PHYSICAL REVIEW B VOLUME 58, NUMBER 24 15 DECEMBER 1998-II

Absorption-edge anisotropy in ReS_2 and $ReSe_2$ layered semiconductors

C. H. Ho and Y. S. Huang*
Department of Electronic Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, Republic of China

K. K. Tiong
Department of Electrical Engineering, National Taiwan Ocean University, Keelung 202, Taiwan, Republic of China

P. C. Liao
Department of Electronic Engineering, Kuang Wu Institute of Technology and Commerce, Peitou, Taipei 112, Taiwan, Republic of China

(Received 11 May 1998)

Polarization-dependent absorption measurements of ReS_2 and $ReSe_2$ single crystals have been carried out in the temperature range between 25 and 500 K. A significant shift towards lower energies has been observed in the transmittance spectra of $\mathbf{E}\parallel\mathbf{b}$ polarization with respect to those corresponding to $\mathbf{E}\perp\mathbf{b}$ polarization. Analysis reveals that the absorption edges of ReS_2 and $ReSe_2$ are indirect allowed transitions. The parameters that describe the temperature dependence of the absorption edges with different polarizations in the van der Waals plane are evaluated. The results indicate that the electron-phonon coupling constants for $\mathbf{E}\parallel\mathbf{b}$ polarization are considerably larger than those of $\mathbf{E}\perp\mathbf{b}$ polarization. [S0163-1829(98)02748-9]

I. INTRODUCTION

ReS_2 and $ReSe_2$ are diamagnetic semiconductors that belong to the family of the layered-type transition-metal dichalcogenides.[1,2] The properties of the transition-metal dichalcogenides have been reviewed by Wilson and Yoffe.[1] The layered-type transition-metal dichalcogenides crystalize in a lattice with strong covalent bonds within a layer and weak interactions, usually of the van der Waals type, between the individual layers. The strong anisotropy in the chemical bonds leads to anisotropy in many material properties, such as their electrical and optical properties parallel and perpendicular to the layers.[3] Unlike most of the layered transition-metal dichalcogenides, ReS_2 and $ReSe_2$ are in a distorted $CdCl_2$ structure, leading to triclinic symmetry.[2,4] Crystals with triclinic symmetry are optically biaxial. Therefore, anisotropic response of ReS_2 and $ReSe_2$ are expected for linearly polarized light, incident normal to the basal plane $[\mathbf{E}\parallel(001),\ \mathbf{k}\perp(001)]$. This behavior differs from that of transition-metal dichalcogenides with hexagonal structure (e.g., 2H-MoS_2, 2H-$MoSe_2$), which are optically uniaxial with the optical axis perpendicular to the van der Waals plane. Although Wilson and Yoffe[1] claimed biaxial behavior in ReS_2 and $ReSe_2$, to our knowledge up to now only a few experimental papers have been reported.[5] Recently, Friemelt, Lux-Steiner, and Bucher[5] reported anisotropy effects in the van der Waals plane of ReS_2 single crystals and mentioned that ReS_2 may be of interest for fabrication of polarization sensitive photodetectors in the visible wavelength region. However, to date, no detailed study on the anisotropy in the absorption edge has been reported.

In this paper, we report on the detailed polarization-dependent optical-absorption study of single crystals of ReS_2 and $ReSe_2$ over temperature ranging from 25 to 500 K. A notable shift towards lower energies was observed in the transmittance spectra of $\mathbf{E}\parallel\mathbf{b}$ polarization with respect to those corresponding to $\mathbf{E}\perp\mathbf{b}$ polarization. Analysis of the absorption curves suggests that the interband transitions in ReS_2 and $ReSe_2$ are indirect and their band gaps are polarization dependent. The polarization-dependent energy gaps of these materials at various temperatures are determined and their temperature dependence is analyzed by the Varshni equation,[6] an empirical expression proposed by O'Donnel and Chen,[7] and an expression containing the Bose-Einstein occupation factor for phonons.[8,9] The parameters that describe the temperature dependence of band gaps are evaluated and discussed.

II. EXPERIMENTAL DETAILS

Single crystals of ReS_2 and $ReSe_2$ were grown using the chemical-vapor transport method with Br_2 as a transport agent. Prior to the crystal growth, quartz tubes containing Br_2 and the elements (Re, 99.95% pure; S, 99.999%; Se, 99.999%) were evacuated and sealed. The quartz tube was placed in a three-zone furnace and the charge prereacted for 24 h at 800 °C with the growth zone at 1000 °C, preventing the transport of the product. The furnace was then equilibrated to give a constant temperature across the reaction tube, and was programmed over 24 h to produce the temperature gradient at which single-crystal growth takes place. Best results were obtained with temperature gradients of approximately 1060→1010 °C for ReS_2 and 1050→1000 °C for $ReSe_2$. Both ReS_2 and $ReSe_2$ formed thin silver-colored, graphitelike platelets up to 2 cm^2 in area and 100 μm in thickness. X-ray diffraction patterns confirmed the triclinic symmetry of ReS_2 and $ReSe_2$ with all parameters consistent with those previously reported.[2,10] Hall effect measurements reveal *n*-type semiconducting behavior. At room temperature, the carrier concentrations were 1×10^{17} and $7\times10^{16}\ cm^{-3}$, the Hall mobilities were 20 and 10 $cm^2/V\,s$ and the resistivities were 3 and 8 Ω cm for ReS_2 and $ReSe_2$, respectively. The weak van der Waals bonding between the layers of the material means that they display good cleavage

©1998 The American Physical Society

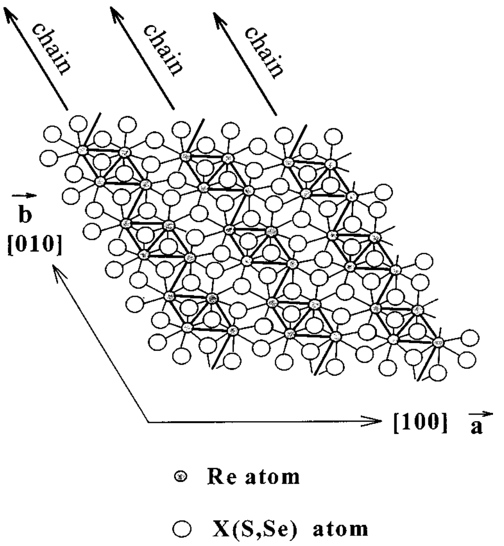

FIG. 1. Top view of the van der Waals plane of ReX_2 ($X = S$, Se) layered structure.

properties parallel to the layers, which can be exploited to obtain thin-single specimens. With a razor blade, thicker samples have been successfully thinned to a limiting thickness of ~10 μm.

Measurements of the reflectance and transmittance at near-normal incidence were made on a Bruker model IFS 120 HR in the range of 8000–13 500 cm^{-1}, with a resolution of 4 cm^{-1}. Transmission intensity was closely monitored to obtain an incidence as close to 90° as possible. The reflectivity studies were done on the as-grown surface (001) and compared against an evaporated gold mirror. The Oriel near-infrared dichroic sheet polarizers were employed for polarization-dependent measurements. Single crystals with a thickness of about 10 μm were used for transmittance measurements. Plate-shaped crystals were selected and mounted on a copper sample holder fitted into a Dewar with optical windows. As shown in Fig. 1, the *b* and *a* axes are the shortest and second shortest axes in the basal plane; the *b* axis is parallel to the cluster chains, which corresponds to the longest edge of the plate.[5,11] Measurements were made at several temperatures between 25 and 500 K with a temperature stability of 0.5 K or better.

III. RESULTS AND DISCUSSION

The transmittance of ReS_2 and $ReSe_2$ were measured at near-normal incidence. The absorption coefficient α was determined from the transmittance T_r by taking into account the spectral dependence of the reflectance R using the relation[12]

$$T_r = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}. \tag{1}$$

Equation (1) assumes that there are multiple reflections within the sample, but that they add incoherently due to sample inhomogeneity or a sufficiently large spread of the incident angles. Since αd is large for the sample crystals, the second term in the denominator of Eq. (1) can be neglected.

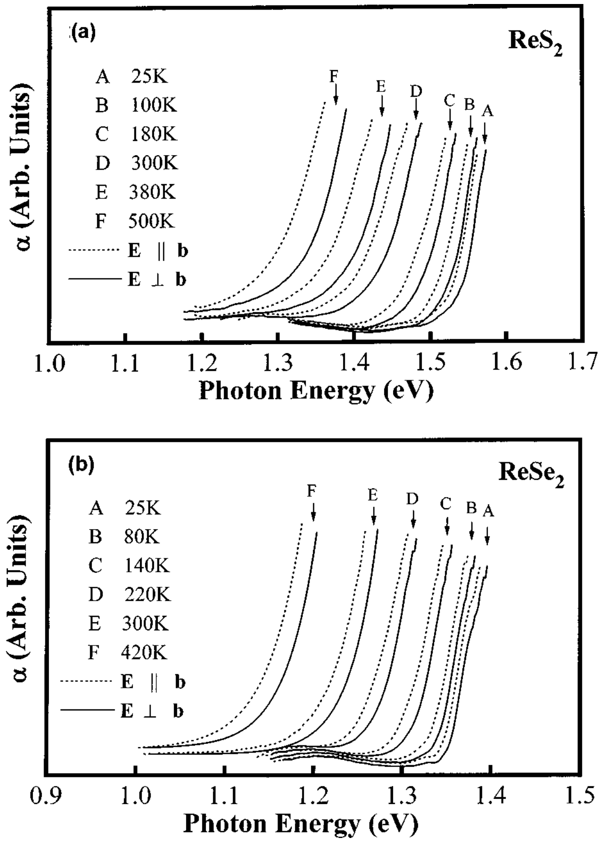

FIG. 2. Polarization-dependent absorption coefficient vs photon energy for (a) ReS_2 and (b) $ReSe_2$ at several representative temperatures between 25 and 500 K. The dashed lines and solid lines are, respectively, deduced from the transmittance spectra of **E**∥**b** and **E**⊥**b** polarizations.

Figure 2 displays the absorption coefficient as a function of photon energy, as determined for (a) ReS_2 and (b) $ReSe_2$ at several representative temperatures between 25 and 500 K. The dashed curves in Fig. 2 correspond to the **E**∥**b** polarization, while the solid curves represent **E**⊥**b** polarization. It is noted that a significant shift towards lower energies for the **E**∥**b** polarization is observed as compared to the **E**⊥**b** polarization. The polarization dependence of the transmittance curves provides conclusive evidence that both optical absorption edges are associated with the interband transitions from different origins. Detailed theoretical study of the anisotropic optical properties in the van der Waals plane of ReS_2 and $ReSe_2$ is needed and is at present beyond the scope of this work. As is generally expected, the absorption edge shifted toward higher energies as the temperature of the sample is lowered. Analysis of the experimental data showed that the absorption coefficient α to be proportional to $(\hbar\omega - E_g)^n$ with $n = 2 \pm 0.1$. This suggests an indirect allowed transition for these materials.

A more complete analysis, taking into account both the absorption and emission phonons, is given as follows. For an indirect allowed transition, the absorption coefficient α for a single-phonon process can be expressed as[12]

$$\alpha\hbar\omega = \frac{A(\hbar\omega - E_g + E_p)^2}{\exp(E_p/kT)-1} + \frac{B(\hbar\omega - E_g - E_p)^2}{1-\exp(-E_p/kT)}, \tag{2}$$

where $\hbar\omega$ is the energy of the incident photon, E_g the band gap, E_p the energy of the phonon assisting the transition, and

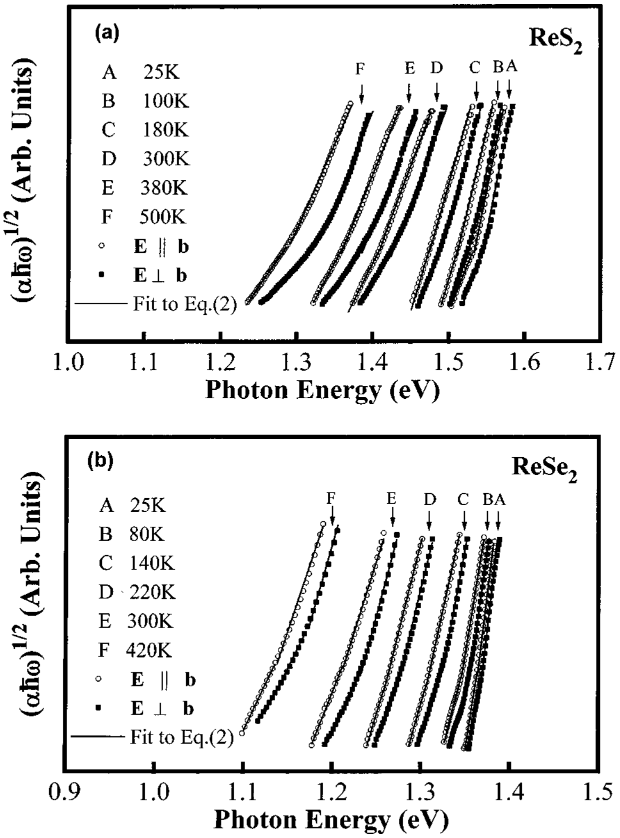

FIG. 3. Experimental points of $(\alpha\hbar\omega)^{1/2}$ vs $\hbar\omega$ that are deduced from polarization-dependent absorption measurements for (a) ReS$_2$ and (b) ReSe$_2$ at several representative temperatures between 25 and 500 K. The hollow circles (solid squares) are data points from the **E**∥**b** (**E**⊥**b**) polarization measurements and the solid lines are the least-squares fits to Eq. (2).

A and B are constants. The first term on the right-hand side of Eq. (2) corresponds to an absorption of a photon and a phonon, whereas the second term corresponds to an absorption of a photon and emission of a phonon and contributes only when $\hbar\omega \geqslant E_g + E_p$. There is a large residual absorption at photon energies below the absorption edge. The large values of the absorption coefficient α below absorption edge of ReS$_2$ and ReSe$_2$ most probably indicate the existence of impurities or defects in the materials. At this point, we have not considered in detail the effect of these impurity or defect states. For simplicity, in our present study, the residual absorption is assumed to be a constant and subtracted out for the evaluation of the band gap E_g and phonon energy E_p. The data of ReS$_2$ and ReSe$_2$ at different temperatures were then to be fitted to Eq. (2). Representative results are shown in Fig. 3, where the hollow circles and solid squares are representative experimental points deduced from different polarization (**E**∥**b** and **E**⊥**b** polarizations, respectively) transmittance spectra and the solid lines are fitted to Eq. (2). The results strongly indicate that ReS$_2$ and ReSe$_2$ are indirect band-gap semiconductors, in which **E**∥**b** polarization exhibits a smaller band gap and a single phonon makes important contributions in assisting the indirect transitions. The nonuniform thicknesses and unsmooth sample surface will tend to deviate the incident angles from the normal direction, resulting in some variations in the absorption spectra. Differing values of E_g and E_p could be obtained by fitting a different energy range, i.e., by rejecting some points at lower or higher photon energies. From this selective omission of data, an error of the order ±0.02 eV can be deduced for the estimation of E_g. Fitting data on different samples give similar parameters, even though there are differences in the absorption spectra due to differences in sample thicknesses.

From our experiments, the indirect gaps at room temperature, denoted as $E_{g\parallel}$ ($E_{g\perp}$), are, respectively, determined to be 1.35±0.02 (1.38±0.02) eV for ReS$_2$ and 1.17±0.02 (1.20±0.02) eV for ReSe$_2$. Here, $E_{g\parallel}$ and $E_{g\perp}$ refer, respectively, to the indirect gap of the **E**∥**b** and **E**⊥**b** polarizations. It is noticed that the values for $E_{g\perp}$ are larger than those of $E_{g\parallel}$, and are similar to those of our previous report of E_g, which determined from the absorption data of the unpolarized incident light.[13] Our values differ slightly from previous published works.[2,14–16] The first available data, 1.33 eV for ReS$_2$ and 1.15 eV for ReSe$_2$, were obtained by Wildervanck and Jellinek[2] from transmittance measurements. Koffyberg, Ouight, and Wold[14] analyzed the photoelectrochemical spectral-response data resulting in a lowest-energy indirect-optical band gap of 1.4 eV for ReS$_2$. From optical-absorption measurements, Marzik *et al.*[15] determined the indirect-optical band gaps of ReS$_2$ and ReSe$_2$ to be 1.32(5) eV for n-type ReS$_2$ and 1.17(5) eV for n-type ReSe$_2$. Recent attempts to determine the energy gaps of p-type ReS$_2$ and p-type ReSe$_2$ using the photoresponse spectra obtained at semiconductor-electrolyte interfaces were carried out by Wheeler, Leland, and Bard.[16] The values obtained were 1.31±0.01 and 1.22±0.01 eV for ReS$_2$ and ReSe$_2$, respectively.

ReX_2 (X=S, Se) can be thought of as distorted 1T-MX_2 dichalcogenides.[17] The 1T-MX_2 phases consist of edge-shared MX_6 octahedra. In each MX_2 layer, the metal-atom sheet is sandwiched by chalcogen-atom sheets, and the metal atoms of an undistorted MX_2 layer form a hexagonal lattice. ReS$_2$ and ReSe$_2$ have a d^3 electron count, and their metal-atom sheets exhibit a clustering pattern of ‘‘diamond chains.’’ The atoms comprising the Re$_4$ diamonds are coplanar, but each diamond unit is canted at a small angle from the basal plane. This canting results in a small variation of the Re atom heights perpendicular to the basal plane. The distortion of the Re atom sheet from perfect hexagonal symmetry further creates a distortion of the chalcogen sheets, both perpendicular and parallel to the basal plane. One consequence of this distortion is the opening of an energy gap in the band structure due to the mutual repulsion of the orbitals around the Fermi energy level. Recently, Kelty *et al.*,[18] and Kertesz and Hoffmann[19] employed simple tight-binding electronic band-structure calculations of the extended Huckel-type on ReS$_2$ and ReSe$_2$, respectively. The results show that the band levels around the band gap are dominated by the Re metal d orbitals. The contribution of chalcogen p_z orbitals are much stronger at the top portion of the valence band than at the bottom portion of the conduction band. For the chalcogen p_x and p_y orbitals, the top portion of the valence band has nearly equal contributions from all chalcogen atoms. The values of the theoretical indirect gap for a single ReS$_2$ layer,[18] the three-dimensional ReS$_2$ (Ref. 18) and ReSe$_2$ (Ref. 19) lattices are 1.27, 0.81, and 0.87 eV, respectively. The value of 1.27 eV for a single layer of ReS$_2$ (Ref. 18) is

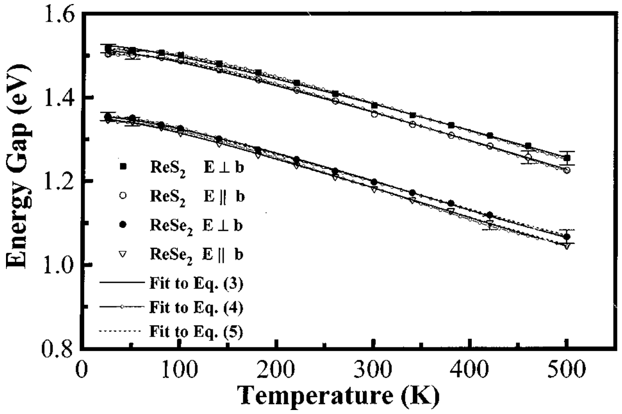

FIG. 4. The temperature dependence of polarization-dependent indirect band gaps of ReS_2 and $ReSe_2$. Representative error bars are shown. The solid lines are least-squares fit to the Varshni equation (see Ref. 6). The dotted curves are least-squares fit to an empirical expression proposed by O'Donnel and Chen (see Ref. 7). The dashed curves are fitted by an expression containing the Bose-Einstein occupation factor of phonon (see Ref. 8).

in approximate agreement with the absorption band gap of 1.35±0.02 (1.38±0.02) eV. However, the calculated value for the three-dimensional lattice[18,19] are much smaller than that actually obtained in our optical-absorption measurements. The calculated value of 0.81 eV for ReS_2 is smaller than that of $ReSe_2$, which is exactly in the opposite trend of the experimental values. These discrepancies indicate the inadequacy of the tight-binding method for studying semiconductors with a layer structure and a more effective method is needed in this area.

Plotted in Fig. 4 are the temperature variations of the polarization-dependent indirect energy gaps of ReS_2 and $ReSe_2$ with representative error bars. A least-squares fit (the solid line) to the Varshni semiempirical relationship[6]

$$E_{gi}(T)=E_{gi}(0)-a_iT^2/(b_i+T) \tag{3}$$

yields parameters as given in Table I. Here $i=\|, \perp$, $E_{gi}(0)$ is the band gap at absolute zero; a_i and b_i are constants referred to as Varshni coefficients. The constant a_i is related to the electron-phonon interaction and b_i is closely related to the Debye temperature. For comparison purposes we have also listed numbers for the polarization-dependent direct band edge excitonic-transition energies of ReS_2 and $ReSe_2$,[20] and the unpolarized results of absorption measurements.[13] The Debye temperature was estimated to be approximately 196 K for ReS_2 and 181 K for $ReSe_2$.[21] Our values of $b_{\|}$ equals 133±50 (150±50) K and $b_{\perp}$ equals 128±50 (140 ±50) K for ReS_2 ($ReSe_2$) are in reasonable agreement with the theoretical estimation. It is noted that the values of a_i are much larger than those obtained from the direct band-edge excitonic transitions.[21] We will discuss the differences in a later section.

The temperature dependence of the indirect band gap in two different polarizations have also been fitted (dotted curves in Fig. 3) by an empirical expression proposed by O'Donnel and Chen,[7]

$$E_{gi}(T)=E_{gi}(0)-S_i\langle\hbar\Omega\rangle[\coth(\langle\hbar\Omega\rangle/2kT)-1], \tag{4}$$

where $i=\|, \perp$, $E_{gi}(0)$ is the indirect band gap at 0 K, S_i is a dimensionless coupling constant related to the strength of electron-phonon interaction, and $\langle\hbar\Omega_i\rangle$ is an average phonon energy. The obtained values of the various parameters are given in Table II. For comparison purposes the numbers from previous reports on direct band-edge excitonic transition energies of ReS_2 and $ReSe_2$,[20] indirect band gaps of Si,[22] RuS_2 and $RuSe_2$ (Ref. 23) are also included in Table II. As shown in Table II, our values of the electron-phonon coupling parameter S_i are much larger than the excitonic transition energies of ReS_2 and $ReSe_2$ as reported in Ref. 20. The values of S_i are also much larger than the indirect gaps of Si,[22] RuS_2, and $RuSe_2$.[23] From Eq. (4), with kT much larger than $\langle\hbar\Omega_i\rangle$, $dE_{gi}(T)/dT=2kS_i$. The calculated values for $dE_{g\|}/dT$ and $dE_{g\perp}/dT$ equal −0.66 (−0.62) and −0.68 (−0.66) meV/K are in good agreement with the val-

TABLE I. Fitting parameters that describe the temperature dependence of polarization-dependent indirect band gaps and direct band-edge excitonic-transition energies of ReS_2 and $ReSe_2$ using the Varshni equation. Also listed are the numbers determined with absorption of the unpolarized incident light.

Materials	Polarization	$E_g(0)$ (eV)	a (meV/K)	b (K)
ReS_2[a]	**E**∥**b**	1.51±0.02	0.73±0.05	133±50
	E⊥**b**	1.52±0.02	0.68±0.05	128±50
$ReSe_2$[a]	**E**∥**b**	1.35±0.02	0.81±0.05	150±50
	E⊥**b**	1.36±0.02	0.76±0.05	140±50
ReS_2 (E_1^{ex})[b]	**E**∥**b**	1.554±0.005	0.37±0.05	175±75
ReS_2 (E_2^{ex})[b]	**E**⊥**b**	1.588±0.005	0.39±0.05	180±75
$ReSe_2$ (E_1^{ex})[b]	**E**∥**b**	1.387±0.005	0.45±0.05	175±75
$ReSe_2$ (E_2^{ex})[b]	**E**⊥**b**	1.415±0.005	0.51±0.05	170±75
ReS_2[c]		1.52±0.02	0.62±0.05	115±50
$ReSe_2$[c]		1.36±0.02	0.75±0.05	135±50

[a] This work.
[b] Reference 20.
[c] Reference 13.

TABLE II. Values of the fitting parameters of the expression proposed by O'Donnel and Chen that describe the temperature dependence of polarization-dependent indirect band gaps and direct band-edge excitonic transition energies of ReS_2 and $ReSe_2$, and indirect band gaps of Si, RuS_2, and $RuSe_2$.

Materials	E_{g0} (eV)	S	$\langle \hbar\Omega \rangle$ (meV)
ReS_2 ($E_{g\parallel}$)[a]	1.50 ± 0.02	4.3 ± 0.5	23 ± 3
ReS_2 ($E_{g\perp}$)[a]	1.51 ± 0.02	4.1 ± 0.5	22 ± 2
$ReSe_2$ ($E_{g\parallel}$)[a]	1.34 ± 0.02	4.5 ± 0.5	18 ± 4
$ReSe_2$ ($E_{g\perp}$)[a]	1.35 ± 0.02	4.34 ± 0.5	16 ± 3
ReS_2 (E_1^{ex})[b]	1.554 ± 0.005	2.0 ± 0.1	19 ± 3
ReS_2 (E_2^{ex})[b]	1.588 ± 0.005	2.0 ± 0.1	20 ± 3
$ReSe_2$ (E_1^{ex})[b]	1.387 ± 0.005	2.8 ± 0.1	25 ± 3
$ReSe_2$ (E_2^{ex})[b]	1.415 ± 0.005	2.8 ± 0.1	21 ± 4
Si (E_{ind})[c]	1.17	1.49	25.5
RuS_2 (E_{ind})[d]	1.43 ± 0.01	2.41 ± 0.2	19.6 ± 2.0
$RuSe_2$ (E_{ind})[d]	0.89 ± 0.01	1.94 ± 0.2	12.5 ± 2.0

[a] This work.
[b] Reference 20.
[c] Reference 22.
[d] Reference 23.

ues of -0.74 (-0.7) and -0.77 (-0.74) meV/K for ReS_2 ($ReSe_2$) as obtained from the linear extrapolation of the experimental data.

The temperature dependence of the polarization-dependent indirect band gaps can also be fitted (dashed curve) by an expression containing the Bose-Einstein occupation factor of phonon:[8,9]

$$E_{gi}(T) = E_{iB} - a_{iB}\left\{1 + \frac{2}{\exp(\Theta_{iB}/T) - 1}\right\}, \qquad (5)$$

where $i = \parallel$ or $\perp$, a_{iB} represents the strength of the electron-phonon interaction, and Θ_{iB} corresponds to the average phonon temperature. The fitted values for E_{iB}, a_{iB}, and Θ_{iB} are given in Table III, and the corresponding values for the direct band-edge excitonic transition energies of ReS_2 and $ReSe_2$,[21] GaAs (Ref. 8) and ZnSe (Ref. 24) are also listed for comparison. The parameter a_i of Eq. (3) is related to a_{iB} and Θ_{iB} of Eq. (5) by taking the high-temperature limit of both expressions. This yields $a_i \approx 2a_{iB}/\Theta_{iB}$. Comparison of Tables I and III shows within error bars this relation is satisfied.

As shown in Tables I, II, and III, the results of the electron-phonon coupling constants a_i in Eq. (3), S_i in Eq. (4), and a_{iB} in Eq. (5), which describe the temperature dependence of the indirect band gaps for ReS_2 and $ReSe_2$ are larger than those for the direct band-edge excitonic-transition energies.[20,21] These results are similar to that of the previous report on 2H-MoS_2 and $MoSe_2$ layered crystals.[25] Goldberg *et al.*[25] reported a detailed study of the low-energy absorption in layered crystals of MoS_2 and $MoSe_2$. The experimental results showed that the temperature shift of the absorption tails is larger than those of the excitons. The phenomena can be interpreted as follows: as the temperature is lowered, the reduction in the thermal broadening of the exciton causes a faster shift of the absorption tail. In addition, it is also noticed that the electron-phonon coupling constants a_i, S_i, and a_{iB} for $E_{g\parallel}$ are larger than those of $E_{g\perp}$. At this point we suspected that the electron-phonon coupling constants for $\mathbf{E}\parallel\mathbf{b}$ polarization are larger than those of $\mathbf{E}\perp\mathbf{b}$ polarization, and may be general characteristics of the crystals with layer structure of triclinic symmetry. However, a more systematic experimentation should be carried out to verify this property.

IV. SUMMARY

In summary, the polarization-dependent optical-absorption study of ReS_2 and $ReSe_2$ single crystals was carried out over temperatures ranging from 25 to 500 K. The transmittance spectra of $\mathbf{E}\parallel\mathbf{b}$ polarization shift towards lower energies with respect to those corresponding to $\mathbf{E}\perp\mathbf{b}$ polarization. Analysis of the absorption curves suggests that the

TABLE III. Values of the Bose-Einstein-type fitting parameters that describe the temperature dependence of band gaps and excitonic transition energies of ReS_2, $ReSe_2$, GaAs, and ZnSe.

Feature	Materials	E_B (eV)	a_B (meV)	Θ_B (K)
$E_{g\parallel}$	ReS_2[a]	1.57 ± 0.02	66 ± 21	194 ± 50
	$ReSe_2$[a]	1.41 ± 0.02	73 ± 22	196 ± 50
$E_{g\perp}$	ReS_2[a]	1.58 ± 0.02	62 ± 18	193 ± 50
	$ReSe_2$[a]	1.42 ± 0.02	68 ± 21	193 ± 50
E_1^{ex}	ReS_2[b]	1.583 ± 0.008	32 ± 10	200 ± 50
	$ReSe_2$[b]	1.428 ± 0.01	45 ± 15	224 ± 75
E_2^{ex}	ReS_2[b]	1.619 ± 0.008	34 ± 10	200 ± 50
	$ReSe_2$[b]	1.462 ± 0.010	53 ± 20	225 ± 75
E_g^d	GaAs[c]	1.512 ± 0.005	57 ± 29	240 ± 102
E_g^d	ZnSe[d]	2.800 ± 0.005	73 ± 4	260 ± 10

[a] This work.
[b] Reference 21.
[c] Reference 8.
[d] Reference 24.

interband transitions in $\mathrm{ReS_2}$ and $\mathrm{ReSe_2}$ are indirect and their band gaps are polarization dependent. The polarization-dependent temperature variation of the energy gaps are analyzed by the Varshni equation, an empirical expression proposed by O'Donnel and Chen, and a Bose-Einstein-type expression. The parameters that describe the temperature dependence of band gaps are evaluated. The results show that the electron-phonon coupling constants for $\mathbf{E}\parallel\mathbf{b}$ polarization are considerably larger than those of $\mathbf{E}\perp\mathbf{b}$ polarization.

ACKNOWLEDGMENT

The authors acknowledge the support of the National Science Council of the Republic of China under Projects Nos. NSC87-2112-M-011-001 and NSC88-2112-M-011-001.

---

*Author to whom correspondence should be addressed. Electronic address: ysh@et.ntust.edu.tw

[1] J. A. Wilson and A. D. Yoffe, Adv. Phys. **18**, 193 (1969).

[2] J. C. Wildervanck and F. Jellinek, J. Less-Common Met. **24**, 73 (1971).

[3] W. Y. Liang, J. Phys. C **6**, 551 (1973).

[4] K. Friemelt, S. Akari, M.-Ch. Lux-Steiner, T. Schill, E. Bucher, and K. Dransfeld, Ann. Phys. **1**, 248 (1992).

[5] K. Friemelt, M.-Ch. Lux-Steiner, and E. Bucher, J. Appl. Phys. **74**, 5266 (1993).

[6] Y. P. Varshni, Physica (Utrecht) **34**, 149 (1967).

[7] K. P. O'Donnel and X. Chen, Appl. Phys. Lett. **58**, 2924 (1991).

[8] P. Lantenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **35**, 9174 (1987).

[9] P. Lantenschlager, M. Garriga, L. Vina, and M. Cardona, Phys. Rev. B **36**, 4821 (1987).

[10] N. W. Alcock and A. Kjekshus, Acta Chem. Scand. **19**, 79 (1965).

[11] B. A. Parkinson, J. Ren, and M.-H. Whangbo, J. Am. Chem. Soc. **113**, 7833 (1991).

[12] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1975).

[13] C. H. Ho, P. C. Liao, Y. S. Huang, T. R. Yang, and K. K. Tiong, J. Appl. Phys. **81**, 6380 (1997).

[14] F. P. Koffyberg, K. Dwight, and A. Wold, Solid State Commun. **30**, 433 (1979).

[15] J. V. Marzik, R. Kershaw, K. Dwight, and A. Wold, J. Solid State Chem. **51**, 170 (1984).

[16] B. L. Wheeler, J. K. Leland, and A. J. Bard, J. Electrochem. Soc. **133**, 358 (1986).

[17] J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).

[18] S. P. Kelty, A. F. Ruppert, R. R. Chianelli, J. Ren, and M.-H. Whangbo, J. Am. Chem. Soc. **116**, 7857 (1994).

[19] M. Kertesz and R. Hoffmann, J. Am. Chem. Soc. **106**, 3453 (1984).

[20] Y. S. Huang, C. H. Ho, P. C. Liao, and K. K. Tiong, J. Alloys Compd. **262–263**, 92 (1997).

[21] C. H. Ho, P. C. Liao, Y. S. Huang, and K. K. Tiong, Phys. Rev. B **55**, 15 608 (1997).

[22] W. Bludau, A. Onoton, and W. Heinke, J. Appl. Phys. **45**, 1846 (1974).

[23] J. K. Huang, Y. S. Huang, and T. R. Yang, J. Appl. Phys. **78**, 2691 (1995).

[24] L. Malikova, W. Krystek, F. H. Pollak, N. Dai, A. Cavus, and M. C. Tamargo, Phys. Rev. B **54**, 1819 (1996).

[25] A. M. Goldberg, A. R. Beal, F. A. Levy, and E. A. Davis, Philos. Mag. **32**, 367 (1975).