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RIGID-LAYER LATTICE VIBRATIONS AND VAN DER WAALS BONDING IN HEXAGONAL MoS_2

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Using a triple Raman spectrometer, we have observed the rigid-layer E^2_{2g} mode in hexagonal MoS_2. The *interlayer* forces are shown to be about 100 times weaker than the *intralayer* forces, and a van der Waals model of the interlayer bonding is proposed.

IN PREVIOUS papers[1,2] it has been pointed out that low-frequency optical lattice vibrations should exist in layered crystals which have more than one layer in the primitive unit cell. Such modes are characterized by entire layers of atoms vibrating rigidly against neighboring layers, and these have been called 'rigid-layer' or 'quasi-acoustical' modes. In the case of hexagonal MoS_2, one of the two rigid-layer modes is Raman active. However, this mode was not previously observed because of an inability to resolve low-frequency Raman lines in the presence of strong Rayleigh scattering at the laser frequency.

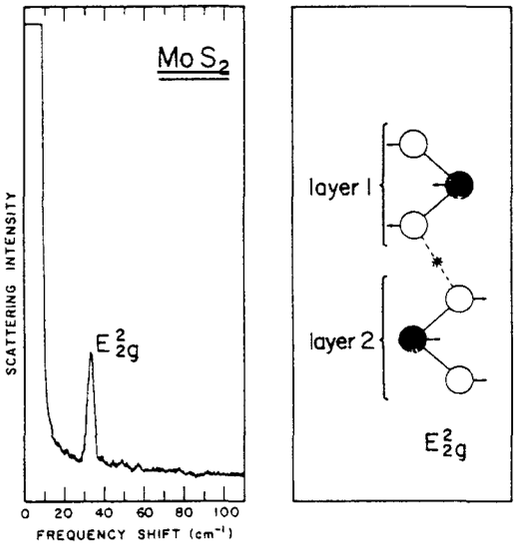
In this paper we report the first observation of the E^2_{2g} rigid-layer mode in MoS_2 using a triple Raman spectrometer. Knowledge of the rigid-layer frequency allows us to compare the strengths of the short-range *intralayer* forces and the much weaker *interlayer* forces. In addition, we obtain a quantitative estimate of the shear interlayer force constant and propose a van der Waals model of the interlayer bonding.

The E^2_{2g} rigid-layer mode has Raman polarizability tensors of the form,

$$\begin{bmatrix} . & d & . \\ d & . & . \\ . & . & . \end{bmatrix} \text{ and } \begin{bmatrix} d & . & . \\ . & -d & . \\ . & . & . \end{bmatrix}.$$

Thus in a back-scattering geometry, the E^2_{2g} mode is allowed for the scattering conditions $z\begin{pmatrix} xx \\ yy \end{pmatrix}\bar{z}$ and $z\begin{pmatrix} xy \\ yx \end{pmatrix}\bar{z}$, where the xy plane is the basal plane of the crystal.

Figure 1(a) shows the low-frequency unanalysed Raman spectrum of MoS_2 at room temperature. The data were taken at Spex Industries on a Spex 1401–1442 triple-spectrometer system.[3] The 5145-Å line from an argon laser operating at ≈ 200 mW was used as the exciting source. The spectrum was obtained with the sample mounted in a helium gas atmosphere in order to eliminate the low-frequency N_2 and O_2 Raman bands caused by scattering from air. The triple-spectrometer system provides excellent scattered-light rejection at low-frequency shifts and thus makes it possible to observe the E^2_{2g} rigid-layer mode at $33.7 \pm 1\ cm^{-1}$. A polarization study of the line showed that it possessed both xx and xy components of the Raman tensor.



a. b.

Fig. 1 (a). The low-frequency unanalysed Raman spectrum of hexagonal MoS_2 obtained with a triple Raman spectrometer. The E^2_{2g} rigid-layer mode is shown at 33.7 ± 1 cm^{-1}.
(b). Atomic-displacement vectors for the six atoms in the unit cell for the E^2_{2g} mode. Molybdenum atoms are represented by the black spheres.

The atomic-displacement vectors for the six atoms in the unit cell for the E^2_{2g} mode are shown in Fig. 1(b). As can be seen, the rigid-layer displacements imply that the only restoring force for this vibration is due to the interlayer bonding. Hence, the frequency of the rigid-layer mode gives a direct measure of the strength of the interlayer interaction in layered crystals.

In a recent paper[4] on GaSe it was shown that a simple classical coupled-oscillator model could be used to compare the interlayer and intralayer bonding forces. This model assumes that two identical oscillators with characteristic resonance frequencies ν_0 are coupled together weakly, such that the coupling frequency $\Delta\nu \ll \nu_0$. Applying this model to the lattice vibrations of MoS_2, we set the resonance frequency ν_0 equal to the frequency of the dipolar mode in the basal plane (384 cm^{-1}), and set the coupling frequency $\Delta\nu$ equal to that of the rigid-layer mode (33.7 cm^{-1}). The ratio $\Delta\nu/\nu_0$ is therefore of the order 0.1. Since in this model the individual frequencies squared are proportional to their respective force constants, the effective interlayer bonding forces are about 100 times weaker than the intralayer forces. This estimate is consistent with similar results obtained for GaSe,[4] As_2S_3, and As_2Se_3.[5]

If we assume that the relatively weak interlayer forces in MoS_2 act only between nearest-neighbor layers, then the shear interlayer force constant can be estimated. (It has been shown[6] previously that this assumption is valid for the longitudinal mode in pyrolytic graphite). The dispersion curve for the rigid-layer mode can be thought of as part of the dispersion curve for a transverse mode in a one-dimensional monatomic lattice. In this analogy the atoms in the linear chain represent the individual layers in the MoS_2 lattice. At the Brillouin-zone edge for a monatomic lattice, the frequency of the transverse mode in the limit of nearest-neighbor interactions is given by

$$\omega^2 = \frac{4K_s}{M}, \qquad (1)$$

where K_s is the shear force constant and M is the atomic mass. Hexagonal MoS_2 has two layers within the primitive unit cell, so that the rigid-layer optical branch is an extension of the acoustical branch, although folded back to the zone center. Thus the E^2_{2g} -mode frequency of 33.7 cm^{-1} represents the zone-edge frequency in equation (1). Substituting the mass of a molecular unit of MoS_2 for M in equation (1), we calculate the shear interlayer force constant to be 2.7×10^3 dyn/cm, which compares well with the value of 3.1×10^3 dyn/cm obtained from inelastic neutron scattering.[7]

Because of the weak interlayer bonding in MoS_2, many authors have postulated that the attractive forces between layers are of the van der Waals type. Evidences in favor of this hypothesis are the easy mechanical cleavage of the crystals along planes parallel to the basal plane; the electronic bonding model,[8] in which the sulfur atoms project closed 3s shells into the interlayer gap; and the small effective charge[2] associated with the infrared-active lattice vibrations. On the other hand, Wildervanck and Jellinek[9] have shown that the hexagonal phase of MoS_2 is stable up to temperatures of at least 1100°C. Thus the question arises as to

whether van der Waals forces can account for the high-temperature stability of the hexagonal phase, as well as the vibrational properties of the rigid-layer modes. In the following model calculation we shall show that it is possible to sstisfy both of these requirements simultaneously.

We begin by assuming that the interlayer forces act only between pairs of sulfur atoms on opposite sides of the gap. The interatomic potential between a pair of sulfur atoms can be represented by the sum of a van der Waals attractive term and an exponential repulsive term,

$$U(R) = -\frac{A}{R^6} + Be^{-\alpha R}. \qquad (2)$$

Here R is the separation between the atoms, and A, B, and α are parameters characteristic of the atoms. In order to evaluate the constants A, B, and α, we make use of three facts: (1) The first derivative of $U(R)$ evaluated at the equilibrium separation R_0 must be zero; (2) the second derivative of $U(R)$ at R_0 is equal to the interatomic force constant Φ; (3) the depth of the potential well at R_0, expressed as a temperature, must be approximately equal to the melting temperature 1185°C. The last fact comes from considerations of the results of polytype-conversion experiments. Wildervanck and Jellinek[9] have shown that the rhombohedral phase of MoS_2 can be converted to the hexagonal phase by prolonged annealing at 1100°C. Since MoS_2 melts at 1185°C, it is reasonable to presume that the hexagonal phase is stable up to the melting point. We therefore set the depth of the potential well equal to the energy equivalent of this temperature.

If we further assume that the sulfur atoms interact through a central force, then the interatomic force constant Φ can be related to the shear and compressional interlayer force constants, K_s and K_c, respectively. Resolving the nearest-neighbor forces into components parallel and perpendicular to the basal plane, we obtain

$$K_s = 2\,\Phi\cos\theta \qquad (3)$$

and

$$K_c = 3\,\Phi\sin\theta\,, \qquad (4)$$

where θ is the angle between the sulfur–sulfur interlayer bond and the basal plane. Since $\theta = 60.1°$, we find $K_s \simeq \Phi$ and $K_c \simeq 2.6\,\Phi$. Thus the ratio of the interlayer force constants is $K_c/K_s \simeq 2.6$, which correlates well with the value $K_c/K_s = 2.35$ determined from the neutron data of Wakabayashi, Smith, and Nicklow.[7]

Using the value[10] $R_0 = 3.66$ Å for the distance between sulfur atoms on opposite sides of the gap, together with our value of K_s, we obtain $A = 2.25 \times 10^{-9}$ erg-Å^6, $B = 1.54 \times 10^{-9}$ erg, and $\alpha = 2.09$ Å^{-1}. The potential function $U(R)$ is shown in Fig. 2 for these values of the parameters.

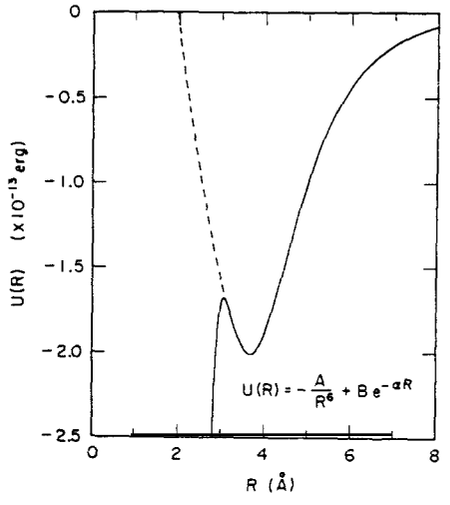


FIG. 2. Interatomic potential of equation (2) vs. R. The values of the parameters are $A = 2.25 \times 10^{-9}$ erg–Å^6, $B = 1.54 \times 10^{-9}$ erg, and $\alpha = 2.09$ Å^{-1}. A more realistic potential for small R is indicated by the dashed curve.

Several points should be made concerning the interatomic potential. First for $R < R_0$ the van der Waals attractive term eventually dominates the exponential repulsive term. Thus a maximum in $U(R)$ occurs at $R = 3.06$ Å, and for $R < 3.06$ Å the function rapidly decreases. We therefore do not expect this potential to be realistic for $R < 3.06$ Å. A more rapidly varying repulsive term would be required to represent the interatomic potential for small R. An example of such a term is shown in Fig. 2 by the dashed curve. Secondly although the depth of $U(R)$ is consistent with the stability of the hexagonal phase at 1100°C, we might expect that a more realistic van der Waals potential would include higher-order multipole attractive terms. Finally, interactions between second-nearest-neighbor sulfur atoms have been neglected, although these interactions may be of some importance.

It should also be noted that a generalized Lennard–Jones potential of the form

$$U(R) = -\frac{A}{R^6} + \frac{B}{R^n} \qquad (5)$$

can not satisfy the high-temperature stability requirement of the hexagonal phase. In particular, there exists no value of $n > 6$ which corresponds to a well depth of 1185°C.

In summary, the E^2_{2g} rigid-layer mode in hexagonal MoS_2 has been observed by Raman scattering. The frequency of this mode has been used to determine the shear interlayer force constant and the parameters in a van der Waals model of the interlayer bonding. Although our results do not prove the existence of van der Waals forces in MoS_2, they do demonstrate the possibility for this type of force in the interlayer bonding.

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Mit Hilfe eines dreifachen Raman Spektrometers haben wir die E^2_{2g} Starrschichtvibration in hexaedrischen MoS_2 beobachtet. Die Kräfte zwischen den Schichten erweisen sich als ungefähr hundert Mal schwächer als die Kräfte innerhalb der Schichten, und ein van der Waals Modell der Bindung zwischen den Schichten wird vorgeschlagen.