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SECOND ORDER RAMAN SPECTRUM OF MoS_2*

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The second order Raman spectra of a layer compound MoS_2 have been measured. Features characteristic of a two-dimensional phonon density of states curve have been observed. Most of the critical points in the second order spectrum are identified.

RECENT results have shown that the second order Raman (SOR) spectra of Ge^1 and $Si^{2,3}$ are mainly due to the overtone process. In this process an incident photon generates two phonons of the same energy with equal and opposite momenta. Since the momentum of each phonon can be anywhere in the Brillouin zone, the SOR spectrum maps out directly the phonon density of state curve of the solid. From the SOR spectrum the phonon frequencies at the critical points in the density of state curve can be determined accurately.[3] While the SOR spectra of transparent materials have been measured extensively,[4] similar measurement on opaque materials are more difficult to obtain. So far detailed results are available for Ge^1 and $Si^{2,3}$ only.

In this paper we report the SOR spectrum of a layer compound MoS_2.[5] This is an opaque semiconductor with a band gap of about 1 eV.[6] Its crystal structure consists of two-dimensional layers of S–Mo–S sandwiches that are weakly bonded to one another along the third dimension. Because of very weak interlayer Van der Waals bonding, the SOR spectrum should correspond to the phonon density of state curve of a two-dimensional solid. The first order Raman and infrared properties of MoS_2[7] have been extensively studied. Some neutron scattering data on layer compounds have also been reported.[8]

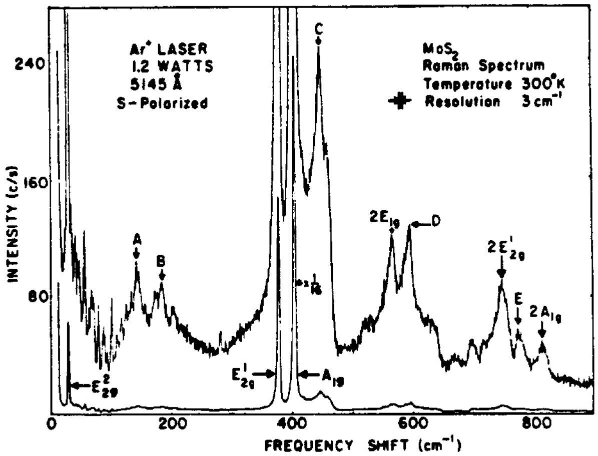

FIG. 1. Raman spectrum of MoS_2 at room temperature with *s*-polarized incident light.

Figures 1 and 2 show the SOR spectrum of MoS_2 obtained with *s* and *p*–polarizations (*E* field perpendicular and parallel to the plane of incidence) respectively of the incident laser light at room temperature. Our equipment includes a 4W Ar laser, a Spex 1401 spectrometer, a thermoelectrically cooled RCA C31034A phototube and photon counting electronics. The dark current was less than 3 counts/sec. There are four first-order Raman active modes in MoS_2, designated E_{1g}(286 cm^{-1}), E^1_{2g}(383 cm^{-1}), A_{1g}(408 cm^{-1}) and E^2_{2g}(32 cm^{-1}).[7] The first three modes are due to vibration of atoms within a S–Mo–S layer. The fourth mode, E^2_{2g}, is due to vibration of two rigid

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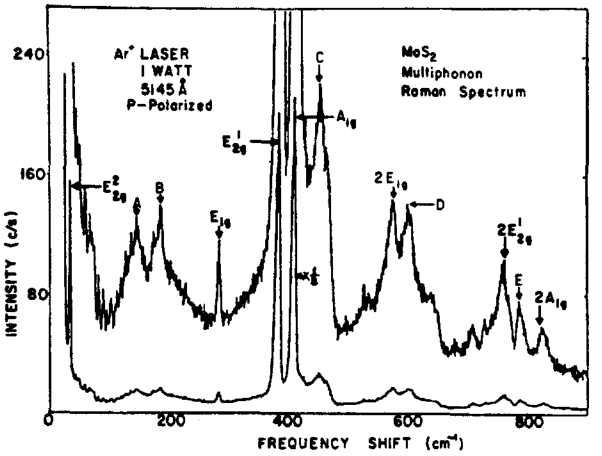

FIG.2. Raman spectrum of MoS_2 at room temperature with *p*-polarized incident light.

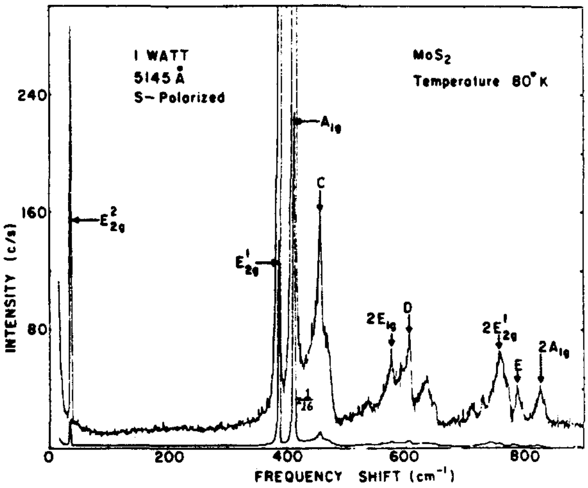

FIG.3. Raman spectrum of MoS_2 at liquid nitrogen temperature with *s*-polarized incident light.

layers against each other. Note that the E_{2g}^2, mode at 32 cm^{-1} is clearly resolved with our double monochromator. In a previous measurement,[9] it was necessary to use a third monochromator to observe this low energy peak. The first order Raman line intensities appear to differ quite appreciably with *s* and *p* polarizations. The first-order E_{1g} mode is much more intense with *p*-polarized light. The other three modes have almost equal intensities in *p*-polarization, while in *s*-polarization the intensity of A_{1g} mode is about twice that of E_{2g} mode and four times that of E_{2g}^2 mode. On the other hand, aside from a slight increase of the intensity in the low frequency part of the spectrum, due to stronger absorption for *p*-polarized incident light, the second order features in the spectrum remain essentially the same. We have observed no appreciable structures beyond 900 cm^{-1}. The energy and intensity of peaks in both first and second order spectra are listed in Table 1. The phonon frequencies given for the first order Raman lines are accurate to within 0.2 cm^{-1}, while the second order peaks are accurate to 0.5 cm^{-1} for sharp peaks and 1 cm^{-1} for less sharp peaks. The accuracy is obtained by using a multichannel scaler for photon counting and by calibrating the spectrometer with the known Ar$^+$ spectral lines.[10] The relative intensities at various points are also reproducible to within 10%.

Compared to the SOR spectra of Ge[1] and Si,[2,3] the second order features of MoS_2 are much sharper. This must be due to the two-dimensional nature of the material, with relatively flat phonon dispersion curves. The shape of the peaks *C* and *D* at 450 cm^{-1} and 596 cm^{-1} resembles closely a logarithmic singularity in a two-dimensional phonon density of state curve,[11] although further theoretical calculation is required to clarify this possibility.

Bromley[12] has calculated the dispersion curves of a single layer of MoS_2 in a central force-nearest neighbor approximation. At this stage, it is not yet possible to make unambiguous identification of all the singular points in our SOR spectrum, based on Bromley's calculation. Among the many features in the spectrum, we can tentatively identify three high energy peaks at 567 cm^{-1}, 757 cm^{-1} and 817 cm^{-1} as due to the overtone process of E_{1g}, E_{2g}^1 and A_{1g} modes respectively. The two low energy peaks, *A* and *B* and 50 cm^{-1} and 188 cm^{-1}, are probably due to the difference process, since at liquid nitrogen temperature (Fig.3) they disappear completely. A difference process, which creates a phonon and absorbs another, has a temperature dependence of the form $n(\omega_1, T)\,[n(\omega_2, T) + 1]$, where $n(\omega, T) = (e^{\hbar\omega/kT} - 1)^{-1}$ is the phonon occupation number and phonons of frequencies ω_1 and ω_2 are absorbed and created respectively. A quick estimation shows that if peaks *A* and *B* were due to the difference process then the intensity at 80°K would be a factor of 20 lower than the intensity at 300°K. On the other hand, if they were due to the overtone or combination process, which has a temperature

Table 1. Phonon frequencies and intensities at the singular points in first and second order Raman spectrum of MoS_2

Peak	Frequency Shift (cm^{-1})		Intensity (counts/sec)				Possible origin of the spectrum
			S-pol.		*P*-Pol.		
	300°K	80°K	300°K	80°K	300°K	80°K	
E_{2g}^2	32.0	33.6	1000	288	1254	412	1st order
A	150.0	–	102	–	132	–	Difference spectrum
B	188.0	–	89	–	130	–	$A_{1g}(M)-LA(M)$
E_{1g}	286.0	288.9	55	–	115	36	1st order
E_{2g}^1	383.0	386.1	2326	2243	1634	2506	1st order
A_{1g}	408.3	410.6	3843	3678	1694	3428	1st order
C	450.2	455.6	249	161	222	173	$2LA(M)$
$2E_{1g}$	567.3	572.9	120	66	147	71	Optical Modes 2nd Order
D	596.0	603.3	128	75	138	84	
$2E_{2g}^1$	750.0	756.7	88	71	97	78	
E	778.0	786.7	53	42	71	46	
$2A_{1g}$	816.7	825.3	46	46	58	51	

dependence of the form $[n(\omega_1, T) + 1] \times [n(\omega_2, T) + 1]$, the intensity should be down only by a factor of 4, and they should still be observable at liquid nitrogen temperature.

Recent neutron data[13] also show that the phonon frequencies of A_{1g} mode and LA mode at the M point of the Brillouin zone are 419 cm^{-1} and 232 cm^{-1} respectively; their difference 187 cm^{-1} is very close to the frequency of peak B. With the aid of neutron data we can also identify peak C as due to the overtone process of longitudinal optical phonon at M point.

We also note that in Fig.3 all the second order features except the peaks A and B are preserved. Furthermore, at liquid nitrogen temperature, the phonon frequencies of the first order Raman lines increase by about 3 cm^{-1}, while the frequencies of the second order peaks increase by about 6–8 cm^{-1}. This also confirms that all the high energy second order peaks are due to either overtone or combination processes.

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Der Raman-Spektren Zweiter Ordnung von Schichtstrukturverbindungen MoS_2 wurde gemessen. Es wurden der verhalten von Zweidimenionalen Zustandsdichten beobachtet. Viele auf der Basis von der Raman-Spektren Zweiter Ordnung sind identifiziert gewurden.