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Urbach tail in the absorption spectra of 2H-WSe_2 layered crystals

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1 Introduction

WSe_2 is a diamagnetic indirect semiconductor with a band gap of around 1.2 eV and strong covalent bonding within the Se–W–Se layers but only rather weak van der Waals interactions between neighboring sandwich layers [1–3]. WSe_2 shows significant anisotropy in its physical properties and plays a key role in a number of technologies like high temperature solid lubrication and rechargeable batteries [4–6]. Due to its high optical absorption, the layered arrangement between the cations, high resistance against photo-corrosion and the magnitude of its band gap, WSe_2 is an important material in photo-electrochemical conversion and photovoltaic solar energy conversion [7, 8]. Recently, WSe_2 has been reported to be a potential candidate for the application in high-mobility field-effect transistors [9]. In spite of its importance in technological applications as a candidate material for optical devices and also for the understanding of its basic physics, so far very little information on the effect of temperature on the optical band gap for the association with the electronic distortion in addition to the influence of electron/exciton-phonon interaction [10, 11].

In this work, we report on the photoconductivity (PC) measurements of optical absorption-edge as a function of photon energy in 2H-WSe_2 layered crystals between 15 and 300 K. Temperature dependence of the indirect band gap and characteristic Urbach's parameters were determined by analyzing the data using Varshni semi-empirical equation [12] and a Bose–Einstein empirical expression [13–15]. The results were applied to estimate the effective phonon energy and the Debye temperature.

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2 Experimental details

Layered crystals of 2H-WSe_2 were prepared by vapor transport technique, employing Br_2 as a transport agent from the elements W (99.99% purity), Se (99.999% purity) having stoichiometric starting materials sealed in evacuated (~10^{-6} Torr). Details of experimental procedure for crystal growth were reported elsewhere [16]. Crystal structure of the as-grown samples was determined by a Rigaku RTP 300RC X-ray diffractometer (XRD) using Cu K_α radiation with a wavelength of 1.542 Å. The XRD patterns showed a good match with the reported patterns for two-layered hexagonal (2H) structure of WSe_2 (space group $P6_3/mmc$). The lattice parameters were calculated as $\boldsymbol{a}$ = 3.29 Å and $\boldsymbol{c}$ = 12.99 Å, which are in good agreement with the reported values for 2H-WSe_2 (JCPDS No. 38-1388). The silver coloured crystal exhibits good optical quality and yields about 2.5 × 2.5 mm^2 large platelets when cleaved perpendicular to the optical $\boldsymbol{c}$-axis. Samples were found to be n-type with the majority carrier concentration of around 7.3 × 10^{15} cm^{-3} by Hall measurements at 300 K. All samples used in this work had about 1.2 × 1.5 mm^2 surface area with a thickness of 20–250 μm. No further polishing and cleaning treatments were required because of the natural mirror-like cleavage faces.

The PC spectra were taken from experiments in the direction perpendicular to the layers. The inset in Fig. 1(a) schematically illustrates the direction of the incident light beam on the surface of 2H-WSe_2 crystals shown as the dotted arrow sign. The electrical connections were provided with four Au wire contacts and the ohmic behavior was confirmed by linear I–V characteristics. The PC measurements were set up by using a monochromator (SpectraPro 300i) with an Oriel 1000 W halogen light source while the signal was measured by a phase sensitive detection instrument (SR530 lock-in amplifier) and recorded by a computer. The sample temperature was varied from 15 to 300 K by a modified and computer controlled LakeShore 321 model temperature controller with an accuracy of ±0.5 K.

3 Results and discussion

The PC spectra of 2H-WSe_2 at 15, 80, 200 and 300 K, respectively, are displayed in Fig. 1(a). The shape of PC spectrum is similar to the results of previous reports and the low-energy absorption-edge has been attributed to the indirect band gap transition [7, 11, 17, 18]. Friemelt et al. have described that the PC intensity is proportional to the absorption coefficient, taking into account both absorption and emission of phonons, the peak position of indirect band gap can be estimated by the following equation

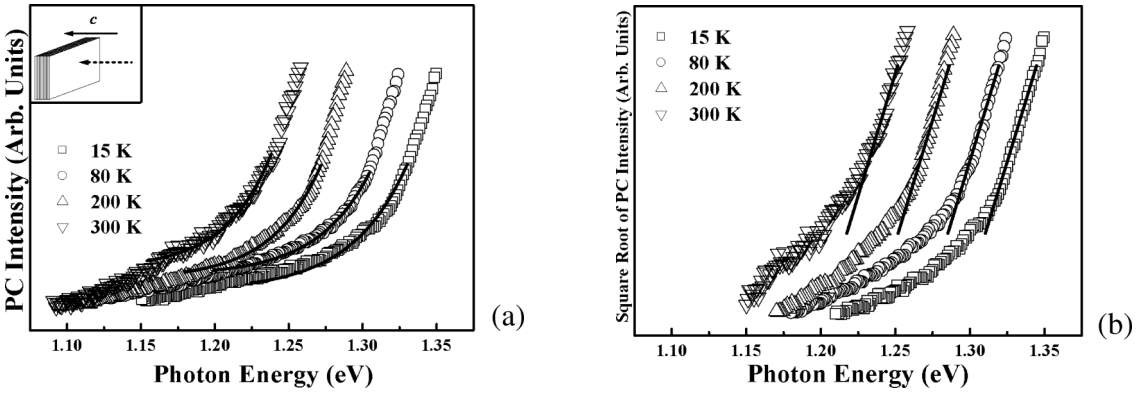

Fig. 1 PC spectra of 2H-WSe_2 at several representative temperatures between 15 and 300 K. (a) Solid lines represent the best fit to Eq. (5) for the Urbach's absorption tail of 2H-WSe_2. (b) The square root of PC intensity depends linearly on the photon energy in the vicinity of the indirect band gap as illustrated and the indirect energy gap of 2H-WSe_2 is estimated by using Eq. (1). The inset in Fig. 1(a) schematically illustrates the direction of the incident light beam shown as the dotted arrow sign.

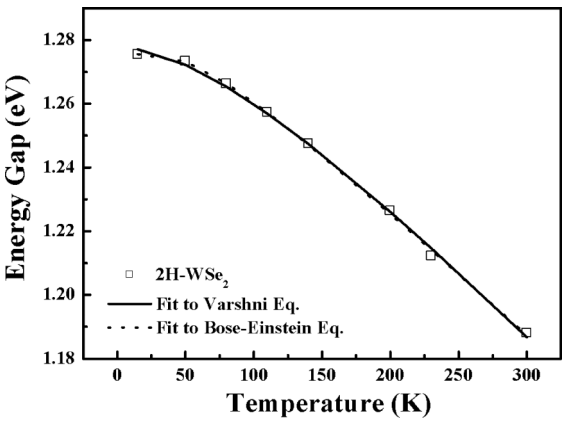

Fig. 2 Experimental values of the temperature dependence of $E_{gi}(T)$ for 2H-WSe_2. Solid lines are best fits to Varshni equation while the dotted lines are best fits to Bose–Einstein equation.

[18, 19]:

$$\text{PC Intensity} \propto \alpha_{\text{indirect}}(h\nu) = \frac{C_1\left(h\nu - E_{gi} + E_p\right)^2}{\exp\left(\frac{E_p}{kT}\right) - 1} + \frac{C_2\left(h\nu - E_{gi} - E_p\right)^2}{1 - \exp\left(-\frac{E_p}{kT}\right)}, \tag{1}$$

where $h\nu$ is the energy of the incident photon, E_{gi} is assigned to be the indirect band gap and E_p is the phonon energy assisting the transitions, C_1 and C_2 are constants. The square root of PC intensity depends linearly on the photon energy in the vicinity of the indirect band gap as illustrated in Fig. 1(b) and the indirect band gap can be determined from the intercept with the energy axis in the plot at different temperatures [19].

The temperature-dependent experimental values of $E_{gi}(T)$ for 2H-WSe_2 are analyzed by the Varshni semi-empirical equation (solid lines in Fig. 2), which is given by [10]:

$$E_{gi}(T) = E_{gi}(0) - \frac{\alpha T^2}{T + \beta}, \tag{2}$$

where $E_{gi}(0)$ is the indirect transition energy at 0 K, α and β are constants referred to as Varshni coefficients. The constant α is related to the electron/exciton–phonon interaction and β is closely related to the Debye temperature (Θ_D) by the relation of $\beta \approx (3/8)\,\Theta_D$ [20]. The obtained values of $E_{gi}(0)$, α and β are listed in Table 1. From the fitted value of β, the value of Θ_D is estimated to be 160 K. The Debye temperature can also be estimated from the Lindemann's formula [21]:

$$\Theta_D \approx 120 T_m^{\frac{1}{2}} A^{-\frac{5}{6}} \rho^{\frac{1}{3}}, \tag{3}$$

where T_m is the melting-point, A is the mean atomic weight and ρ is the mean density of the material. 2H-WSe_2 decompose without melting at the temperature of 1050 °C [16]. Therefore taking this to be the decomposition temperature T_m in Eq. (3) with A = 113.92 g/mol [22] and ρ = 9.0 g/cm^3 [22] leads to $\Theta_D \approx 156$ K. The experimentally fitted Debye temperature agrees well with the theoretical estimation.

Table 1 Values of the parameters $E_{gi}(0)$, E_B, α, a_B, β and Θ were obtained from a fit to Eqs. (2) and (4).

	$E_{gi}(0)$ [eV]	E_B [eV]	α [meV/K]	a_B [meV]	β [K]	Θ [K]
Varshni	1.28		0.47		60	
Bose–Einstein		1.30		28		120

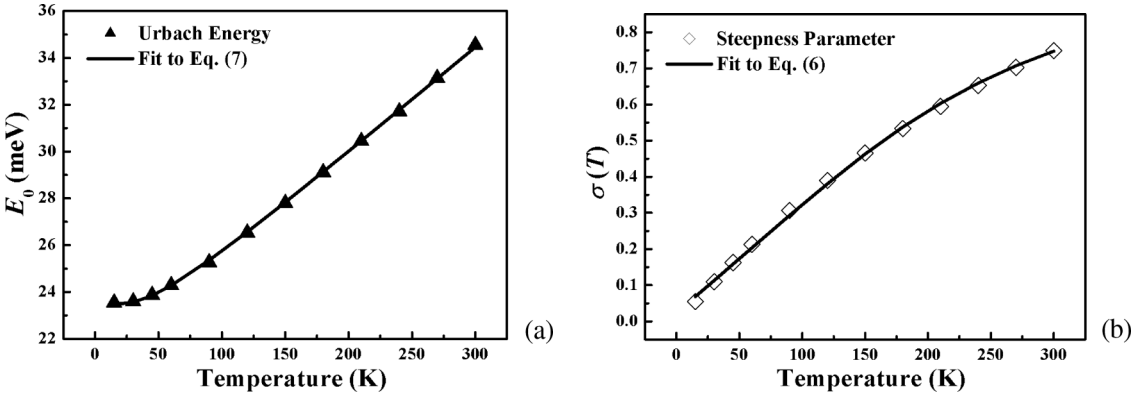

Fig. 3 (a) Variation of the Urbach energy, E_0 (closed triangles), as a function of temperature for 2H-WSe_2 and the solid line represents the best fit to the Einstein oscillator model of Eq. (7). (b) The steepness parameters, $\sigma(T)$ (diamonds), as a function of temperature for 2H-WSe_2 and the solid line represents the best fit by using Eq. (6).

The temperature dependence of indirect transition energies have also been fitted (dotted lines in Fig. 2) by an expression containing the Bose–Einstein occupation factor for phonons [13–15]:

$$E_{gi}(T) = E_B - a_B\left(1+\frac{2}{\exp\left(\frac{\Theta}{T}\right)-1}\right), \tag{4}$$

where a_B represents the strength of the electron/exciton–phonon interaction and Θ corresponds to the average phonon temperature. The fitted values for E_B, a_B and Θ are also given in Table 1 and the fitted value of Θ is consistent of the relation of $\Theta \approx (3/4)\,\Theta_D$ [20]. The parameters obtained from both fitting procedures using Eqs. (2) and (4), are checked for consistency. For example, at high temperature limit, the value of α of Eq. (2) is related to a_B and Θ of Eq. (4) by the relation $\alpha \approx 2a_B/\Theta$. Within the error limits, this relation holds fairly well. The temperature shifts of the energies are due to both the lattice variations and interactions with relevant acoustic and optical phonons. Our results agreed favourably with the previous Ref. [13].

In the temperature range of 15 to 300 K, the PC spectra of 2H-WSe_2 sample exhibits an absorption tail due to residual absorption at photon energies below the absorption edge. Such observation as pointed out by Ho et al. [23] is an indication of the existence of impurities and defects in the layered materials. Abay et al. [10, 24] attributed the absorption tail to the interaction of electrons/excitons with phonons in the layered semiconductors. Therefore, the absorption tail should be considered for understanding the effect of these phonon effects or defect states in 2H-WSe_2 material. The absorption tail has been firstly discussed by Urbach and the absorption coefficient near the absorption edge has an exponential shape which can be expressed as [25]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_0}\right), \tag{5}$$

where α_0 is a constant; E_0 is the Urbach energy describing the distribution of tail states extending into the forbidden gap. From Eq. (5), we have fitted the Urbach's tail of the absorption edge. A very good fit to the experimental results using Eq. (5) can be obtained and displayed as solid lines in Fig. 1(a). From the fits, we obtain the Urbach energy E_0 as a function of temperature and the dependence is illustrated in Fig. 3(a) as closed triangles.

The Urbach energy of the absorption edge can also be expressed by an inverse logarithmic slope relation $E_0 = kT/\sigma(T)$, where $\sigma(T)$ is called the steepness parameter [10, 24]. The temperature-dependent

steepness parameter was then calculated from the slope of the fitted Urbach energy (via Eq. (5)) of 2H-WSe_2 and the dependences are shown in Fig. 3(b) (diamonds). The derived temperature dependence of $\sigma(T)$ can be analyzed by the empirical temperature-dependent relation [26, 27] given as:

$$\sigma(T) = \frac{2kT\sigma_0}{h\nu_p} \tanh\left(\frac{h\nu_p}{2kT}\right), \tag{6}$$

where σ_0 is a temperature-independent but material-dependent constant. The term $h\nu_p$ is attributed to the effective phonon energy describing the electron/exciton–phonon interaction. The solid lines in Fig. 3(b) represent the best fits to the derived $\sigma(T)$ data by using Eq. (6). From the fits, the values of $h\nu_p$ for light illuminated on the surface of 2H-WSe_2 crystals are determined to be 29.4 meV. Mead et al. have recorded the Raman spectra of 2H-WSe_2 that show a peak at about 178 cm^{-1} (22 meV) and has assigned to be the E_{1g} mode [28]. The values of $h\nu_p$ = 29.4 meV is well correlated with the E_{1g} mode. Kranjcec et al. [29] and Desnica et al. [30] have also observed similar phenomena. They attributed the larger value of phonon energy to the structural disorders induced by the cation-cation disorder, cation vacancies and interstitial in the mixed crystals.

Moreover, the contribution to E_0 as a function of temperature for the 2H-WSe_2 crystal can come from both static structural and dynamic phonon disorders [31]. E_0 is directly corresponded to the thermal-induced disorder in semiconductor of high crystalline quality, but it becomes larger because of the contributions from both thermal and structural disorders for non-ideal single crystals. The value of E_0 can be described by an Einstein oscillator model [31], which takes into consideration the contributions from both the thermal and structural disorders. This model can be expressed as:

$$E_0 = A\left(\frac{1}{\exp\left(\frac{\Theta_E}{T}\right)-1}\right) + B, \tag{7}$$

where A and B are constants related to thermal and structural disorders and Θ_E is the Einstein temperature. The solid line calculated by Eq. (7) is shown in Fig. 3(a) and the closed triangles are the experimentally derived values. The Einstein temperature, Θ_E = (125 ± 5) K is close to the value of average phonon temperature Θ from the fit of Eq. (4), implying that the physical origin of the Urbach energy should come from the electron/exciton–phonon interaction and structural disorder [24]. The structural disorder may likely result from the existence of multiple structural defects associated with the two-dimensional dislocation or stacking faults of the constituent elements in the layered 2H-$MoSe_2$ lattice as observed in the layered crystals [32]. The values of the adjustable parameters, A and B are, respectively, 5.68 meV and 23.47 meV. The contributions to E_0 are also assumed to be a linear addition of the thermal and structural disorders. The thermal-induced disorder (the first term of Eq. (7)) is evaluated to be about 11 meV at room temperature, while the structural disorder (given by B) is temperature-independent. Comparing with the structural disorder, our analysis reveals that structural disorder is dominant at low temperature. Although the contribution from the thermal disorder gradually increases, it is still not comparable to the structural disorder at room temperature in the 2H-WSe_2 materials [33]. The obtained values of A, B and Θ_E, respectively, are listed in Table 2.

Table 2 Values of the parameters h_{vp}, σ_0, Θ_E, A and B were obtained from a fit to Eqs. (6) and (7).

h_{vp} (meV)	σ_0	Θ_E (K)	A (meV)	B (meV)
29.4 ± 0.3	0.51 ± 0.01	125 ± 5	5.68	23.47

4 Conclusion

The temperature dependence of the energy gap $E_{gi}(T)$ of 2H-WSe_2 has been fitted with the Varshni and Bose–Einstein expressions. The fitting parameters obtained from both models show good consistency within the investigated temperature ranges. From the temperature dependence of the Urbach tail, the associated effective phonon energies have been evaluated to be 29.5 meV and correlated well to the E_{1g} mode. The temperature variation of Urbach energy is also analyzed via the Einstein oscillator model which takes into consideration the contributions from electron/exciton–phonon interaction (thermal-induced disorder) and temperature independent structural disorder. The structural disorder is found to be dominant at low temperature region, while the contribution from the thermal disorder is not comparable to the structural disorder even at room temperature.

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