

RAMAN INVESTIGATION OF MoS_2 SINGLE MOLECULAR LAYERS AND RESTACKED FILMS

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Raman Scattering experiments have been carried out in single layer particles of MoS_2 in an aqueous suspension and on restacked films prepared from these particles. The results indicate that the Mo atoms are octahedrally coordinated while the particles are in suspension and that the MoS_2 structure is distorted to form a $2a \times 2a$ superlattice. When the particles are restacked into the films, the more usual single crystal trigonal prismatic coordination of the Mo atoms is gradually recovered as the films are aged or thermally annealed. The spectral features associated with the superlattice also gradually disappear as the restacked films are aged over a period of a few days.

I. INTRODUCTION

Molybdenum disulphide is a semiconducting member of the large family of transition metal dichalcogenides which crystallizes in a layered structure with weak Van der Waals interlayer bonding. It is relatively easy to intercalate foreign atoms or molecules into the interlayer region of these compounds. Both the intercalated and nonintercalated compounds have many potential applications. For example, MoS_2 has been used in diverse applications such as catalysis [1], battery electrodes [2] and, because of its anti friction properties, as a lubricant [3,4]. The last-named application is a direct consequence of the weak Van der Waals-type forces between the MoS_2 layers. In many applications it is desirable to have a very small particle size to increase the effective surface area of the sample. A relatively simple procedure has been developed to prepare small particles of MoS_2 [5]. This procedure involves the intercalation of MoS_2 with Li and the subsequent exfoliation of LiMoS_2 into single layers of MoS_2 . This paper describes the results of a Raman spectroscopy study that has been carried on MoS_2 single layers in suspension in water and in films prepared by restacking and drying the single layers [6].

II. EXPERIMENTAL DETAILS

A. Sample Preparation

MoS_2 powder was intercalated with lithium by immersing it in an n-butyllithium-hexene

mixture for at least 48 hours. Exfoliation into single layers is accomplished by adding water to the LiMoS_2 system. Indeed, the rather violent hydrogen gas emission that results from the formation of lithium hydroxide pushes the MoS_2 layers apart by overcoming the weak Van der Waals interlayer bonding. After a washing process to remove LiOH and organic compounds, a MoS_2 single layer aqueous suspension is obtained and films can be made from this material by using a spreading technique [6]. The MoS_2 restacked films used in this study were deposited on glass substrates and the resulting films had thicknesses that varied between a few hundred angstroms and 2000 Å. Some films were thermally annealed in an Ar atmosphere for an hour at 300°C to simulate the effects of aging and reduce the time involved in this process.

B. Raman Scattering Measurements

The spectra were excited with either the 488.0 and 514.5 nm lines of an argon ion laser at room temperature. The incident light was focused on the sample with a cylindrical lens to minimize laser heating effects. The scattered light from the sample was collected in a near back scattering geometry and focused at the entrance slit of a triple spectrometer. The signal was detected with an ITT Mepsicon imaging detector and the data stored and processed in an IBM personal computer.

III. RESULTS AND DISCUSSION

The symmetry of the structure of 2H- MoS_2

can be described by the D_{6h}^4 space group. The primitive unit cell contains two molybdenum atoms occupying sites with symmetry D_{3h} and four sulphur atoms in sites with symmetry C_{3v} . Mo and S atoms are coordinated in a trigonal prism configuration, as shown in Fig. 1(a). Using group theory analysis, it is found that the complete decomposition of the 18 normal modes into irreducible representations at the zone center Γ of the hexagonal Brillouin zone is [7]:

$$\Gamma = A_{1g} + 2A_{2u} + 2B_{2g} + B_{1u} + E_{1g} + 2E_{1u} + 2E_{2g} + E_{2u},$$

where A_{2u} and E_{1u} correspond to translational acoustic modes, $A_{1g} + E_{1g} + E_{2g}$ are Raman active modes and $A_{2u} + E_{1u}$ are infrared active. The modes B_{2g} , B_{1u} and E_{2u} are inactive. Figure 2 shows the room temperature Raman spectra obtained from (a) a freshly prepared MoS_2 single layer suspension, (b) a film prepared two hours before the spectrum was obtained and (c) a two-month old film. The spectrum shown in Fig. 2(c) is very similar to those obtained from single crystals of MoS_2 [8]. The two very strong peaks at 383 cm^{-1} and 409 cm^{-1} correspond to the Raman allowed E_{2g}^1 and A_{1g} modes respectively. A weaker feature at 287 cm^{-1} , which is difficult to observe on the scale of Fig. 2(c), corresponds to the E_{1g} mode. In single crystals of MoS_2 a peak is also observed at 32 cm^{-1} which is due to the E_{2g}^2 rigid layer mode [8].

As is evident from figure 2(a), the single layer suspension spectrum contains additional strong peaks at 156 cm^{-1} (J_1), 226 cm^{-1} (J_2) and at 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

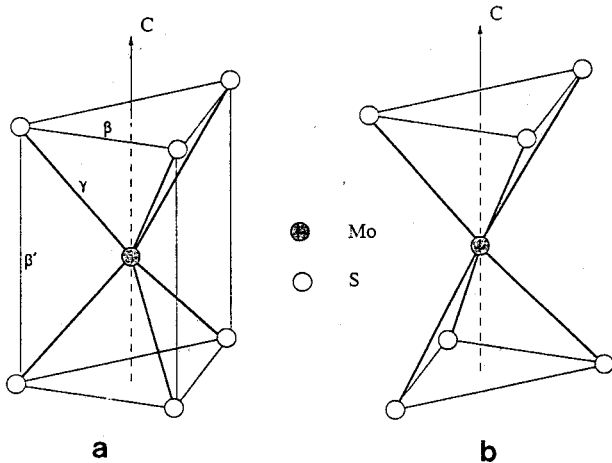


Figure 1. Schematic diagram of MoS_2 with (a) trigonal prism coordination and (b) octahedral coordination.

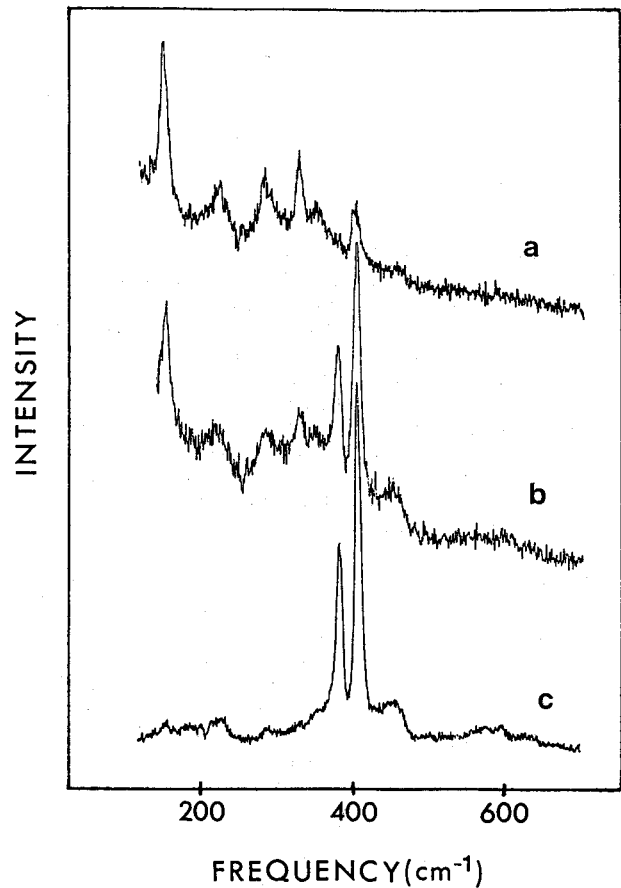


Figure 2. Room temperature Raman spectra of (a) MoS_2 single layers in aqueous suspension, (b) a two-hour old restacked film and (c) a two-month old restacked film.

by neutron scattering experiments [9]. These zone boundary modes would be normally inactive because of the wave-vector conservation rule. However, if the M-point of the Brillouin zone is folded into Γ , due to the formation of a $2a_0 \times 2a_0$ superlattice, these zone edge modes become Raman allowed and can be observed through Raman scattering experiments [10]. The correlation between the appearance of the peaks J_1 , J_2 and J_3 and the formation of a $2a_0 \times 2a_0$ superlattice agrees with the results of X-ray diffraction studies, which also indicate the formation of a $2a_0$ superlattice in MoS_2 single layers [11].

It is clear from figures 2(b) and (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 over a period of a few days. A similar behavior is observed when the films are thermally annealed at 300°C for an hour.

One of the most interesting features in figure 2(a) is the total absence of the peak at 383 cm^{-1} , which is usually very strong in spectra obtained from single crystals of MoS_2 , as is evident in Fig. 2(c). In order to gain insight into this peculiarity, a lattice

dynamics model was used to explore the possibility of having octahedral Mo coordination (1T-MoS₂). It has been suggested previously that MoS₂ undergoes a phase transition, from trigonal prismatic coordination (Fig. 1(a)) to octahedral (Fig. 1(b)), when it is intercalated with lithium [12].

We have considered a single layer model with nearest-neighbor interactions in the Born-Von Kármán approximation to calculate the eigenvalues ($\omega^2(q)$) and eigenvectors of the dynamical matrix. The force constants used in the calculation are: α for Mo-Mo interaction, β (β') for S-S interaction when the atoms are in the same (different) plane(s), and γ for the Mo-S interaction. In the case of trigonal prismatic molybdenum coordination, one can use the set of secular equations given by Bromley [13]. When the dynamical matrix is evaluated at Γ , all the matrix elements have expressions only in terms of γ and β' . The eigenvalues ($\omega^2(q)$) are thus obtained as a function of γ and β' only. Therefore, if one uses the experimental frequencies (table 1), it is possible to determine the force constants. Unfortunately, because of the characteristics of the model, the force constants derived in this way are not unique in the sense that two different, but approximately equal, values can be obtained for the same force constant if one uses two different analytical expressions that involve different frequencies. We have determined values for the force constants that provide a very good compromise with the experimental values (table 1), which are the following:

$$\gamma = 189.0 \times 10^3 \text{ dyn/cm}$$

$$\beta' = 32.5 \times 10^3 \text{ dyn/cm.}$$

The difference between trigonal prismatic and octahedral coordination is a 60° rotation around the c-axis of one of the sulphur basal planes. After this rotation, the interplanar S-S distance is increased by 15%. If one considers the potential function for sulphur atom pairs given by Rinaldi and Pawley [14], one can estimate the change in β' for 1T-MoS₂ in the Born-Von Kármán approximation. This results in a value of $\beta' = 21.4 \times 10^3 \text{ dyn/cm}$, and the following frequencies for the vibrational modes of 1T-MoS₂:

$$\begin{aligned} \omega(E_g) &= 311 \text{ cm}^{-1} \\ \omega(A_{1g}) &= 429 \text{ cm}^{-1} \\ \omega(E_{2u}) &= 383 \text{ cm}^{-1} \\ \omega(A_{2u}) &= 469 \text{ cm}^{-1}. \end{aligned}$$

The symmetries of the modes have been assigned by using the eigenvectors obtained from the dynamical matrix along with the irreducible representations of the modes at Γ for a 1T structure [15]:

$$\Gamma = A_{1g} + 2A_{2u} + E_g + 2E_{2u}.$$

Here the acoustic modes correspond to the

Table 1. Experimental and Calculated frequencies for the vibrational modes of hexagonal MoS₂.

Mode	Experimental (cm ⁻¹) [16]	Calculated (cm ⁻¹)	Activity
E _{1g}	287	296	Raman
E _{2g} ¹	383	383	Raman
E _{2g} ²	32	---	Raman
A _{1g}	409	409	Raman
E _{1u}	384	383	Infrared
A _{2u}	470	469	Infrared

irreducible representations $A_{2u} + E_{2u}$, the two infrared active modes to $E_{2u} + A_{2u}$ and the two Raman active modes to $A_{1g} + E_g$, in contrast to the trigonal prism case where four Raman modes are allowed. The 383 cm⁻¹ mode is thus Raman inactive for 1T-MoS₂, in agreement with the spectrum of Fig. 2(a), in which this peak is clearly absent. This indicates that the molybdenum atoms are octahedrally coordinated in the MoS₂ single layers, a result that is also in agreement with X-ray diffraction studies [11]. The difference between experimental and calculated Raman frequencies of 1T-MoS₂ for the E_g and A_{1g} modes is 8% and 5%, respectively.

IV CONCLUSIONS

A lattice dynamics model has been used to analyze the room temperature Raman spectra of MoS₂ single layers in aqueous suspension. In this case, comparison of the calculated and experimental results indicate that Mo atoms have octahedral coordination. The spectra of the MoS₂ single layers also contain strong peaks that are consistent with the formation of a 2a₀ × 2a₀ superlattice. The Raman spectra show that, when the layers are restacked to form films, the peaks associated with the superlattice decrease considerably in intensity upon aging and/or thermal annealing. This result indicates that, in the restacked films, there is a strong tendency for the Mo atoms to recover the more usual, and presumably more stable, trigonal prism coordination.

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