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RESONANCE RAMAN SCATTERING IN TRANSITION-METAL DICHALCOGENIDES

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Resonance Raman scattering has been studied in group VIB transition-metal dichalcogenides, 2H-MoS_2, -WS_2, -$MoSe_2$ and -WSe_2. Raman intensities of A_{1g} phonons are enhanced at A and B exciton levels, and in addition at A' and B' exciton levels in diselenides. For E_{2g} phonon of 2H-$MoSe_2$ the resonance enhancements occur at A' and B' exciton levels but the E_{2g} phonon has anomalous polarization near the A and B exciton levels. This fact was observed in MoS_2 and WS_2, too.

I. Introduction

Transition-metal dichalcogenides are layered compounds and have two-dimensional structures. Group VIB transition-metal dichalcogenides MX_2 (M=Mo, W and X=S, Se) are semiconductors and their optical measurements [1] have been extensively carried out. The symmetry of 2H-polytype belongs to the space group D_{6h}^4 and there are 12 modes of lattice vibrations at Γ point. Among them Raman-active modes are A_{1g}, E_{1g} and two E_{2g}. With X=[100], Y=[010] and Z=[001] these Raman tensors are given as follows,

$$A_{1g}: \begin{bmatrix} a & & \\ & a & \\ & & b \end{bmatrix}, \quad E_{1g}: \begin{bmatrix} & & c \\ & & \\ c & & \end{bmatrix}, \begin{bmatrix} & & -c \\ & & \\ -c & & \end{bmatrix} \quad \text{and} \quad E_{2g}: \begin{bmatrix} & d & \\ d & & \\ & & \end{bmatrix}, \begin{bmatrix} d & & \\ & -d & \\ & & \end{bmatrix}. \qquad (1)$$

Raman scattering of these compounds has been done by some workers [2-7]. In back-scattering experiment on a surface perpendicular to c axis, the E_{1g} phonon is forbidden and one of E_{2g} phonons is a "rigid-layer" mode and its frequency is very small.

In the group VIB compounds a few sharp peaks due to excitons appear at fundamental absorption edges, i.e. two excitons A and B and in addition two other excitons A' and B' at higher energies in diselenides. But the origin of these excitons is still not well understood. Then we study the resonance Raman scattering of 2H-MoS_2, -WS_2, -$MoSe_2$ and -WSe_2 in the energy region of excitonic absorption for A_{1g} and higher-frequency E_{2g} phonons.

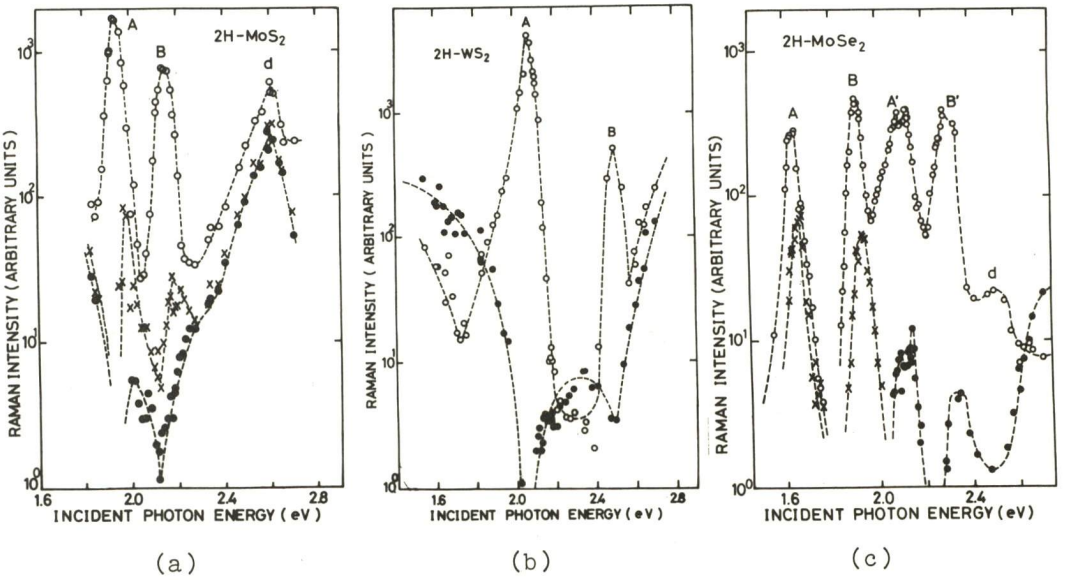
II. Experimental Details

Resonance Raman scattering measurements have been performed using 450-800 nm laser lines at liquid He temperature. We obtained these laser lines by operating an argon and a krypton ion lasers and a dye laser excited by the ion lasers. The experiments were carried out by nearly back-scattering method with cleaved or as-grown surfaces of samples grown by sublimation method or of natural samples. Raman

spectra were obtained by multichannel detector (IDARSS) of Tracor Northern through a Spex 1401 double monochromator.

III. Results and Discussion

Figure 1 shows Raman intensities (RIs) of 2H-MoS_2, -WS_2, -$MoSe_2$ and -WSe_2 for A_{1g} and higher-frequency E_{2g} phonons. These spectra were corrected for instrumental response, but not for the absorption and reflection coefficients of these samples, and they clearly show several peaks due to excitons and direct band-to-band transitions, as mentioned below. (RI, which is not corrected for the absorption and reflection coefficients, often does not exhibit resonance enhancements and only after this correction exhibits the resonance enhancements [8].)



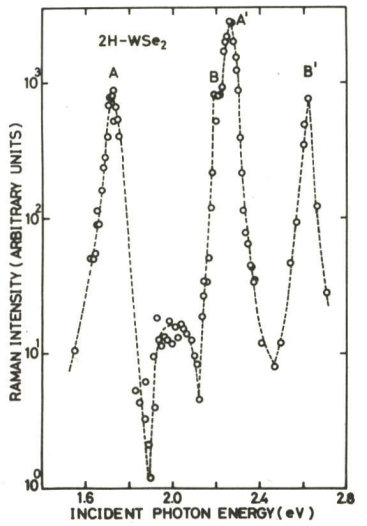


Fig.1 Raman intensities vs. incident photon energy in 2H-MoS_2, -WS_2, -$MoSe_2$ and -WSe_2
(a) 2H-MoS_2: o, A_{1g} phonon in $Z(XX+XY)\bar{Z}$; ×, E_{2g} phonon in $Z(XX)\bar{Z}$ and •, E_{2g} phonon in $Z(XY)\bar{Z}$
(b) 2H-WS_2: o, A_{1g} phonon in $Z(XX+XY)\bar{Z}$ and •, E_{2g} phonon in $Z(XY)\bar{Z}$
(c) 2H-$MoSe_2$: o, A_{1g} phonon in $Z(XX+XY)\bar{Z}$; •, E_{2g} phonon in $Z(XX+XY)\bar{Z}$ and ×, E_{2g} phonon with $Z(XX)\bar{Z}$ component in $Z(XX+XY)\bar{Z}$
(d) 2H-WSe_2: o, A_{1g} phonon in $Z(XX+XY)\bar{Z}$
In (a)-(d) the dashed lines are for clarity only.

In 2H-MoS_2 two sharp peaks at 1.93 eV and 2.15 eV and a broad peak at 2.61 eV were observed for A_{1g} phonon. When the intermediate states are excitonic in Raman process, the scattering cross section is enhanced more strongly than that when the intermediate states are free electron-hole pairs. Therefore two sharp peaks were attributed to A and B excitons, and the broad peak to direct band-to-band transition "d", whose energies agree with the absorption data [9]. On the other hand, RI of the E_{2g} phonon is enhanced by the band-to-band transition "d" but not by the A and B excitons in $Z(XY)\bar{Z}$ configuration, where the dips at these two exciton levels are expected to become flat by correcting the RI for the absorption and reflection coefficients. But in $Z(XX)\bar{Z}$ configuration, it is enhanced at these two exciton levels, where the peak shifts to about 30 meV at higher energy side. This fact shows that the E_{2g} phonon does not have usual Raman tensors as shown in eq. (1) near the A and B exciton energies.

In 2H-WS_2 we obtained the same result as in 2H-MoS_2 near the energies of A (2.07 eV) and B (2.52 eV) excitons and of a direct band-to-band transition at higher energy than 2.7 eV, though the $Z(XX)\bar{Z}$ component of E_{2g} phonon is not shown in Fig. 1(b). The existence of the A' and B' excitons in the disulfides is always questioned [10], and our results obviously deny it.

In 2H-$MoSe_2$ the resonance behavior of the A_{1g} and E_{2g} phonons near A (1.64 eV) and B (1.91 eV) exciton levels are the same as in MoS_2 and WS_2. At A' (2.11 eV) and B' (2.31 eV) exciton levels the resonance enhancements were observed for the A_{1g} phonon and for the E_{2g} phonon having the same intensities in $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$ configurations. The RI of the A_{1g} phonon is enhanced weakly by a band-to-band transition "d" at about 2.5 eV, which was not clear in the absorption data [9]. The RI of the E_{2g} phonon also is enhanced by a direct band-to-band transition at higher energy than 2.7 eV, which may be probably "C" transition [9].

In 2H-WSe_2 E_{2g} phonon has a frequency very close to A_{1g} phonon [7] and its intensity is very weak, and we were unable to separate the E_{2g} phonon from the A_{1g} phonon even in $Z(XY)\bar{Z}$ configuration. However we obtained the resonance enhancements at A (1.72 eV), B (2.19 eV), A' (2.27 eV) and B' (2.62 eV) exciton levels for A_{1g} phonon.

The usual Raman tensors are second rank and when the incident photon energy approaches to exciton levels and we assume that the wave vectors of an incident and a scattered photon are zero, it is given as follows [11],

$$R_{lz} \propto \sum_{\substack{n c v \\ n' c' v'}} \frac{U_{cvn}(0)\, U^{*}_{c'v'n'}(0)\, \langle v|\vec{\varepsilon}_2\cdot\vec{p}|c\rangle \{\langle c|\Xi|c'\rangle \delta_{vv'} - \langle v'|\Xi|v\rangle \delta_{cc'}\} \langle c'|\vec{\varepsilon}_1\cdot\vec{p}|v'\rangle}{[E_n(cv) - \hbar\omega_1 + \hbar\omega_0][E_{n'}(c'v') - \hbar\omega_1]} \quad , \quad (2)$$

where $E_n(cv)$, $\hbar\omega_1$ and $\hbar\omega_0$ are energies of exciton, incident photon and phonon, respectively. $U_n(r)$ is an envelope function of exciton with quantum number n. $|v\rangle$ ($|v'\rangle$) and $|c\rangle$ ($|c'\rangle$) are wave functions of valence and conduction bands. $\vec{p}$ and $\vec{\Xi}$ are momentum vectors of electrons and deformation potential. $\vec{\varepsilon}_1$ and $\vec{\varepsilon}_2$ are polarizations of incident and scattered photons. Band calculation [12] and recent modulation spectroscopy [13] suggested that the A and B excitons originate from the d-d band transition at Γ point, while the A' and B' excitons from the p-d band transition and that the splittings between the A and B excitons and between the A' and B' excitons are due to spin-orbit interaction. By considering the spin-orbit interaction

the representations of all bands at Γ point are restricted to be $\Gamma_7^{\pm}$, $\Gamma_8^{\pm}$ and $\Gamma_9^{\pm}$. Then the matrix elements $\langle c|\Xi|c\rangle$ and $\langle v|\Xi|v\rangle$ of the E_{2g} (Γ_6^+) phonon are forbidden for all bands at Γ point in the intraband exciton-phonon scattering process, but those of A_{1g} (Γ_1^+) phonon are allowed. This selection rule explains that the RIs of the A_{1g} phonons are enhanced by the A and B excitons but the RIs of the E_{2g} phonons are not enhanced in $Z(XY)\bar{Z}$ configuration at these two exciton levels. Since Frohlich interaction, which is important for LO phonon [14], is not necessary to be considered in this case, the higher order effect due to impurities or surface effect or strain may probably give rise to the enhancements of the E_{2g} phonons in $Z(XX)\bar{Z}$ configuration.

On the other hand, the RI of the E_{2g} phonon of 2H-$MoSe_2$ is enhanced at the A' and B' exciton levels both in $Z(XX)\bar{Z}$ and $Z(XY)\bar{Z}$ components. For the A_{1g} phonon the intraband exciton-phonon scattering process is predominant near these two exciton levels, because in interband scattering process Raman tensor has weaker divergences at exciton levels than that in intraband scattering process. Though the RI of the E_{2g} phonon is much weaker than that of the A_{1g} phonon near the A' and B' exciton energies, the resonance behavior of the E_{2g} phonon is very similar to that of A_{1g} phonon. Therefore it is good to consider that the intraband exciton-phonon scattering process is predominant in the E_{2g} phonon. It is concluded that the A' and B' excitons originate from some bands at other than Γ point in Brillouin zone.

In conclusion we observed the resonance enhancements of the Raman scattering by the A_{1g} phonons at the A and B exciton levels in 2H-MoS_2, -WS_2, -$MoSe_2$ and -WSe_2 and in addition at the A' and B' exciton levels in diselenides. The RI of the E_{2g} phonon is enhanced at the A' and B' exciton levels in 2H-$MoSe_2$, but its selection rule is broken near the A and B exciton energies. The same results were observed in MoS_2 and WS_2. According to this fact it is good to consider that the A and B excitons originate from the bands at Γ point but the A' and B' excitons from some bands at other than Γ point in Brillouin zone.

References

1) B.L. Evans: Optical and Electrical Properties ed. by P.A. Lee (Reidel, Dordrecht, 1976) p. 1.
2) T.J. Wieting and J.L. Verble: Phys. Rev. B12 (1971) 4286.
3) J.M. Chen and C.S. Wang: Solid State Commun. 14 (1974) 857.
4) T. Sekine, T. Nakashizu, K. Toyoda, K. Uchinokura and E. Matsuura: to be published in Solid State Commun.
5) T. Sekine, M. Izumi, T. Nakashizu, K. Uchinokura and E. Matsuura: to be published in J. Phys. Soc. Japan.
6) T.J. Wieting, A. Griesel and F. Levy: Physica 99B (1980) 337.
7) D.G. Mead and J.C. Irwin: Can. J. Phys. 55 (1977) 379.
8) J. Camassel, T.C. Chiang, Y.R. Shen, J.P. Voitchovsky and N.M. Amer: Solid State Commun. 19 (1976) 483.
9) A.R. Beal, J.C. Knights and W.Y. Liang: J. Phys. C5 (1972) 3540.
10) K. Saiki, M. Yoshimi and S. Tanaka: Phys. Stat. Sol. (b)88 (1978) 607.
11) A.K. Ganguly and J.L. Birman: Phys. Rev. 162 (1967) 806.
12) L.F. Mattheiss: Phys. Rev. B8 (1973) 3791.
13) M. Tanaka, H. Fukutani and G. Kuwabara: J. Phys. Soc. Japan 45 (1978) 1899.
14) R.M. Martin and T.C. Damen: Phys. Rev. Lett. 26 (1971) 86.