RAMAN SPECTRA OF IVB AND VIB TRANSITION METAL DISULFIDES USING LASER ENERGIES NEAR THE ABSORPTION EDGES

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Abstract—In this paper, we present Raman spectra of ZrS_2 , HfS_2 , MoS_2 and WS_2 using laser energies near the energies of the absorption edges. The Raman spectra probe the properties of the first-excited electronic state and the nature of the electron-phonon coupling. The spectra of the IVB disulfides are independent of the laser excitation energy, suggesting weak electron-phonon interaction. In contrast, additional Raman bands appear in the spectra of the VIB disulfides as the laser energy approaches the band gap energy. The new modes in the spectra of MoS_2 and WS_2 cannot be assigned as first-order processes nor as combination bands of the phonons with zero momentum. The resonance Raman scattering of MoS_2 is analyzed in terms of second-order scattering due to the coupling of phonon modes of nonzero momentum with an electronic transition associated with excitonic states.

INTRODUCTION

The layered transition metal dichalcogenides are characterized by anisotropic properties related to the quasi-two-dimensional character of their crystal structure [1–3]. These materials range from insulators to metals and have a diversity of properties including charge density waves [4], superconductivity [5], sharp exciton peaks in the optical spectra [6], catalytic activity [7] and a rich intercalation chemistry [8]. The superconductivity and charge density waves in the metallic layered materials suggest strong electronphonon interaction. In this paper, we probe the electron-phonon coupling in the semiconducting layered disulfides by resonance Raman spectroscopy.

The semiconducting group IVB and VIB dichalcogenides have a layered structure consisting of a hexagonal array of metal atoms sandwiched between arrays of hexagonally ordered chalcogens. The group IVB metals occupy trigonally distorted octahedral sites between the anion layers, whereas the VIB metals are in trigonal prismatic sites. The chalcogenmetal-chalcogen layers are stacked such that the repeat distance is one layer in the IVB compounds and two layers in the VIB compounds. While the bonding within a layer is strong, adjacent layers are held together by weaker van der Waals interaction.

The semiconducting layered compounds considered in this paper have band gap energies at room temperature as follows: E_g (ZrS₂) ~ 1.68 eV [9], E_g (HfS₂) ~ 1.96 eV [9], E_g (MoS₂) ~ 1.7 eV [1] and E_g (WS₂) ~ 1.9 eV [1]. Although these materials are structurally and chemically related, the details of their band structures are different [10–12]. The group IVB materials, with distorted octahedral coordination about the metal, have a filled valence band derived primarily from chalcogen s and p orbitals and an empty conduction band of the energetically similar metal d_{z^2} , $d_{x^2-y^2}$ and d_{xy} orbitals [10, 11]. The group VIB materials, with trigonal prismatic coordination about the metal, have a filled d_{z^2} valence band overlapping the filled chalcogen sp orbitals. The conduction band is derived from the degenerate metal $d_{x^2-y^2}$ and d_{xy} orbitals that overlap the empty antibonding chalcogen sp orbitals [10, 12, 13].

The optical spectra in Fig. 1 show the differences in the band structures. A simple valence to conduction band electronic transition is observed in the optical spectra of ZrS_2 and HfS_2 [1, 14]. In contrast, the absorption spectra of MoS_2 and WS_2 show complex excitonic features at the adsorption edge attributed to electronic transitions between the filled and empty *d* bands [1, 6, 15].

In this paper, we present Raman spectra of ZrS_2 , HfS_2 , MoS_2 and WS_2 for laser energies close to the energies of the absorption edges (see Fig. 1). The Raman spectra obtained probe the properties of the first-excited electronic state of these materials and the nature of the electron-phonon coupling. The resonance Raman scattering of MoS_2 is analyzed in some detail using the band structure calculated by Mattheiss [10] and the phonon dispersion measured by inelastic neutron scattering by Wakabayashi *et al.* [16]. The importance of second-order scattering from phonons with nonzero momentum is emphasized.

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Fig. 1. Transmission spectra for the IVB and VIB disulfides at room temperature: (a) 1*T*-ZrS₂, (b) 1*T*-HfS₂, (c) 2H-MoS₂ and (d) 3R-WS₂ (after ref. [1]). Data for 2H-WS₂ are not available but the positions of the excitons in 2H-WS₂ and 3R-WS₂ are similar [1]. The laser excitation energies used in the Raman experiments are indicated.

EXPERIMENTAL

Powder samples of 1T-ZrS₂, 1T-HfS₂, 2H-MoS₂ and 2H-WS₂ were prepared by high-temperature reactions of stoichiometric mixtures of high-purity elements sealed in quartz ampoules and evacuated to less than 10^{-5} Torr. The indicated structural polytypes were verified by powder X-ray diffraction. The resulting powders were sealed in spectrosil tubing for the Raman experiments. The group IVB materials were handled without exposing the powders to air.

The Raman experiments were carried out in the backscattering geometry. The 676.4, 647.1 and 530.9 nm lines of a Coherent Radiation Model CR-500K cw krypton ion laser were used with powers below 100 mW. The *p*-polarized laser light was focused to a line image on the sample using a cylindrical lens, with an angle of incidence near 45° . The Raman scattered light was analyzed with a Spex Model 1400-II double monochromator and detected with an RCA 31034 photomultiplier by photon counting. A Ratheon Data Systems Model 500 Computer was used to acquire the data. The spectra were calibrated with a neon lamp and the spectrometer band pass was 3 cm⁻¹.

RESULTS

Previous studies of the Raman spectra of the transition metal dichalcogenides include Raman scattering from soft modes due to charge density waves [17] and by superconducting gap excitations [18] in the VB compounds as well as the normal Raman scattering with 514.5 nm (2.41 eV) laser excitation for the IVB and VIB compounds [19-24]. Sekine et al. [25] have studied the variation in the intensity of the first-order Raman modes in the VIB materials as the laser excitation energy is varied between 1.8 and 2.8 eV. We compare the spectra at 514.5 nm for the IVB and VIB disulfides with spectra that we have obtained at excitation energies of 676.4 nm (1.83 eV), 647.1 nm (1.92 eV) and 530.9 nm (2.34 eV). Additional peaks appear in the spectra of MoS₂ and WS2 that cannot be assigned as one-phonon processes nor second-order combinations of phonons with zero momentum (i.e. at the Γ point of the Brillouin zone). We compare the unusual resonance Raman scattering observed for MoS₂ and WS₂ with the normal Raman scattering always observed for HfS₂ and ZrS₂, even for laser energies near the energies at the absorption edges.

The Raman spectra of ZrS_2 ($E_g \sim 1.68 \text{ eV}$) and HfS_2 ($E_g \sim 1.96 \text{ eV}$) with 647.1 nm (1.92 eV) excitation are shown in Fig. 2. The energies of the A_{1g} and E_g modes observed are in agreement with previous studies [19]. Only the absolute intensities of these two modes change with the laser excitation energy; no additional peaks are observed.

The Raman spectra of MoS₂ ($E_g \sim 1.7 \text{ eV}$) at three excitation wavelengths are compared in Fig. 3. The VIB compounds have four Raman-active modes [20]. The E_{2g}^1 and A_{1g} modes observed at 383 and 409 cm⁻¹, respectively, with 530.9 nm laser light are in agreement with previous reports [20]. The E_{1g} mode (287 cm⁻¹) is not observed due to the laser polarization chosen and the random orientation of the crystallites in the powder sample. We did not



Fig. 2. Raman spectra of (a) 1*T*-ZrS₂ and (b) 1*T*-HfS₂ powders at room temperature using 647.1-nm light.



Fig. 3. Raman spectra of 2H-MoS₂ powder at room temperature for three different incident photon energies. (a) 676.4 nm; (b) 647.1 nm and (c) 530.9 nm.

probe below 100 cm⁻¹ to look for the E_{2g}^2 rigid-layer lattice vibration previously observed at 34 cm⁻¹ [21]. The broad feature centered near 400 cm⁻¹ in Figs. 3(b) and 3(c) is a weak Raman band due to the container.

The resonance Raman spectra of MoS_2 at 676.4 and 647.1 nm have many new peaks not observed at 530.9 nm. The frequency shifts of the new bands are similar to the frequencies of the weak second-order peaks in the spectrum obtained by Chen and Wang [23] with 1.2 W of 514.5 nm light. The relative intensities of the various bands vary dramatically with the excitation energy and the asymmetric shapes of the bands at 177, 466, 601 and 643 cm⁻¹ are striking.

The Raman spectra of WS₂ ($E_g \sim 1.9 \text{ eV}$) at three excitation wavelengths are compared in Fig. 4. Of the four Raman-active modes, only the band at 421 cm⁻¹ can be identified unambiguously as the A_{1g} mode. The E_{2g}^1 mode is expected to occur near 352 cm⁻¹ [24]. However, the wavelength dependence and the linewidth of the band at 352 cm⁻¹ suggests that this intense peak is due to a second-order process that overlaps the E_{2g}^1 . Above 250 cm⁻¹, five weak bands are observed, in agreement with the spectrum obtained by Sekine *et al.* [24] with 514.5-nm excitation.

DISCUSSION

Crystalline semiconductors exhibit first-order Raman scattering only by phonons of approximately zero momentum. If the laser energy is in the region of an electronic transition, multiphonon Raman scattering may be observed; the resonance Raman spectra of the post-transition metal semiconductors and some rare-earth chalcogenides show overtone and combination bands of the phonons with zero momentum [26, 27]. Combination bands of phonons with nonzero momentum are possible in second-order by creating two phonons of equal and opposite momentum, but there are few examples of such scattering [26–28]. In our analysis of the resonance Raman spectra of MoS_2 and WS_2 , we suggest that scattering by phonons with nonzero momentum occurs.

The Raman spectra of ZrS_2 and HfS_2 show no multiphonon scattering, even for laser energies 0.05 eV below the absorption edge. Band-structure calculations [10, 11] show these materials to be indirect gap semiconductors with the lowest energy direct transition at the Γ point of the Brillouin zone. No excitonic peaks are observed in the optical spectra of these materials [9]. The lack of excitonic peaks and multiphonon Raman scattering indicates that the excited state resulting from the electronic transition from the valence band of chalcogen *sp* orbitals to the conduction band of metal *d* orbitals is not coupled strongly to the phonon modes.

A rich multiphonon Raman spectrum is observed for MoS_2 , even for laser energies 0.2 eV below or above the absorption edge. The calculation of the band structure of MoS_2 by Mattheiss [10] shows an indirect gap between the Γ and T points and the lowest-energy direct transition is at the K point. Sharp features in the optical spectra near the absorption edge, labelled A and B, have been attributed to excitons [1, 6, 15]; in 2H-MoS₂, the A and B excitons



Fig. 4. Raman spectra of 2H-WS₂ powder at room temperature for three different incident photon energies. (a) 676.4 nm; (b) 647.1 nm and (c) 530.9 nm.

are at 1.9 and 2.1 eV [1], respectively. Although there is still much controversy as to the origins of these excitons, most authors agree that the A and B peaks are due to d to d transitions from the filled d_{z^2} orbital to the pair of states which are a mixture of the d_{xy} and $d_{x^2-y^2}$ orbitals that are split by spin-orbit coupling [1, 10, 12, 13, 29, 30]. Except for a recent paper by Khan and Goldsmith [31], most analyses assign the excitons to transitions at the Γ point. The resonance Raman scattering suggests that these electronic transitions are coupled strongly to the phonon modes.

The resonance Raman scattering of MoS₂ can be interpreted in some detail using the inelastic neutron scattering data (in the $\Gamma - M[100]$ direction) of Wakabayashi *et al.* [16]. The neutron data show the four modes with zero momentum (Γ point) observed in the normal Raman spectrum. The energy dispersions of A_{1g} , E_{2g}^1 and E_{1g} modes in the Γ -*M* direction are small. The energy of the rigid-layer E_{2g}^2 mode at the Γ point increases in the Γ -*M* direction to a longitudinal acoustic mode LA(M) $\cong 232$ cm⁻¹ at the *M* point.

Chen and Wang [23] assign the weak multiphonon scattering peaks in their spectrum of MoS_2 taken with 514.5 nm light as combination bands of phonons at the *M* point of the Brillouin zone. We agree with their assignments and find additional peaks due to combination bands of phonons at the *M* point. The assignments for the various Raman bands are given in Table 1. Many of the new bands are combination and difference bands coupled with the longitudinal acoustic mode LA(M). The large asymmetric peak at 466 cm⁻¹ is assigned as twice the fundamental frequency of LA(M). If LA(M) has a frequency of 233 cm⁻¹, then from the sum and difference modes at 643 cm⁻¹ [$A_{1g}(M) + LA(M)$] and 177 cm⁻¹ [$A_{1g}(M) - LA(M)$], we predict that the frequency of $A_{1g}(M)$ is 410 cm⁻¹. Likewise, we suggest that the frequency of $E_{1g}(M)$ is 296 cm⁻¹ from the assignment of the band at 529 cm⁻¹ [$E_{1g}(M) + LA(M)$] and from the bands at 601 cm⁻¹ [$E_{1g}(M) + LA(M)$] and 780 cm⁻¹ [$A_{1g}(M) + E_{2g}^{1}(M)$], we suggest $E_{2g}^{1}(M)$ has a frequency of 368 cm⁻¹. Table 2 compares these predictions for the frequencies of the phonon modes at the M point with the frequencies of the modes at the Γ point and M point measured by Wakabayashi *et al.* [16], with good agreement.

All the multiphonon bands involving LA(M) are asymmetric. While the dispersions of A_{1g} , E_{2g}^1 and E_{1g} in the Γ -*M* direction are small, the frequency of the LA mode vs momentum has an inverse parabolic shape near the *M* point. The electronic transitions of wavevector $\Gamma \pm \delta$, for small δ , will couple to phonons of momentum $M \pm \delta$. Combination bands that are sum bands will tail to lower frequency due to contributions of the lower energy LA(M $\pm \delta$) modes. (The phonon dispersion is concave down at the *M* point.) Similarly, as expected for a difference band, the band at 177 cm⁻¹ has a tail on the highfrequency side. The asymmetric shape of the combination bands involving the LA phonons therefore supports our assignments.

Chen and Wang draw their conclusions based on the temperature dependences of the intensities of several of the bands. We hesitate to interpret the temperature dependences of our spectra due to the large temperature dependence of the magnitude and energy of the excitonic absorption bands [6]. Such

| Frequency (cm ⁻¹) | Assignments | | |
|-------------------------------|----------------------|-----------------------------------|--|
| | 1st Order | 2nd Order | |
| 34† | $E_{2g}^{2}(\Gamma)$ | | |
| 152 | | Spurious? | |
| 177 | | $A_{1g}(M)$ -LA(M) | |
| 287† | E1g(1) | -0 | |
| 383 | $E_{2g}^{1}(\Gamma)$ | | |
| 409 | Α _{1g} (Γ) | | |
| 466 | | 2LA(M) | |
| 529 | | $E_{10}(M) + LA(M)$ | |
| 572 | | $2E_{1g}(\Gamma)$ | |
| 601 | | $E_{2\sigma}^{1}(M) + LA(M)$ | |
| 643 | | $A_{1g}(M) + LA(M)$ | |
| 780 | | $A_{1g}^{-1}(M) + E_{2g}^{1}(M)$ | |
| 820 | | $2A_{1g}(\Gamma)$ or $2A_{1g}(M)$ | |

Table 1. Frequencies and assignments of the bands observed in the resonance Raman spectrum of MoS₂ with 676.4-nm excitation

 \dagger Since these modes are not observed in our spectra of MoS₂ powder, the frequencies have been taken from refs. [20] and [21].

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| Table 2. | The frequencies | of the first-ord | er phonon n | nodes of MoS | b_2 at the Γ | and M poin | nts of the | Brillouin |
|----------|-----------------|------------------|-------------|--------------|-----------------------|------------|------------|-----------|
| | | | ZC | one | | | | |

| | Phonon Frequencies (cm ⁻¹) | | | | |
|-----------------|--|-----|-----|--|--|
| | Г | Mţ | M‡ | | |
| A _{1g} | 409 | 397 | 410 | | |
| E_{2g}^{1} | 383 | 373 | 368 | | |
| E _{1g} | 287 | 294 | 296 | | |
| LA | | 234 | 233 | | |
| E_{2g}^2 | 34 | | | | |

 \dagger Frequencies of the phonon modes at the M point obtained from the neutron scattering data in ref. [16].

 \ddagger Frequencies of the phonon modes at the M point as predicted from the resonance Raman data.

large changes in the optical properties of MoS_2 with temperature complicate the analysis of the changes in the intensities of the Raman bands as a function of temperature. We prefer to argue on the basis of the shapes of the sum and difference bands.

In contrast to the strong multiphonon scattering observed in the spectra of MoS₂, the second-order features in the spectra of WS₂ are weak relative to the first-ordering scattering. The A and B excitons in 2H-WS₂ are at 2.0 and 2.4 eV, respectively, compared to 1.9 and 2.1 eV for 2H-MoS₂ [1]. We speculate that the intense, asymmetric band at 352 cm⁻¹ corresponds to the 466-cm⁻¹ band in the spectrum of MoS₂; the 352-cm⁻¹ band is an overtone of a longitudinal acoustic mode (LA) of frequency 176 cm⁻¹ and nonzero momentum. The weak band at 525 cm⁻¹ can be assigned to E_{2g}^1 + LA and the band at 584 cm⁻¹ as A_{1g} + LA. A calculation of the band structure of 2H-WS₂ and inelastic neutron scattering data are necessary before a detailed comparison between the resonance Raman spectra of WS₂ and MoS₂ can be made.

In conclusion, the resonance Raman data of MoS_2 and WS_2 in comparison to HfS_2 and ZrS_2 demonstrate strong electron coupling to phonons of nonzero momentum. We hope the richness of these resonant spectra can be used to help unravel the nature of the excitons in these materials.

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