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# Temperature dependence anisotropic photoconductivity in 2H-$MoSe_2$ single crystals

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**Abstract**

Single crystals of 2H-$MoSe_2$ were investigated by the anisotropic photoconductivity (PC) measurements as a function of temperature in the range of 12–300 K. A significant shift towards lower energy has been observed in the PC spectra of the edge plane with respect to the van der Waals plane. The anisotropy in the indirect energy gap is being attributed to crystal anisotropy. The parameters that describe the temperature dependence of the anisotropic indirect energy gap are evaluated and discussed utilizing the Varshni and Manoogian–Woolley semi-empirical relationships. The Debye temperature of the sample has also been estimated by the fitted values.


*Keywords:* Semiconductor; Anisotropy

## 1. Introduction

Molybdenum diselenide ($MoSe_2$) is a diamagnetic indirect semiconductor and belongs to the family of transition metal dichalcogenides (TMDCs) [1,2]. From recent investigations, these compounds have been attractive in a variety of important technologies such as solid lubricants [3–5], photovoltaic solar cells [6–9], nanocrystallites [10], etc. The layered-type TMDCs crystallize in a lattice with strong covalent bonds within a layer and weak interaction, usually of the van der Waals (VdW) type, between the individual layers. The strong anisotropy in the chemical bonds leads to anisotropy of the electrical and optical properties of the materials parallel and perpendicular to the layers [2]. 2H-$MoSe_2$ is optically uniaxial with the optical axis (*c*-axis) perpendicular to the VdW plane. Therefore, anisotropic response is expected for a linearly incident light beam along the *c*-axis (VdW plane) or perpendicular to the *c*-axis (edge plane) of the 2H-$MoSe_2$ crystals. However, to our knowledge, no detailed temperature dependence studies on the anisotropic photoconductivity (PC) have been reported.

In this work, we report on the anisotropic PC studies of 2H-$MoSe_2$ single crystals over the temperature range from 12 to 300 K. A notable shift towards lower energy was observed in the PC spectra corresponding to the edge plane with respect to the VdW plane of the crystal. The indirect energy gaps from the anisotropic PC spectra of this material at various temperatures were estimated carefully. The parameters that describe the temperature dependence of the anisotropic PC spectra were evaluated and discussed by the Varshni semi-empirical relationship [11] and a semi-empirical equation proposed by Manoogian–Woolley [12].

## 2. Experimental

Single crystals of 2H-$MoSe_2$ were grown by chemical vapor transport method, using $Br_2$ as a transport agent. Silver-colored, graphite-like, single crystalline platelets of samples with sizes up to 2.5 mm × 2.5 mm surface area and 100 μm in thickness have been extracted from the larger pieces. All obtained crystals are n-type in nature and the majority carrier concentration is determined to be about $3.5 \times 10^{15}$ $cm^{-3}$ from Hall measurements at 300 K. From the evaluation of the X-ray powder diffraction pattern in Fig. 1, we may conclude that the

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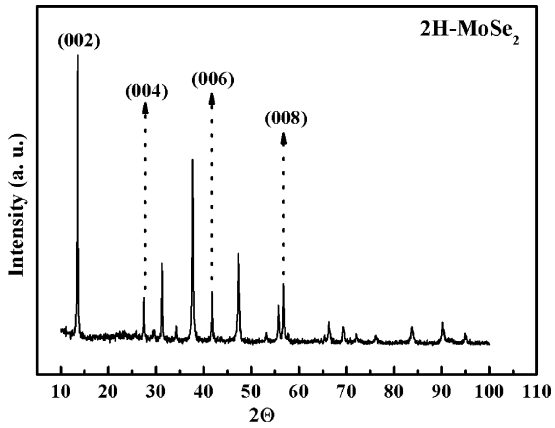


Fig. 1. X-ray powder diffraction pattern shows the as-grown samples are of two-layered hexagonal (2H) structure of $MoSe_2$ from the observed diffraction peaks of (0 0 2), (0 0 4), (0 0 6) and (0 0 8).

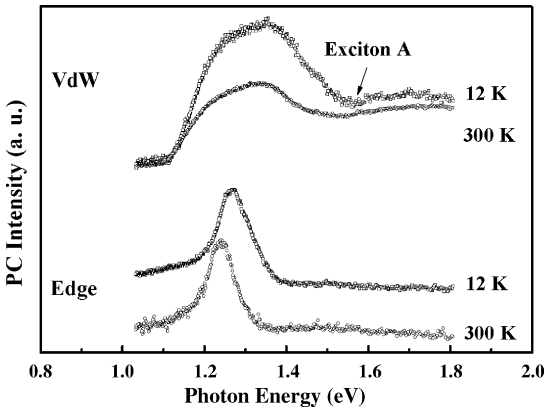


Fig. 2. Anisotropic PC spectra of VdW plane and edge plane, respectively, for 2H-$MoSe_2$ single crystals at 12 and 300 K over the extended energy range ∼1.0 to 1.8 eV.

as-grown samples are of two-layered hexagonal (2H) structure of $MoSe_2$ from the observed diffraction peaks of (0 0 2), (0 0 4), (0 0 6) and (0 0 8). The lattice parameters were calculated as $a = 3.286$ Å and $c = 12.901$ Å, which are in good agreement with the reported values for 2H-$MoSe_2$ (JCPDS No. 77–1715).

For the anisotropic PC measurements, a selected sample was oriented and cut into a rectangular shape. The anisotropic PC spectra were recorded on a standard experimental set-up with light beam incident onto the edge plane or VdW plane of the crystals under a constant current source [13]. The light source was an Oriel 1000 W halogen light filtered by a SpectraPro 300i monochromator. Electrical connections to the crystal were made by means of four gold wires laid across the VdW surface of the crystal and attached to the crystal surface by means of highly conducting silver epoxy which showed good ohmic contact qualities. Phase sensitive detection instrument (Stanford SR530) was used to measure the PC signals at several temperatures between 12 and 300 K. A CTI model SC closed-cycle cryogenic refrigerator equipped with a LakeShore model 321 digital thermometer controller was used for the low temperature measurements. The measurements were made between 12 and 300 K with a temperature stability of 0.5 K or better.

## 3. Results and discussion

To understand the optical properties from indirect to direct excitonic transitions, the PC spectra (VdW plane and edge plane) of 2H-$MoSe_2$ in the extended energy range from ∼1.0 to 1.8 eV at 12 and 300 K, respectively, were recorded and displayed in Fig. 2. In the energy range of 1.0 to ∼1.3 eV, the PC intensity increases to a maximum and then decreases, a photoresponse corresponding to electron–hole pair creation at the indirect gap of 2H-$MoSe_2$ is observed. For the PC spectrum on the VdW plane at 12 K, we are able to detect an energy dip at about 1.58 eV which is being identified to be the exciton A feature [7]. The excitonic peak position corresponds to the direct transition of the lowest energy interpreted as a $K_4 \rightarrow K_5$ optical transition by Coehoorn et al. [14]. The electron-hole pair creation above this gap will provide the most important contribution to the photoresponse. However, our current work is focused on the temperature-dependent indirect transitions of 2H-$MoSe_2$. Displayed in Fig. 3(a and b) are the PC spectra on the VdW plane and edge plane, respectively, in the vicinity of the indirect energy gap of 2H-$MoSe_2$ at several representative temperatures between 12 and 300 K in the energy range of 1.0–1.25 eV. The insets are the anisotropic configuration of PC measurement with an incident light beam. The results indicate that a notable shift towards lower energy was observed in the PC spectra for the edge plane with respect to VdW plane of the crystal.

The Moss's rule is commonly used for calculation of energy gap from spectral distribution of the photoconductivity. According to Moss's rule [15], the spectral sensitivity $S(E)$, defined as the ratio of the photoconductivity $\Delta\sigma(E)$ to its maximum value $\Delta\sigma_{max}$, can be represented by the following expression:

$$S(E) = \frac{1}{1 + \exp[C(E_{gi} - E)]} \quad (1)$$

where $C$ is a constant and $E_{gi}$ is the indirect energy gap. From the expression we see that the spectral falls to one-half when the photon energy $E$ is equal to the indirect energy gap $E_{gi}$. Utilizing Moss's rule as expressed by Eq. (1) (shown in the inset of Fig. 4), the indirect energy gap of 2H-$MoSe_2$ for VdW plane at 12 K is determined to be about 1.212 eV. In addition, Friemelt et al. have shown that the PC intensity is proportional to the absorption coefficient [16]. For an indirect allowed transition,

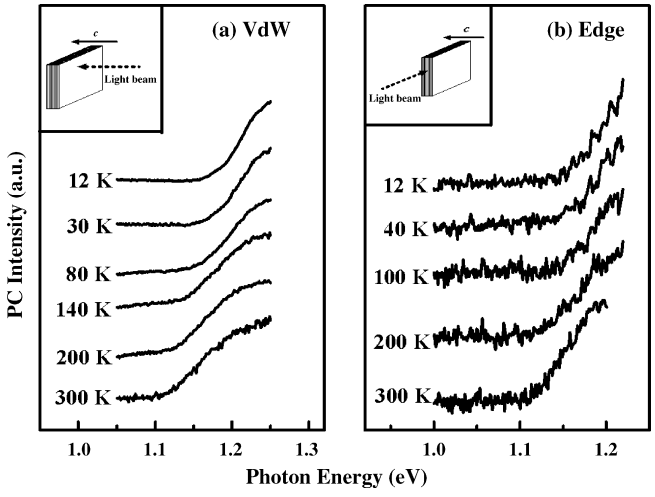


Fig. 3. The PC spectra of 2H-$MoSe_2$ at several temperatures between 12 and 300 K for (a) VdW plane and (b) edge plane. The insets are the anisotropic configuration of PC measurements with an incident light beam for VdW plane and edge plane, respectively.

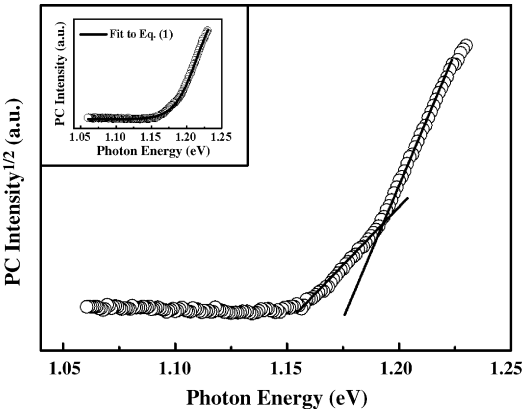


Fig. 4. A representative scheme (at 12 K for the VdW plane of 2H-$MoSe_2$) for the determination of the indirect band gap using the interception of the two slopes for the square root of the PC intensity, while the inset is the linear fit applied by Moss's rule to estimate the indirect band gap for the PC intensity.

taking into account both absorption and emission of phonons, the exact position of indirect energy gap can also be calculated by the following equation [17]:

$$\text{PC intensity} \propto \alpha_{\text{indirect}}(h\nu) = \frac{(h\nu - E_{\text{gi}} + E_{\text{p}})^2}{\exp(E_{\text{p}}/kT) - 1} + \frac{(h\nu - E_{\text{gi}} - E_{\text{p}})^2}{1 - \exp(-E_{\text{p}}/kT)} \quad (2)$$

where $h\nu$ is the energy of the incident photon, $E_{\text{gi}}$ is assigned to be the indirect energy gap and $E_{\text{p}}$ is the phonon energy. As illustrated in the interception of the two slopes for the square root of the PC intensity in Fig. 4, the absorption edge of 2H-$MoSe_2$ for VdW plane at 12 K is obtained to be about 1.161 eV by using Eq. (2). However, it is shown that the calculated value from Moss's rule is higher than the determined value from Eq. (2). Moreover, similar results have been investigated by Tsay et

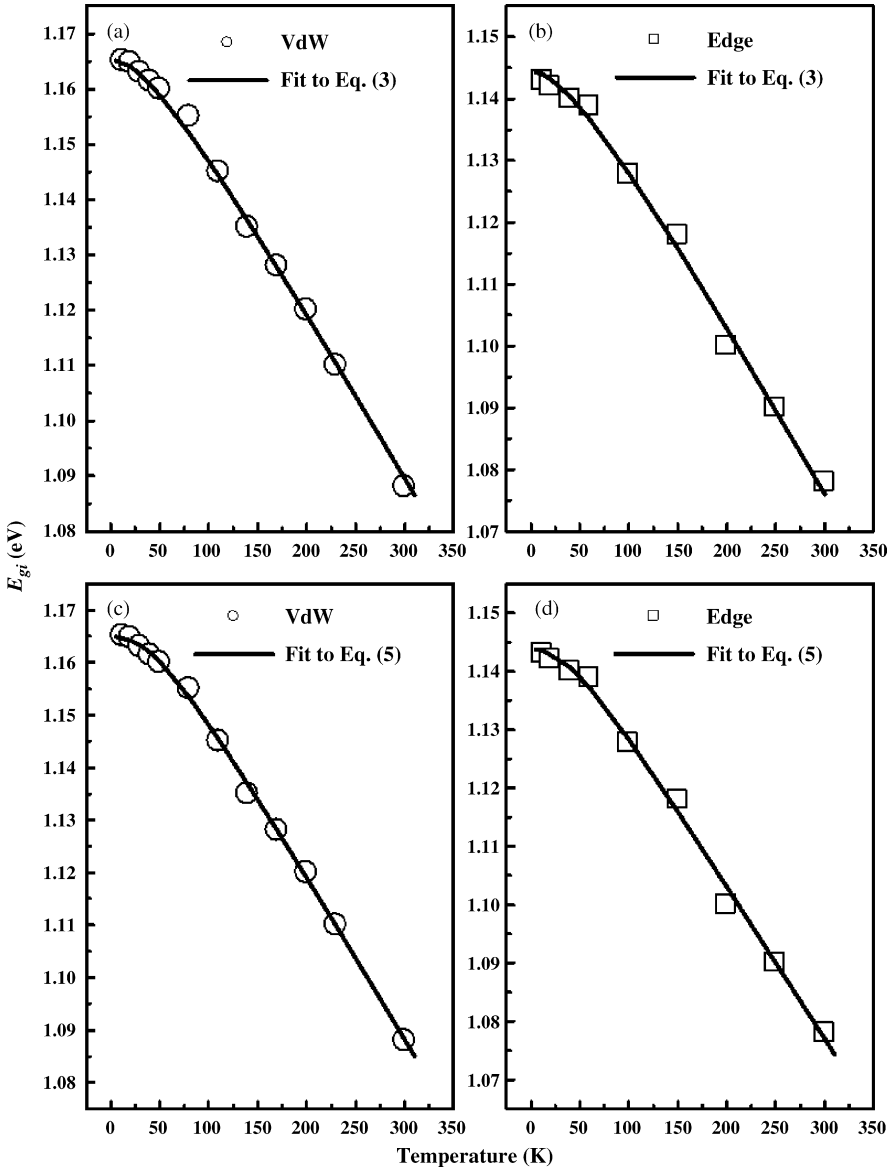


Fig. 5. The temperature variations of the anisotropic indirect energy gaps, $E_{\text{gi}}(T)$ of 2H-$MoSe_2$. The solid lines are least-squares fits to Eq. (3) for (a) VdW plane and (b) edge plane, respectively, and Eq. (5) for (c) VdW plane and (d) edge plane, respectively.

Table 1
Values of the parameters $E_{gi}(0)$, $\alpha$, $\beta$, $\theta$, $U$, $s$ and $V$ obtained from a fit to Eqs. (3) and (5), respectively

| | $E_{gi}(0)$ (eV) | $\alpha$ (meV/K) | $\beta$ (K) | $\theta$ (K) | $U$ (meV/K) | $s$ | $V$ (meV/K) |
|---|---|---|---|---|---|---|---|
| Varshni (VdW plane) | $1.165 \pm 0.004$ | $0.29 \pm 0.03$ | $73 \pm 5$ | – | – | – | – |
| Varshni (edge plane) | $1.144 \pm 0.004$ | $0.28 \pm 0.03$ | $73 \pm 5$ | – | – | – | – |
| Manoogian–Woolley (VdW plane) | $1.161 \pm 0.004$ | – | – | $143 \pm 5$ | $0.07 \pm 0.01$ | $1.0 \pm 0.1$ | $1.1 \pm 0.3$ |
| Manoogian–Woolley (edge plane) | $1.142 \pm 0.004$ | – | – | $143 \pm 5$ | $0.05 \pm 0.01$ | $1.0 \pm 0.1$ | $1.2 \pm 0.3$ |

al. [18] and Elkorashy [19]. From the estimated results of indirect energy gap, it is suggested that the higher energy gap extracted from photoconductivity spectra by Moss's rule may originate from the phonon effect in the indirect transition region.

Plotted in Fig. 5(a) for VdW plane and Fig. 5(b) for edge plane are the temperature variations of the anisotropic indirect energy gaps, $E_{gi}(T)$ of 2H-$MoSe_2$. A least-squares fits (the solid lines) to the Varshni semi-empirical relationship [11]:

$$E_{gi}(T) = E_{gi}(0) - \frac{\alpha T^2}{\beta + T} \quad (3)$$

where $E_{gi}(0)$ is the indirect transition energy at 0 K, and $\alpha$ and $\beta$ are constants referred to as Varshni coefficients. The constant $\alpha$ is related to the electron/exciton-phonon interaction and $\beta$ is closely related to the Debye temperature ($\Theta_D$) and has been shown that $\beta \approx 3/8\Theta_D$ [11]. For comparison purposes, the obtained anisotropic values of $E_{gi}(0)$, $\alpha$ and $\beta$ for both VdW plane and edge plane are listed, respectively, in Table 1. It is noted that the anisotropic value of $E_{gi}(0)$ for edge plane with respect to VdW plane is around 20 meV while $\alpha$ is almost the same for both VdW plane and edge plane. From the fitted value of $\beta$, the value of $\Theta_D$ is estimated to be 195 K. Debye temperature can also be estimated from the Lindemann's formula [20]:

$$\Theta_D \approx 120 T_m^{1/2} A^{-5/6} \rho^{1/3} \quad (4)$$

where $T_m$ is the melting-point, $A$ is the mean atomic weight and $\rho$ is the mean density of the material. 2H-$MoSe_2$ decomposes without melting at a temperature of 1170 °C [21]. Therefore, taking this to be the decomposition temperature $T_m$ in Eq. (4) with $A = 84.62$ g/mol [21] and $\rho = 6.9$ g/cm$^3$ [21] leads to $\Theta_D \approx 193$ K. The value of $\Theta_D$ estimated using the Lindemann's formula agreed well with that derived from the fitted parameter of $\beta$.

The $E_{gi}(T)$ behavior can also be analyzed with a model proposed by Manoogian–Woolley described as [12]:

$$E_{gi}(T) = E_{gi}(0) - UT^s - V\theta \left[ \coth\left(\frac{\theta}{2T}\right) - 1 \right] \quad (5)$$

The empirical model includes the lattice dilation term described as $UT^s$ and the last term represents the electron/exciton-phonon interaction. The parameters $E_{gi}(0)$, $U$, $s$, $V$ and $\theta$ in Eq. (5) are adjustable and almost independent of temperature. However, the fitted value of parameter $\theta$, being the mean frequency of phonon excitation is similar to $\Theta_D$ in Eq. (4) and the relationship is $\theta \approx (3/4)\Theta_D$ [12]. The values of $E_{gi}(0)$, $U$, $s$, $V$ and $\theta$ obtained from the best fit to Eq. (5) are given, respectively, in Table 1 and the corresponding solid lines are shown in Fig. 5(c and d). The anisotropy of $E_{gi}(0)$ for edge plane with respect to VdW plane is around 20 meV which agreed well with the fitted results of Eq. (3). The $\Theta_D$ value for 2H-$MoSe_2$ is estimated to be 191 K using the value of $\theta = 143 \pm 5$ K obtained from the fitted value of Eq. (5). The experimentally fitted Debye temperature agrees well with the theoretical estimation.

In our present case for the 2H-$MoSe_2$ single crystal, a reasonably good fit using the two models over the entire temperature range from near zero to room temperature of the experimentally observed variation of the anisotropic energy gap is demonstrated. It is suggested that temperature shift of the indirect energy gap is probably due to the interaction with relevant acoustic and optical phonons [22]. By comparing with the indirect gap anisotropy, we see that the mechanism of crystal anisotropy as a result of van der Waals interaction has an influence on the indirect gap and this finding concurred well with the study on other layered structure compounds such as $MoS_2$ [23] and $WSe_2$ [24].

## 4. Summary

In this work, we have successfully investigated the temperature dependence anisotropy of photoconductivity of 2H-$MoSe_2$ single crystals in the temperature regions between 12 and 300 K. The $E_{gi}(T)$ dependence show good consistency with both Varshni and Manoogian–Woolley semi-empirical models. The temperature shift of the indirect energy gap is probably due to the interaction with relevant acoustic and optical phonons, while the anisotropy in the energy gap is being attributed to crystal anisotropy. The small deviation of the two models at low temperature are compared and discussed. Parameters obtained from the fits allowed us to estimate the Debye temperature which shows good agreement with both models and with the theoretical Lindemann's formula.

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