l)$ lines and no $(hk.l)$ $(l \neq 0)$ mixed lines. After deintercalation of water the crystal

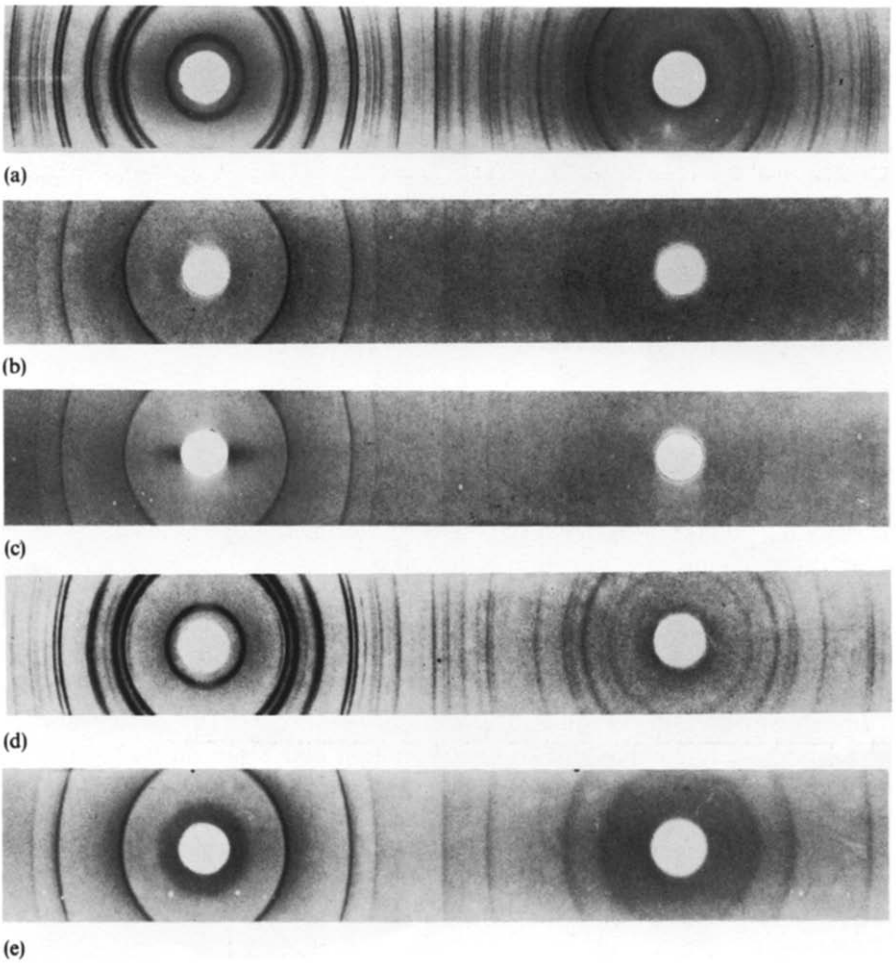

Fig. 1. The X-ray powder patterns for (a) part of the original 2H-TaS_2 crystal (made into powder), (b) the water-expanded TaS_2 (immediately after the intercalation of water), (c) the sample as in (b) with partial deintercalation of water from some of the sample, (d) the restacked TaS_2 from the water-expanded crystal after complete deintercalation of water and (e) the randomly stacked TaS_2 film obtained by drying a single-layer suspension on glass.

gave a pattern similar to the original 2H-TaS_2 pattern. The positions of (*hk*.0) lines for either the water-expanded crystal (Fig. 2(b)) or the deintercalated crystal (Fig. 2(c)) relative to the original crystal indicated that there is no significant change in the layer *a* axis to within 1%.

In the pattern shown in Fig. 1(c) the diffuse diffraction arcs in the low angle region indicate the deintercalation of water. In this diffuse background, three (00.*l*) lines can be identified at 4.8°, 6.0° and 7.25° which correspond to spacings between neighbouring layers of 3.6_9 nm, 3.6_9 nm and 3.6_7 nm if the lines are taken to be (00.4), (00.5) and (00.6) respectively (this nomenclature refers to only one layer per unit cell). The consistency of the spacing indicates that these lines are not due to three different interlayer spacings. It appears that this 3.7 nm spacing corresponds to

a phase between the completely water-expanded crystal and the totally deintercalated crystal. This spacing is about six times the initial spacing of 2H-TaS_2 and is consistent with the observed crystal expansion on complete water intercalation of about 30 times. From our observation we can safely say that before the deintercalation of water the average spacing between neighbouring layers of the water-expanded crystal is more than 10 nm. Similar diffraction lines were observed with the deintercalation of water-expanded NbS_2 crystals at 5.6°, 7.0° and 8.45° giving spacings of 3.1_6 nm, 3.1_6 nm and 3.1_5 nm respectively if these lines correspond to the (00.4), (00.5) and (00.6) reflections.

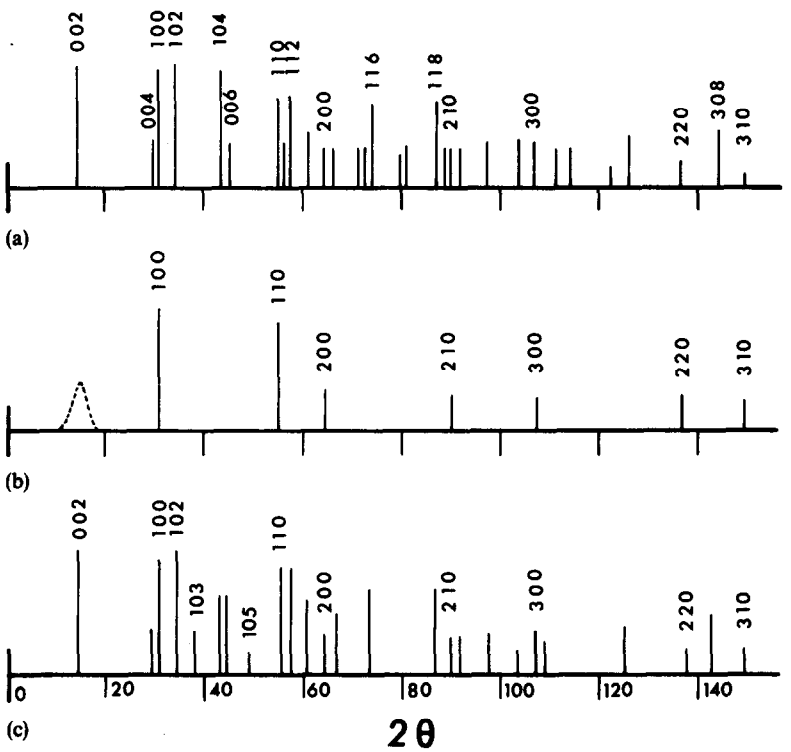

Fig. 2. Qualitative intensities for (a) the original 2H-TaS_2, (b) the water-expanded TaS_2 (– – –, the (00.2) linewidth expected for a hypothetical two-layer group structure) and (c) TaS_2 after deintercalation of water.

The X-ray diffraction pattern of the random stacking TaS_2 films obtained by drying a single-layer suspension on glass (Fig. 1(e)) shows a very broad (00.2) line in the low angle region implying that the particle size along the *c* axis is very small. It is hard to determine the linewidth because part of the line falls into the punch hole region; however, the pattern indicates that the particle size along the *c* axis is only a few layers thick. It was also noted that the positions of the (*hk*.0) lines in Fig. 1(e) are slightly displaced towards larger angles compared with the original 2H-TaS_2 pattern and that they also appear to be somewhat asymmetric, falling off more gradually to larger angles. These features conform to the analysis of two-

dimensional diffraction by Warren[5] and support the view that this material consists of randomly stacked layers. The line shape of the pattern shown in Fig. 1(b) is not significantly affected, however. This is mainly because before the ultrasonic treatment the lateral dimensions of layers are large. Along the c axis the large and probably non-uniform spacing of water between neighbouring layers results in the absence of the $l \neq 0$ lines.

Figure 1(d) shows that, when the water deintercalates, the layers mostly restack back to the original 2H structure. The increasing intensity of the (10.3) and (10.5) lines and other changes in the high angle region in Fig. 1(d) show that stacking faults and possibly some other (stacking) sequences result during the restacking process.

The absence of all the $l \neq 0$ lines in Fig. 1(b) indicates that water molecules have intercalated into every van der Waals gap. It is easy to show[6] that for a group of N parallel layers the scattering profile of a (00.l) reflection is of the form

$$I = \frac{\sin^2(2\pi N d \sin\theta/\lambda)}{N \sin^2(2\pi d \sin\theta/\lambda)} \tag{1}$$

where I represents the intensity and the other symbols have their usual meanings. From this expression we can see that at a Bragg angle the peak intensity decreases and the linewidth increases as N decreases. For $N = 2$ the (00.l) lines get maximally broadened and for $N = 1$, *i.e.* single-layer groups, there will be no (00.l) lines. From both the theoretical calculation and the experimental observation we know that for 2H-TaS_2 the relative intensity of the (00.2) reflection is about 2.6 times higher than the (10.0) and about 3 times higher than the (11.0) reflection. If the water-expanded TaS_2 crystal contains significant numbers of two-layer groups, a broad (00.2) line should appear in the X-ray pattern as shown by the broken curve in Fig. 2(b). No evidence for such (00.2) scattering is seen in Fig. 1(b), so that we can conclude that the sample contains no significant number of two-layer or other multiparallel layer groups. We can thus call the pattern shown in Fig. 1(b) a single-layer X-ray pattern.

The presence of large amounts of water between the layers greatly reduces the strength of the interlayer bonding so that single-layer suspensions are readily obtained by a small amount of ultrasonic dispersion. The single-layer form of particles in suspension is confirmed by the electron microscope results. The specimens made from single-layer suspensions show many clusters of particles. Their electron diffraction pattern consists of rings corresponding to the $hk.0$ reflections from the basal plane of the 2H-TaS_2 structure showing that the particles are randomly normal to the c axis. In addition, very thin isolated platelets are also observed. Electron diffraction patterns from such platelets were usually of single-crystal type, again corresponding to the basal plane $hk.0$ reflections.

A graph of contrast *versus* thickness for 2H-TaS_2 is shown in Fig. 3. Using this graph, some thin platelets obtained from the single-layer suspension were estimated to be 1.2 nm thick. The errors are in the range of $\pm 30\%$. Thinner platelets were also observed but their thickness could not be estimated because the change in contrast was too low to be measured, and we conclude that they were single molecular layers corresponding to a thickness of 0.6 nm as expected from the X-ray patterns of the water-expanded samples.

Finally, Fig. 4(a) shows an electron microscope photograph of a thin single-crystal platelet obtained from a TaS_2 suspension and Fig. 4(b) is the electron

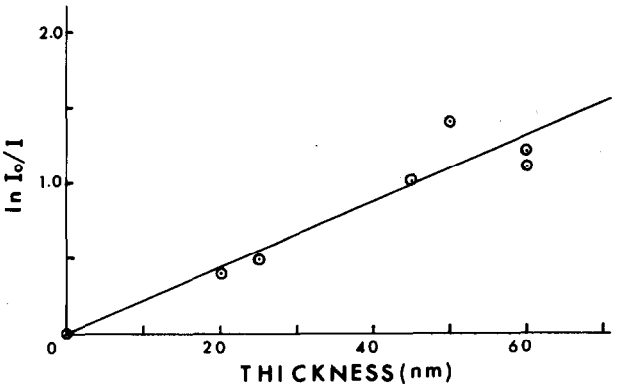

Fig. 3. A graph of the electron microscope image contrast $\ln(I_0/I)$ *vs.* crystal thickness for 2H-TaS_2 single crystals, where I is the transmitted intensity and I_0 is the incident intensity.

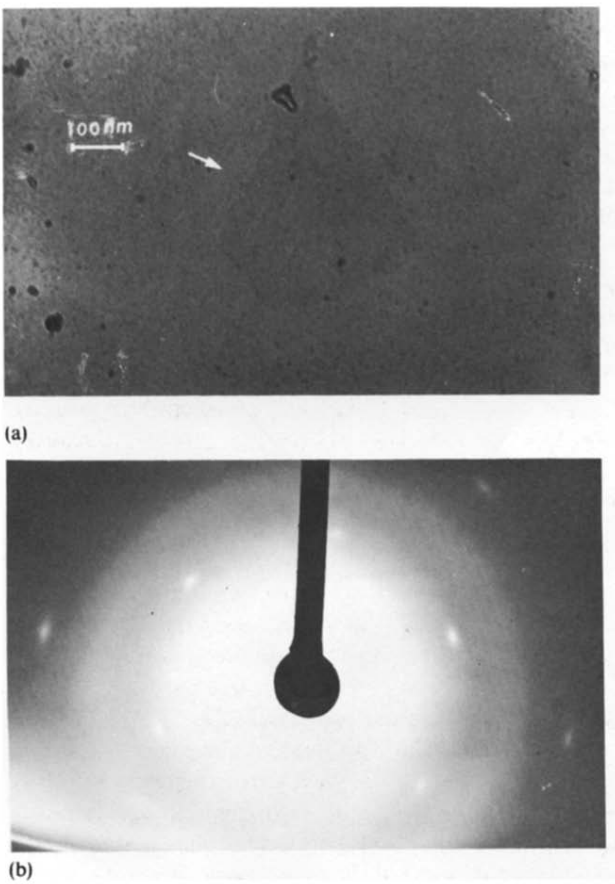

Fig. 4. (a) Electron microscope photograph of a thin single-crystal TaS_2 platelet probably two layers thick. The arrow points to the edge of the platelet. The contrast has been increased photographically to maximize the observability. (b) Electron diffraction pattern of the TaS_2 platelet shown in (a) at 25 K. The 100 kV electron beam is in the [000.1] direction. The six reflections closest to the centre of the figure are $(10\bar{1}.0)$ reflections and the other reflections are $(11\bar{2}.0)$ reflections.

diffraction pattern of this platelet at 25 K. Figure 4(b) shows no charge density wave (CDW) superlattice diffraction pattern while with the original 2H-TaS_2 a CDW superlattice diffraction pattern is seen below 75 K [7]. The failure to observe a CDW diffraction pattern in Fig. 4(b) has a number of possible explanations. The signal-to-noise level for the spots in the pattern will decrease as the specimen thickness decreases; thus for very thin specimens the CDW diffraction pattern may not be detectable above the noise. There may also be a physical effect such that a CDW simply does not form in crystals a few layers thick. Finally the method of specimen preparation may lead to a loss of stoichiometry and this could cause the absence of CDWs.

Further work is needed to account for the absence of a CDW diffraction pattern in Fig. 4(b).

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