Structure of single-molecular-layer MoS_2

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An analysis of x-ray diffraction line shape and Raman-scattering results shows that single-molecular-layer MoS_2, prepared by exfoliation of lithium-intercalated MoS_2 powder in water, has a structure in which the Mo atoms are octahedrally coordinated, in contrast to the trigonal prismatic coordination of Mo in bulk MoS_2. The octahedral coordination of single-layer MoS_2 is strongly distorted, with a $2a_0$ superlattice. For a restacked film, the octahedral coordination of MoS_2 appears to be a metastable structure. On heating or aging, it transforms back to the trigonal prismatic coordination.

Single-molecular-layer MoS_2,[1,2] prepared by exfoliation of lithium-intercalated MoS_2 powder in water, provides a good system for a study of the physical and chemical properties of a two-dimensional semiconducting material. One question which arises in the study of single layers of MoS_2 is whether the structure is the same as the bulk $2H$-MoS_2. Layered compounds of the MoS_2 type have the general formula TX_2, where T is a transition-metal atom from group IVB, VB, or VIB and X is one of the chalcogens sulfur, selenium, or tellurium. These compounds have a structure with strongly bonded two-dimensional X-T-X sandwiches, which are loosely coupled to each other by weak van der Waals bonding. Within a layer of such compounds, the metal atom can be coordinated by six chalcogen atoms in either an octahedral or trigonal prismatic arrangement.[3] However, only the trigonal prismatic coordination of the Mo atom is found in bulk $2H$- and $3R$-MoS_2 materials. On the other hand, it has been reported that a structural transformation from trigonal prismatic to octahedral coordination occurs when MoS_2 is intercalated by lithium and it is suggested that the transformation is driven by a lowering of the electronic energy for the octahedral structure when electrons are donated from Li to the MoS_2 layers on intercalation.[4] The octahedral transformation in Li_xMoS_2 starts at $x = 0.1$ and completes around $x = 1$.[4,5] Recent electron diffraction work on Li-MoS_2 has shown this transformation is accompanied by a $2a_0 \times 2a_0$ superlattice.[5]

Our optical and electrical observations have shown that exfoliated MoS_2 single layers and freshly restacked MoS_2 films may have a structure which differs from that of bulk $2H$-MoS_2. In this paper, the problem is investigated by x-ray diffraction and Raman scattering. The preparation of single-layer MoS_2 in suspension in water has been described previously.[1] X-ray diffraction patterns were obtained with a Philips diffractometer using nickel-filtered Cu $K\alpha$ radiation. The MoS_2 samples used here are in a wet pastelike form, after being washed with water and centrifuged three or four times. The sample holder is made of a glass slide with a well of depth 1 mm. The scattering from the sample holder with only water in

the well was measured and the data used for background subtraction.

Figure 1(a) shows a typical experimental x-ray pattern of MoS_2 single layers in suspension in water. The x axis in Fig. 1 is the x-ray scattering wave vector s, where $s = 4\pi \sin\theta/\lambda$ or $s = 2\pi/d$, 2θ is the diffraction angle, λ is x-ray wavelength (1.542 Å), and d is the interplanar spacing. There are several noticeable features in the pattern of Fig. 1(a).

(a) Only $(hk0)$ peaks are present in the pattern. All $(00l)$ lines and mixed (hkl) lines are absent, indicating that the sample is made up of single layers.[6]

(b) The (200) peak ($s = 2.25$ Å^{-1}) is very asymmetric with a sawtooth shape. This strong asymmetry in the (200) peak is one of the most interesting features in the x-ray pattern of single-layer MoS_2. It should be pointed out that the asymmetry of the (200) line is not simply due to the Warren effect in two-dimensional lattices,[7] which would be much weaker. The (200) peak here corresponds to the (100) peak in bulk MoS_2. This is due to the existence of a $2a_0$ superlattice which will be discussed in some detail below.

(c) The (220) peak, which is equivalent to the (110) peak in an undistorted MoS_2 system, is not as asymmetrical as the (200) peak. The slight asymmetry in the shape of the (220) is due to the Warren effect. The (220) peak seems to be a doublet, with a separation of 0.06 Å^{-1} ($s = 3.86$ and 3.92 Å^{-1}).

(d) Four peaks that can be attributed to a $2a_0$ superlattice are observed: the (210) peak at $s = 2.95$ Å^{-1}, the (300) peak at $s = 3.32$ Å^{-1}, the (320) peak at $s = 4.84$ Å^{-1}, and the (410) peak at $s = 5.11$ Å^{-1}. The intensity of the superlattice peaks indicates the system is strongly distorted.

(e) The a_0 spacing of single-layer MoS_2, calculated from the (220), (210), (300), (320), and (410) peaks, is 3.27 ± 0.015 Å, which is 3.5% larger than the single-crystal value of 3.16 Å. One should be careful in determining the a_0 spacing from the (200) peak by simply using Bragg's law. Our modeling studies show that the peak position shifts to a higher angle due to the strong asymmetry. Table I compares the a_0 spacings of $2H$-

	2H-MoS$_2$ crystal	Li-MoS$_2$ crystal[a]	MoS$_2$ single layer[b]
Coordination	trigonal prism	octahedral	octahedral
a_0 spacing (Å)	3.162	3.36	3.27
Expansion (%)	0	+6.0	+3.5

[a]References 4 and 5.
[b]This work.

MoS$_2$, Li-MoS$_2$, and single-layer MoS$_2$.

In order to understand the x-ray scattering for single molecular layer MoS$_2$, a modeling study was carried out. Assuming that the material is randomly oriented, the average scattering power I, in electron units, is given by the Debye formula[8]

$$I(s) = \sum_m \sum_n f_m f_n \frac{\sin(sr_{mn})}{sr_{mn}} , \qquad (1)$$

where r_{mn} is the distance between mth and nth atoms and f_m and f_n are the atomic scattering factors of the mth and nth atoms. Equation (1), along with a polarization factor, is used in the numerical calculation.

Figure 2 gives calculated patterns of undistorted MoS$_2$ single layers of various configurations for a particle size of 20×20 MoS$_2$ units. The particle size of 20×20 is chosen here because it fits the experimental linewidths well. Figure 2(a) is for a two-dimensional hexagonal Mo structure without sulfur atoms. There are three peaks in the calculated range: (100), (110), and (200). The asymmetry of these peaks is due to the so-called Warren effect, a special feature associated with a two-dimensional structure.[6] The effect arises from the fact that the reciprocal lattice for a two-dimensional layer becomes a line perpendicular to the layer, hence a continuous distribution of diffraction intensity appears for higher diffraction angles.
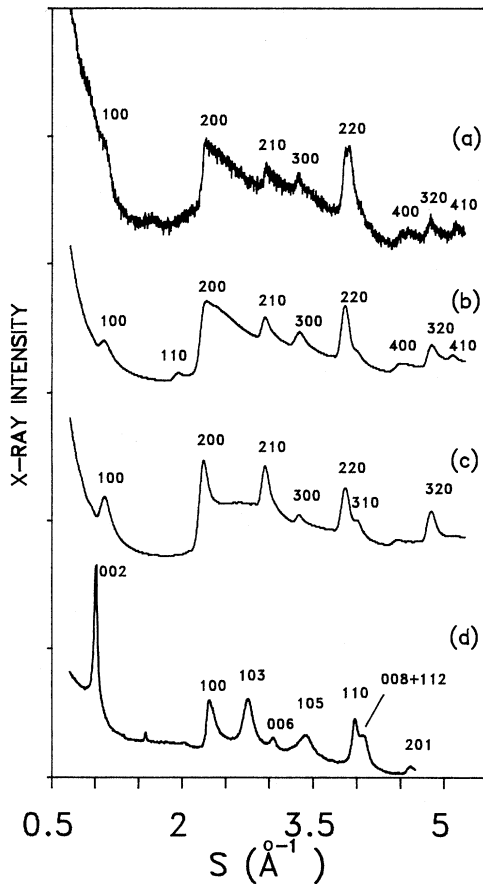

FIG. 1. X-ray diffraction patterns of MoS$_2$. (a) Experimental pattern of single-layer MoS$_2$ suspended in water. The background due to water and substrate has been subtracted. (b) Calculated pattern of distorted octahedral MoS$_2$ single layer. A $2a_0 \times 2a_0$ superstructure is introduced with a distortion of 0.14. The layer size is 20×20 MoS$_2$ units. An $a_0 = 3.27$ Å was used. (c) Calculated pattern of distorted trigonal prismatic MoS$_2$ single layer. All parameters are the same as (b). (d) Experimental x-ray diffraction pattern of restacked, dried, and baked MoS$_2$ sample. All (00l) lines and mixed lines of crystalline 2H-MoS$_2$ reappear and the a_0 spacing shifts back to 3.16 Å.
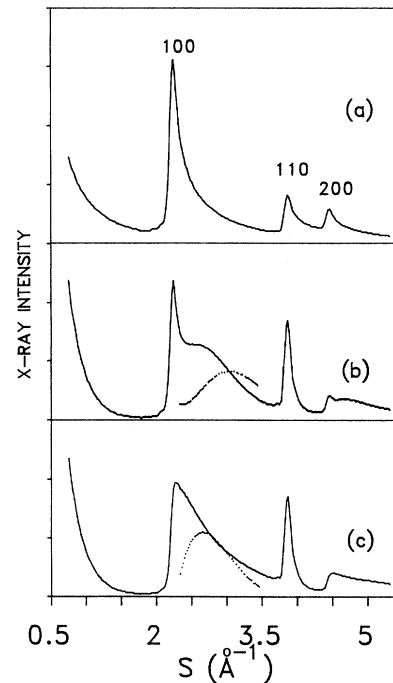
FIG. 2. Calculated x-ray diffraction patterns of undistorted system for (a) two-dimensional hexagonal Mo lattice, (b) trigonal prismatic MoS$_2$ single layer, and (c) octahedral MoS$_2$ single layer. The particle size is 20×20 MoS$_2$ units. The a_0 spacing is 3.27 Å. The dotted lines in (b) and (c) show variations of the structure factor along the c axis for the (100) line.

Figures 2(b) and 2(c) give calculated patterns of undistorted trigonal prismatic and octahedral MoS_2 single layers, respectively. Several interesting features are evident in comparing the two figures. The (110) peaks are identical in both cases. The asymmetry due to the Warren effect can be seen in the (110) peak. A significant difference appears between trigonal prismatic and octahedral coordination for the (100) peak in Figs. 2(b) and 2(c). The (100) peak for trigonal prismatic MoS_2 single layers has the form of a sharp spike at $s = 2.24$ Å^{-1} followed by a broad shoulder around $s = 2.8$ Å^{-1}. With increasing layer size, the spike becomes narrower and the shoulder smaller. On the other hand, the shape of the (100) peak for the octahedral arrangement has a sawtooth shape and no significant Bragg spike is seen until the size of the layer is larger than about 50×50 MoS_2 units. The Bragg spike is relatively small even for 100×100 MoS_2 units. We have carried our simulation for up to twenty MoS_2 layers with 20×20 MoS_2 units in each layer. The distinction in the shape of the (100) line between the trigonal prismatic and octahedral coordination is essentially lost for more than one layer.

Why the line shape of the (100) line depends on the structure of unit cell for a molecular layer can be visualized in terms of the following. Since a reciprocal lattice in a two-dimensional system becomes a line or rod, a $(hk0)$ line actually is the integration of the (hkl) line, where index l is a continuous variable from $-\infty$ to $+\infty$. Apart from the interference effect between unit cells, the structure factor $F^2(hkl)$ also varies continuously with l, and modulates the interference function, affecting both the amplitude and the shape of the diffraction. The dotted lines in Figs. 2(b) and 2(c) show the variations of the structure factor $F^2(10l)$ along the c direction in reciprocal space. The rapid increase in F^2 for the octahedral structure in Fig. 2(c) partially compensates the dramatic decrease in the interference function [Fig. 2(a)], yielding a slow decrease in the (100) line. For the trigonal prismatic structure [Fig. 2(b)], F^2 remains constant until s reaches 2.5 Å^{-1}, resulting in a spike followed by a broad shoulder for the (100) line.

A $2a_0$ type of superlattice is suggested by our experimental results [Fig. 1(a)] and we have carried out a number of diffraction simulations using various $2a_0$ distortions. Figure 3 shows a possible model for a $2a_0 \times 2a_0$ superlattice, where four Mo atoms in a unit cell are distorted in such a way that they form a smaller rhombus. Figures 1(b) and 1(c) compare the calculated pattern for the structure in Fig. 3 for the octahedral and trigonal prismatic coordination, for a distortion factor $\mathscr{D} = 0.14$ and layer size of 20×20 MoS_2 units, where $\mathscr{D} = \delta(a_0)/a_0$, and $\delta(a_0)$ is the displacement of distorted atoms along the primitive vectors. This distortion gives a good fit to the experimental x-ray data and corresponds closely to the two Mo-Mo bond lengths (2.8 and 3.8 Å) observed for single layer MoS_2 in water suspension by extended x-ray absorption fine structure.[2] Two Mo-Mo distances are also observed in other materials.[9] It should be noted that the $2a_0 \times 2a_0$ distortion shown in Fig. 3 is one of a number of possibilities. Simulations on other $2a_0 \times 2a_0$ distortions and on $2a_0$ distortions in one direction only give
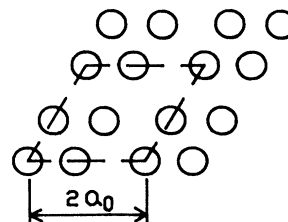

FIG. 3. Model for a $2a_0 \times 2a_0$ superlattice. The four Mo atoms in a unit cell are distorted to form a smaller rhombus. Dashed lines show a unit cell. Only Mo atoms are displayed.

curves quite similar to those shown in Figs. 1(b) and 1(c).

From a comparison of the experimental pattern in Fig. 1(a) and the calculated patterns in Figs. 1(b) and 1(c), it can be concluded that MoS_2 single molecular layers in suspension in water have the octahedral coordination. This is clearly seen from the sawtooth shape of the (200) peak as well as the strengths of the (220), (300), and (410) peaks. The 3.5% expansion of a spacing is also an indication of the phase transition from trigonal prismatic to octahedral arrangement.

We have found that the octahedral configuration of MoS_2 is a metastable phase. An irreversible transformation from the octahedral phase to the trigonal prismatic phase occurs when the sample is annealed above 150 °C. Figure 1(d) shows a diffraction pattern for a sample that has been dried, restacked, and baked in Ar (300 °C, 1 h). All $(00l)$ lines and mixed (hkl) lines of crystalline $2H$-MoS_2 reappear in the pattern, the a spacing shifts back to 3.16 Å, and the superlattice lines disappear, indicating the sample has, to a large extent, converted back to the trigonal prismatic $2H$ phase. For MoS_2 obtained from single layer suspensions, the Li content is less than 1% atomic as measured by inductively coupled plasma mass spectrometry. This is at least a factor of 10 lower than the Li required in the structural transformation in bulk MoS_2,[4,5] and since on drying the single layers revert back to the bulk form it can be concluded that residual Li is not a factor in the single-layer configuration.

Raman spectra also provide evidence for the existence of a $2a_0$ superlattice in single-layer MoS_2. The Raman spectra were obtained at room temperature in a near-backscattering geometry with the 488.0- or 514.5-nm excitation line of an argon ion laser. Figure 4 shows the room-temperature spectra obtained from (a) a freshly prepared MoS_2 single-layer water suspension, (b) a restacked film prepared 2 h before the spectrum was obtained, and (c) a 2-month old restacked film. The restacked films were prepared from single-layer MoS_2 using a spreading technique on a glass substrate.[10] With this process, water is removed from the MoS_2 basal planes. As is evident from Fig. 4(a), the single-layer suspension spectrum contains strong peaks at 156 cm^{-1} (J_1), 226 cm^{-1} (J_2), and 330 cm^{-1} (J_3). These peaks correspond well with the frequencies at the M point of the Brillouin zone of MoS_2 which have been measured by neutron scattering experiments.[11] These zone boundary modes would normally be Raman inactive because of the wave vector conservation rule. They can be observed in Ra-
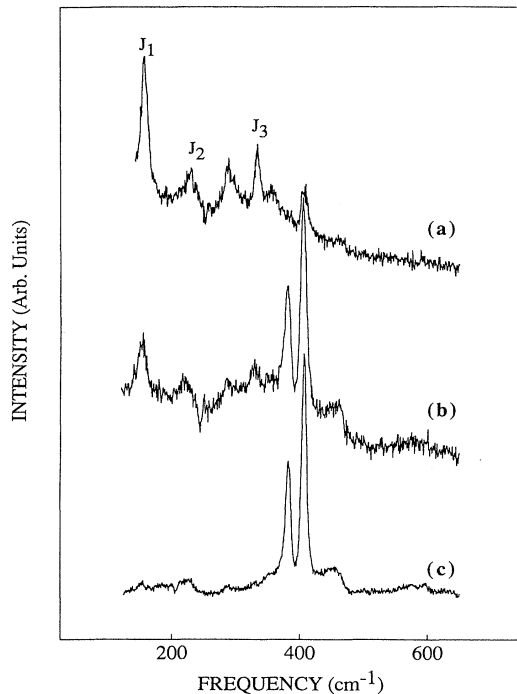
FIG. 4. Room-temperature Raman spectra of (a) fresh MoS$_2$ single-layer suspension, (b) 2-h old restacked film, and (c) a 2-month old restacked film.

man scattering, however, if the M point of the Brillouin zone is folded into the center due to the formation of a $2a_0$ superlattice.[12] The appearance of the J_1, J_2, and J_3 modes is thus consistent with the formation of a $2a_0$ superlattice in single-layer MoS$_2$, as indicated by the x-ray diffraction measurements. It is also clear from Figs. 4(b) and 4(c) that the J_1, J_2, and J_3 peaks become much weaker in the restacked films and decrease further as the film is aged. The spectrum of Fig. 4(c) is in fact very similar to that of single-crystal MoS$_2$.[13] Another interesting feature of Fig. 4(a) is the absence of a peak at 383 cm^{-1} which is usually very strong in spectra obtained from MoS$_2$ [Fig. 4(c)] and corresponds to scattering from the E_{1g} mode of 2H-MoS$_2$.[13] Group theory can be used to show[14] that this mode corresponds to the E' vibration of single layers of MoS$_2$ that retain the trigonal

prismatic coordination (1H-MoS$_2$). Because there is no longer a center of inversion in 1H-MoS$_2$, this mode is both Raman and infrared active. In octahedral coordinated layers (1T-MoS$_2$), however, there is a center of inversion and group theoretical correlations[14] show that the E' mode becomes the E_u mode of 1T-MoS$_2$. Thus in 1T-MoS$_2$ the 383-cm^{-1} phonon is infrared, rather than Raman active and the absence of the 383-cm^{-1} peak in Fig. 4(a) can be attributed to an octahedral coordination of Mo atoms. The results described above have been confirmed by a direct lattice dynamics calculation which will be described in detail in a future publication.

Figures 1 and 2 reveal some interesting features of the diffraction patterns of monomolecular layers. In three-dimensional structures, the rearrangement of atoms inside a unit cell will affect the intensity of Bragg lines, as determined by the structure factor, but it has no effect on the shape of Bragg lines. For a single molecular layer, on the other hand, the structure of the unit cell can play an important role in determining the form of the diffraction profile. Single molecular layer MoS$_2$ in suspension in water provides an excellent system for demonstrating that analysis of line shape of x-ray diffraction patterns for monomolecular layers can give information on the structure of the unit cell.

In conclusion, the experimental results of x-ray diffraction and Raman scattering indicate that the structure of single-layer MoS$_2$ in suspension in water has the octahedral coordination, a structure which does not exist in bulk MoS$_2$. The single-layer system is strongly distorted, with a $2a_0$ superlattice. The a_0 spacing expands to 3.27 Å, about 3.5% larger than the bulk MoS$_2$ value of 3.16 Å. Octahedrally coordinated MoS$_2$ is a metastable structure: on drying by heating or aging, it transforms back to the trigonal prismatic coordination. It is not clear what factors stabilize the octahedral coordination for the single layers in suspension. Some form of ordered water on the basal plane is one possibility and further work is required here.

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