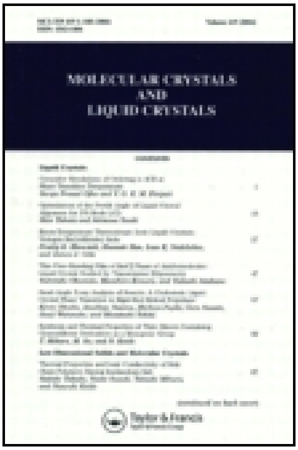

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Restacking Exfoliated Layered Compounds

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RESTACKING EXFOLIATED LAYERED COMPOUNDS

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Abstract Single-molecular-layer MoS_2, prepared by exfoliation of lithium-intercalated MoS_2 in water or alcohols, was deposited on supports such as carbon black and alumina. X-ray diffraction patterns show that the stacking of MoS_2 layers can be perfectly turbostratic. The restacked MoS_2 may or may not have water-bilayers between them, depending on the deposition conditions. A special form of the Debye fomula for a turbostratically stacked layer system is introduced and calculated diffraction patterns are compared with the experimental results. On heating, the turbostratic stacking converts to an ordered stacking, accompanied by a structural transformation of the MoS_2 layers from a distorted octahedral coordination to a trigonal-prismatic coordination along with dramatic changes in the optical and electrical properties

1 INTRODUCTION

Single-molecular-layer MoS_2 in suspension, prepared by exfoliation of lithium-intercalated MoS_2 in water or alcohols[1], provides a interesting system for study of the physical and chemical properties of two-dimensional materials. A detailed experimental study shows that the physical properties of single layer MoS_2 differ from those of crystalline MoS_2 significantly in several ways: the structure of single layer MoS_2 has the octahedral coordination, which does not exist in crystalline MoS_2; single layer MoS_2 adopts a strongly distorted structure with a 2x1 superlattice; single layer MoS_2 is a semimetal, in contrast to its semiconducting counter-part in the crystalline phase.[2,3]

One interesting feature of single layer MoS_2 is that they can be restacked turbostratically on various substrates to form a quasi-two-dimensional system. A turbostratocally stacked system is like a pile of randomly stacked cards, where the individual cards are parallel to each other at the same interlayer spacing, but random in translation and in rotation about the normal to the cards. The diffraction patterns for turbostratic stacking consist of two type of peaks: the (00l) peaks and (hk0) peaks. The (00l) peaks are of a three-dimensional lattice type and the (hk0) peaks are of a two-dimensional lattice type. All the mixed (hkl) peaks are suppressed completely by the randomness in translation and rotation.

Turbostratic disorder is commomly found in synthetic carbons and clays. To calculate the diffraction pattern for a turbostratically-stacked layer system, a common approach is to use numerical integration over the reciprocal lattice.[4] In this paper, we first introduce a special form of the Debye formula for a turbostratically stacked layer system. Then calculated diffraction for turbostratically stacked MoS_2 using the new approach is presented. Finally, the experimental evidence for turbostratically restacked MoS_2 and some physical properties of the system are discussed.

2. CALCULATION OF POWDER X-RAY DIFFRACTION PATTERNS FOR A TURBOSTRATICALLY STACKED LAYER SYSTEM

For very small systems, the powder diffraction pattern can be directly generated by computer using the Debye formula[5]. This was first done for microcrystallites of 2H-MoS_2 by Chien[6]. For a powdered material, the average scattering power per unit cell, I, in electron units, is given by the Debye formula

$$I(s) = \frac{1}{N_t}\sum_{i=1}^{N_t}\sum_{j=1}^{N_t} f_i f_j \frac{\sin(2\pi s r_{ij})}{2\pi s r_{ij}} \qquad (1)$$

where N_t is the total number of atoms in the cluster, f_i is the atomic scattering factor of the i-th atom, $s=2\sin\theta/\lambda$, and r_{ij} is the distance between the i-th and the j-th atoms.

Now consider a turbostratically stacked layer system which has M layers and N atoms in each layer (so MN is the total number of atoms in the cluster). The Debye formula for such a system can be rewritten as

$$I = I_{intra} + I_{inter} \qquad (2)$$

I_{intra} is the scattering intensity due to the intra-layer interference and is given by

$$I_{intra} = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} f_i f_j \frac{\sin(2\pi s r_{ij})}{2\pi s r_{ij}} \qquad (3)$$

I_{intra} is exactly the X-ray diffraction pattern for a two-dimensional system. It gives only (hk0) peaks, which have a strongly asymmetric line shape. Note that I_{intra} is independent of M, the number of layers of the cluster.

The second term in Eq.(2) represents the interlayer interference effect. For a turbostratically stacked system, each atomic sheet can be treated as a uniform sheet of electron density. In the case of MoS_2, there are three atomic sheets in each MoS_2 layer. It can be shown that

$$I_{inter} = \frac{D}{M\pi s^2}\sum_{n=1}^{M-1}(M-n)\sum_{i=1}^{3}\sum_{j=1}^{3} f_i f_j \cos\left[2\pi s(nc_0 + d_{ij})\right] \qquad (4)$$

where D is the surface atomic density of the sheets, c_0 is the spacing between MoS_2 layers, and d_{ij} is the separation of the i-th atomic sheet from the j-th atomic sheet. Eq.(4)

has peaks at $s=l/c_0$, the locations of (00l) peaks. Note that I_{inter} in Eq.(4) does not depend on N (the size of layers).

In calculating diffraction patterns the use of Eq.(2)-(4) will save computation time dramatically. Since the double sum in Eq.(3) goes over atoms in a layers only, the computation time is less than that using Eq.(1) by a factor of at least $1/M^2$. The computation time for Eq.(4) is negligible in comparison with that for Eq.(3).

Fig.1 shows the calculated diffraction intensity of turbostratically-stacked trigonal-prism MoS_2 for 1, 2, 4, and 10 layers, respectively. The layer size is 20x20 MoS_2 units for all curves in Fig.1. For the single layer MoS_2 (Fig.1(a)), only (hk0) peaks, i.e., (100), (110) and (200) in the calculation region, are present in the pattern. They all have a strongly asymmetric lineshape. The shape of the high angle tails varies from peak to peak due to the modulation of the structure factor. Of particular interest, the (100) peak has the form of a sharp spike at s=0.37 Å^{-1} followed by a broad shoulder around s=0.45 Å^{-1}. This special shape of the (100) peak denotes the trigonal-prism coordination of the MoS_2 structure.

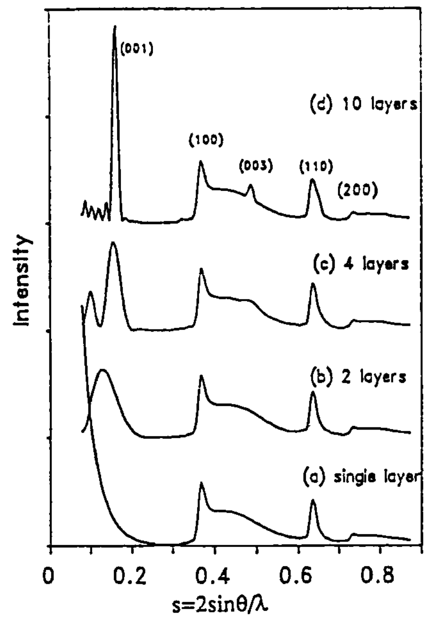

Fig.1 Calculated diffraction patterns of turbostratically-stacked trigonal-prism MoS_2 for 1, 2, 4 and 10 layers. The layer size is 20x20 for all curves.

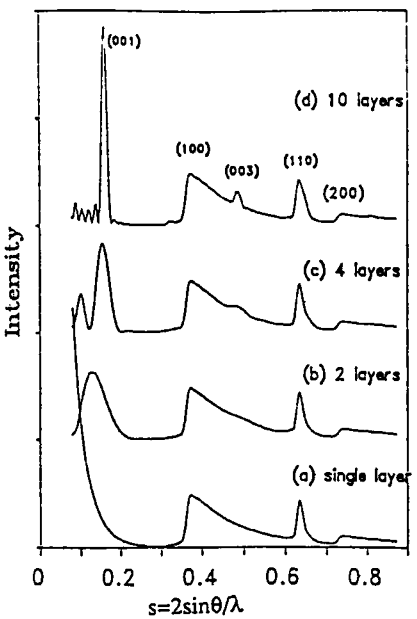

Fig.2 Calculated diffraction patterns of turbostratically-stacked octahedral MoS_2 for 1, 2, 4 and 10 layers. The layer size is 20x20 MoS_2 units for all curves.

When two layers are stacked (Fig.1(b)), the (001) peak shows up strongly. As the number of layers increases, the (001) peak sharpens and higher order (00l) peaks appear. The number of layers, however, has no effect on the (hk0) peaks. Similarly, the width of (00l) peaks is independent of the layer size. The structure seen on the low angle side of the (001) peak is due to the finite munber of layers. Such systems may be regarded as quasi-two-dimensional in that they display diffraction peaks characteristic of a two-dimensional lattice.

Fig.2 shows the calculated diffraction patterns for another turbostratically stacked MoS_2 system in which all parameters are the same as those in Fig.1 except the MoS_2 unit is octahedrally coordinated. The only difference between patterns in Fig.1 and Fig.2 occurs in the (100) peak. The (100) peak for octahedral two-dimensional MoS_2 layers has a saw-tooth shape. This structure dependent lineshape is a unique feature of low dimensional materials, and can aid in structure identification.

3. EXPERIMENTAL RESULTS

Turbostratically stacked layer systems can be obtained from exfoliated MoS_2 single layers by restacking on various supports and substrates. Fig.3 shows two examples of randomly restacked MoS_2. In Fig.3(a), MoS_2 is coated on fine alumina (0.05-0.5 micron size) where the use of a powder substrate provides random orientation for the restacked MoS_2. Water is intercalated between MoS_2 layers in this sample, as evidenced by the strong $(001)_w$ and $(002)_w$ peaks. The suffix "w" is appended to the (00l) indices to indicate the presence of water layers. The interlayer spacing in the sample is 11.8 Å, which is 5.6 Å larger than the c-spacing of crystalline MoS_2 (6.15 Å). The increase of 5.6 Å in interlayer spacing indicates that two layers of water of diameter 2.8 Å (possibly some Li-water complex[7]) are included between MoS_2 layers. The absence of mixed (hkl) peaks and the asymmetric lineshape of (hk0) peaks show that the restacking is turbostratic. The saw-tooth shape of the (100) peak indicates the MoS_2 unit cell is octahedrally coordinated. Based on our computer simulations, we can use the (110) peak to determine that the a-spacing for Fig.3(a) expands to 3.27±0.02 Å, 3.5 % larger than the 3.16 Å for trigonal-prism 2H-MoS_2. Fig.3(a) is in good agreement with patterns obtained for water-bilayer MoS_2 without the fine alumina powder[2], although the superlattice peaks observed in single layer MoS_2 are not well resolved in Fig.3(a).

Fig.3(b) shows the experimental diffraction pattern of MoS_2 restacked in the presence of carbon black. Again, the strong (001) peak, asymmetric (hk0) peaks and no mixed peaks indicate that MoS_2 layers are restacked turbostratically. There is no water inclusion between MoS_2 layers in this case. The c-spacing is 6.40 Å, 4 % larger than that of crystalline MoS_2. Possibly the presence of the carbon black encourages the formation of water pockets in the region of the carbon particles rather than the formation of the water bilayer phase. The shape of the (100) peak and the position of the (110) peak indicate a structure in which the Mo atoms have trigonal-prism coordination. The correlated layer size is about 25x25 unit cells with a correlation thickness of about 10 layers in both cases in Fig.3.

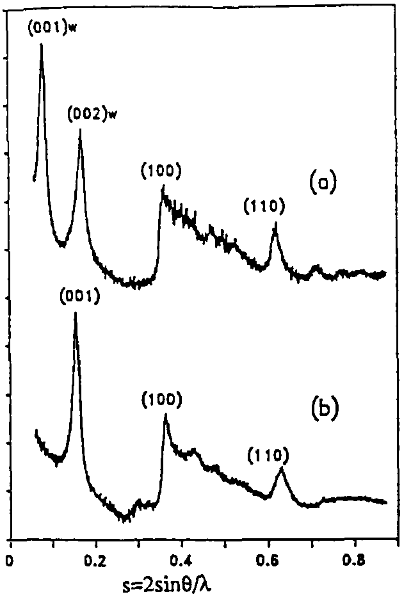

Fig.3 Experimental powder X-ray diffraction patterns of restacked MoS_2 coated on (a) fine alumina powder, and (b) carbon black. Support background is subtracted.

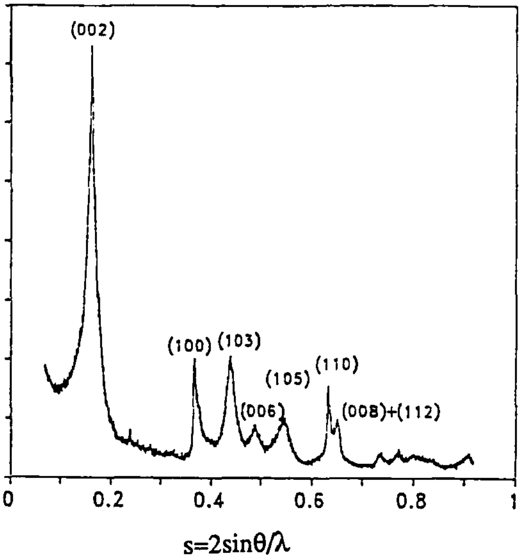

Fig.4 The powder X-ray diffraction pattern for a baked restacked MoS_2.

It has been found that the octahedral configuration of MoS_2 is only seen in the water bilayer or single layer form. A irreversible transformation from the octahedral phase to the trigonal prismatic phase occurs when the sample is dried. Fig.4 shows a diffraction pattern for a water bilayer sample that has been baked at 600 °C for 1 hour in an Argon environment. All mixed (hkl) peaks of crystalline 2H-MoS_2 reappear in the pattern and the a-spacing shifts back to 3.16 Å, indicating the sample has, to a large extent, converted back to the trigonal prismatic 2H-MoS_2. However, the intensities of the (103) and (105) lines in Fig.4 are somehow weaker than those for perfect 2H-MoS_2, likely due to the presence of stacking faults or a mix of the 2H and 3R naturally-occuring polytypes of MoS_2.

Fig.5(a) shows the optical transmission spectrum at 77 K for a restacked MoS_2 film in the water-bilayer phase (around 100 layers thick). The band gap at 700 nm for crystalline 2H-MoS_2 disappears and the spectrum gives a very flat response with strong absorption extending into IR region. The spectrum for the same sample after baking at 600 °C in an Argon atmosphere for 1 hour (Fig5.(b)) clearly shows the recovery of the interband absorption edge around 700 nm as well as the exciton peaks A and B. Our experimental results also show that the room temperature conductivity of the octahedral MoS_2 is 2 to 3 orders of magnitude higher than that of trigonal-prism MoS_2. Thus it appears that the structural transformation from octahedral MoS_2 to trigonal-prism MoS_2 is accompanied by a semi-metal (or metal) to semiconductor transition, in agreement with the work on recently synthesized metallic octahedral MoS_2[8].

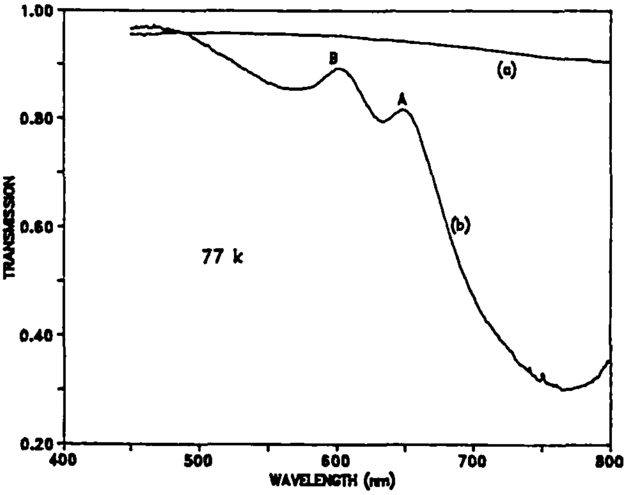

Fig.5. Optical transmission spectra at 77 K for (a) a restacked MoS_2 film in water bilayer phase, and (b) the same sample after baking .

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