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Temperature dependence of energies and broadening parameters of the band-edge excitons of ReS_2 and $ReSe_2$

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We have measured the temperature dependence of the spectral features in the vicinity of the direct gaps E_g^d of ReS_2 and $ReSe_2$ in the temperature range between 25 and 450 K using piezoreflectance (PzR). From a detailed line-shape fit to the PzR spectra we have been able to determine accurately the temperature dependence of the energies and broadening parameters of the band-edge excitons. The parameters that describe the temperature variation of the transition energies and broadening function have been evaluated. [S0163-1829(97)00324-X]

I. INTRODUCTION

ReS_2 and $ReSe_2$ are diamagnetic indirect semiconductors and belong to the family of transition-metal dichalcogenides crystallizing in the distorted octahedral layer structure of triclinic symmetry (space group $P\overline{1}$).[1,2] In recent investigations, these compounds have been attractive as electrode or photoelectrode materials because of their catalytic properties and favorable stability.[3–7] In particular, considerable attention has been focused on ReS_2. It is of considerable interest as a catalytic material having potential application as a sulfur-tolerant hydrogenation and hydrodesulfurization catalyst,[3,4] as a promising solar-cell material in electrochemical cells,[5,6] and as a material for fabrication of polarization sensitive photodetectors in the visible wavelength region.[8] Despite their various technological applications, the theoretical and experimental understanding of the solid-state properties of ReS_2 and $ReSe_2$ are still relatively incomplete. Recently Friemelt *et al.*[9] reported the temperature dependence of the direct-energy gap E_g^d by optical absorption, photoconductivity, and photoacoustic measurements. However, they did not determine the temperature variation of the broadening function and the experiments were performed only in the range of 50–300 K.

In this paper we report a study of the temperature dependence of the piezoreflectance (PzR) measurements in the spectral range near the direct fundamental band gaps of ReS_2 and $ReSe_2$ single crystals from 25 to 450 K. PzR has been proven to be useful in the investigation and characterization of semiconductors.[10,11] The derivative nature of modulation spectra suppresses uninteresting background effects and greatly enhances the precision of transition energies. The sharper line shapes as compared to the conventional optical techniques have enabled us to achieve a greater resolution and hence to detect weaker features. The PzR spectra are fitted with a form of the Aspnes equation of the first-derivative Lorentzian line shape.[12] From a detailed line shape fit we have been able to accurately measure the temperature dependence of the energies and broadening parameters of the interband excitonic transitions near band edge.[1,9] We have analyzed the temperature variation of the transition energies by the Varshni equation,[13] an empirical expression proposed by O'Donnel and Chen,[14] and an expression containing the Bose-Einstein occupation factor for phonons.[15,16] The parameters that describe the temperature dependence of excitonic-transition energies are evaluated and discussed. The temperature dependence of the broadening function also has been studied in terms of a Bose-Einstein equation that contains the electron (exciton)-longitudinal optical (LO) phonon-coupling constant.[15,16]

II. EXPERIMENT

Single crystals of ReS_2 and $ReSe_2$ were grown by chemical vapor transport method, using either Br_2 or ICl_3 as a transport agent, leading to n-type or p-type conductivity, respectively. Prior to the crystal growth quartz tubes containing the transport agent and elements (Re: 99.95% pure, S: 99.999%, Se: 99.999%) were evacuated and sealed. To improve the stoichiometry, sulfur or selenium with 2 mol % in excess was added with respect to rhenium. 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 give the temperature gradient at which single crystal growth took place. Best results were obtained with temperature gradients of about 1060→1010 °C for ReS_2 and 1050→1000 °C for $ReSe_2$. Both ReS_2 and $ReSe_2$ formed silver-colored, graphite-like, thin hexagonal platelets up to 2 cm^2 in area and 100 μm in thickness. X-ray diffraction patterns of single crystals were obtained using Ni-filtered Cu Kα radiation. The patterns confirmed the triclinic symmetry of ReS_2 and $ReSe_2$ with all parameters consistent with those previously reported.[2] The weak van der Waals bonding between the layers of these materials means that they display good cleavage properties parallel to the layers, which can be exploited to obtain thin single specimens. Using a razor blade the thicker samples

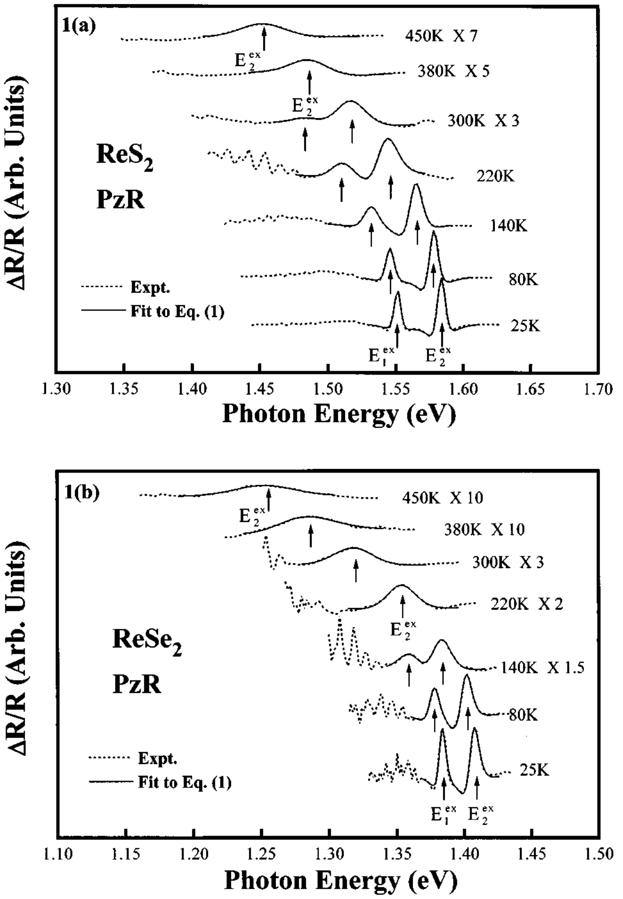

FIG. 1. The experimental PzR spectra (dashed curves) of (a) ReS$_2$ and (b) ReSe$_2$ at 25, 80, 140, 220, 300, 380, and 450 K, respectively. The full curves are least-squares fits to Eq. (1) which yields the excitonic-transition energies (E_1^{ex} and E_2^{ex}) indicated by the arrows.

have been successfully thinned to a limiting thickness of $\sim$10 μm.

The PzR measurements were achieved by gluing the thin single crystal specimens on a 0.15 cm thick lead-zirconate-titanate (PZT) piezoelectric transducer driven by a 200 V_{rms} sinusoidal wave at 200 Hz. The alternating expansion and contraction of the transducer subjects the sample to an alternating strain with a typical rms $\Delta l/l$ value of $\sim 10^{-5}$. A 150 W tungsten-halogen lamp filtered by a model 270 McPherson 0.35 m monochromator provided the monochromatic light. The reflected light was detected by an EG&G type HUV-2000B silicon photodiode, and the signal was recorded from an NF model 5610B lock-in amplifier. A RMC model 22 closed-cycle cryogenic refrigerator equipped with a model 4075 digital thermometer controller was used for low-temperature measurements. For high temperature experiments the PZT was mounted on one side of a copper finger of an electrical heater, which enable us to stabilize the sample temperature. The measurements were made between 25 and 450 K with a temperature stability of 0.5 K or better.

III. RESULTS AND DISCUSSIONS

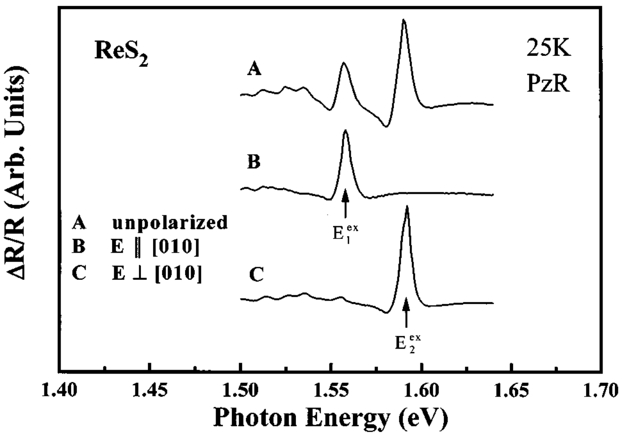

FIG. 2. Polarization dependence of the PzR spectra of ReS$_2$ at 25 K.

Displayed by the dashed curves in Figs. 1(a) and 1(b) are the PzR spectra, first-derivative spectroscopy, in the vicinity of E_g^d of ReS$_2$ and ReSe$_2$, respectively, for several temperatures between 25 and 450 K. At lower temperatures the nature of the lineshape indicates the presence of two oscillators on the high-energy side of the spectra. The oscillations on the lower-energy side are caused by the interference effects. Figure 2 shows the polarization dependence of the PzR spectra of ReS$_2$ in the vicinity of E_g^d at 25 K. The results indicate that feature 1 is absent in $E \perp [010]$ polarization whereas feature 2 disappears in $E \parallel [010]$ polarization. We believe this provides conclusive evidence that both features 1 and 2 are associated with the interband excitonic transitions from different origins. Detailed 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. We have fitted the experimental line shape to a functional form appropriate for excitonic transitions that can be expressed as a Lorentzian line-shape function of the form[12,17]

$$\frac{\Delta R}{R} = \mathrm{Re}\left[\sum_{i=1}^{2} A_i^{ex} e^{j\phi_i^{ex}} (E - E_i^{ex} + j\Gamma_i^{ex})^{-2}\right], \qquad (1)$$

where A_i^{ex} and ϕ_i^{ex} are the amplitude and phase of the line shape, and E_i^{ex} and Γ_i^{ex} are the energy and broadening parameter of the interband excitonic transitions. As shown by the solid curves in Fig. 1 for the low-temperature spectra are the least-squares fits using Eq. (1). The fits yield the parameters A_i^{ex}, E_i^{ex}, and Γ_i^{ex}. However, for high-temperature spectra, i.e., when temperature is higher than 300 K for ReS$_2$ and 220 K for ReSe$_2$, good fits can be achieved using only one oscillator. The obtained values of E_1^{ex} and E_2^{ex} are indicated by arrows in the figures. We note that the amplitude of feature 1 A_1^{ex} decreases as the temperature is increased. If the temperature of the sample is high enough so that $kT > E_b$, where E_b is the excitonic binding energy of exciton 1, exciton 1 will dissociate and the associated feature disappeared. The lowest temperature (T_{md}) for such occurrence is related to the dissociation (binding) energy of exciton as $E_b = kT_{md}$. A more accurate estimate can also be performed by acting that the temperature dependence of A_1^{ex} may be expressed as $A_1^{ex}(T) = A_0 \exp(-E_b/kT)$, where E_b is as defined earlier. An Arrhenius plot of the amplitude of feature 1 will give a good estimated value for E_b. We

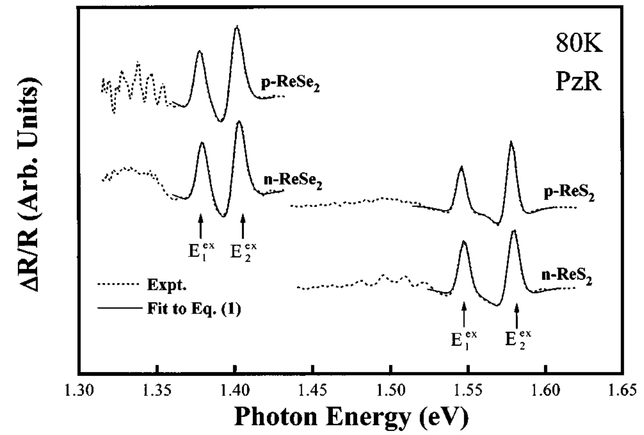

FIG. 3. The PzR spectra of both the n-type and p-type ReS$_2$ and ReSe$_2$, respectively, at 80 K. The oscillations on the lower energy side of the spectra are caused by interference effects. The full curves are least-squares fit to Eq. (1) that yield the excitonic-transition energies indicated by the arrows.

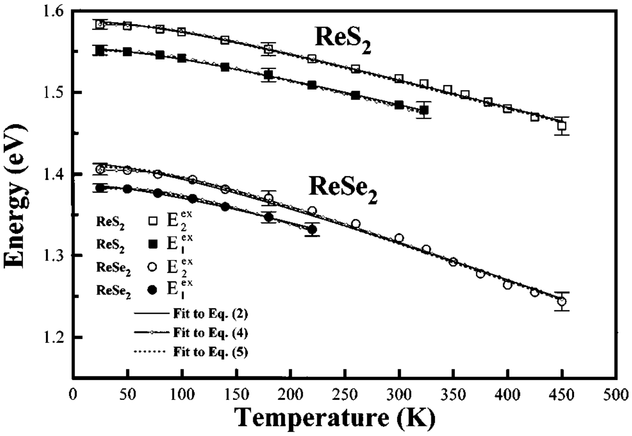

FIG. 4. The temperature dependence of the excitonic-transition energies of ReS$_2$ and ReSe$_2$. Representative error bars are shown. The full curves are least-squares fit to Eq. (2), the dotted curves are least-squares fit to Eq. (4) and the dashed curves are least-squares fits to Eq. (5).

have performed the estimation of E_b using both methods and the result is consistent. The excitonic binding energy of exciton 1 is estimated to be 31±5 meV for ReS$_2$ and 22±3 meV for ReSe$_2$. From the estimates, we can deduce the lowest direct gap ($E_d^g = E_1^{ex} + E_b$) for ReS$_2$ and ReSe$_2$ to be 1.579 and 1.401 eV at 80 K, and 1.517 and 1.322 eV at 300 K, respectively. The value of E_g^d at 80 K for ReS$_2$ is comparable with that of the previously reported value of 1.55 eV at the same temperature.[9] Friemelt *et al.*[9] have studied the temperature dependence of the direct band gap of ReS$_2$ by optical absorption, photoacoustic spectroscopy, and photoconductivity. Their results indicate that the direct band gap for p-type ReS$_2$ is 0.03 eV larger than that of n-type materials. However, from our experiments, the deduced values of E_g^d (from Fig. 3, within experimental error) for both n-type and p-type ReS$_2$ and ReSe$_2$ are similar. The discrepancy might be due to the larger uncertainty of the methods Friemelt *et al.*[9] used for the band-gap determination. Since the band gap is generally expected to be the same for the nondegenerate n-type and p-type semiconductors.

ReX$_2$ ($X = S$, Se) can be thought of as distorted $1T$-MX$_2$ dichalcogenides.[18] 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 by a small angle from the basal plane. The result is 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 distorting of the S or Se 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 level. Kertesz and Hoffmann employed simple tight-binding energy-band structure calculations of the extended Huckel type on ReSe$_2$.[19] The results show that the main part of both the conduction and the valence band in ReSe$_2$ is derived from nonbonding Re d orbitals. The calculated direct gap at Γ is 1.16 eV and the value of the indirect gap is 0.87 eV for ReSe$_2$. The calculated value of the direct gap is much smaller than that actually obtained by our PzR measurements. The fact that the calculated gap is smaller than the experimental value is a general problem associated with tight-binding method for studying semiconductors.[20]

Plotted in Fig. 4 are the experimental values of the temperature dependence of $E_1^{ex}(T)$ and $E_2^{ex}(T)$ for ReS$_2$ and ReSe$_2$. Representative error bars are shown. The full curves in Fig. 4 are the least-squares fit to the Varshni empirical relationship[13]

$$E_i(T) = E_i(0) - \frac{a_i T^2}{(b_i + T)}, \tag{2}$$

where $i = 1$ or 2, $E_i(0)$ is the transition energy at 0 K, and a_i and b_i are constants referred to as Varshni coefficients. The constant a_i is related to the electron (exciton)-phonon interaction and b_i is closely related to the Debye temperature. The obtained values of $E_i(0)$, a_i and b_i for the excitonic transitions for ReS$_2$ and ReSe$_2$ are listed in Table I. For comparison purposes we also have listed numbers for indirect band gaps of ReS$_2$ and ReSe$_2$ (Ref. 21). Debye temperature can be estimated from the Lindemann's formula[22]

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

where T_m is the melting temperature, A the atomic weight, and ρ is the density of the material. ReS$_2$ and ReSe$_2$ decompose without melting at temperatures of 1150 and 1100 °C, respectively. Therefore taking these decomposition temperatures as T_m in Eq. (3), $A = 83.44$ g/mol or 99.07 g/mol, $\rho = 7.613$ g/cm^3 (Ref. 2) or 9.237 g/cm^3 (Ref. 23) leads to $\Theta_D \approx 196$ K for ReS$_2$ and 181 K for ReSe$_2$. Our values of b equals 175±75 K for E_1^{ex} and 150±75 K for E_2^{ex} for both ReS$_2$ and ReSe$_2$ are in reasonable agreement with the theoretical estimation. It is noticed that the values of a_i are much smaller than that obtained from the indirect gaps.[21] We will discuss the differences in later sections.

TABLE I. Values of the Varshni-type fitting parameters which describe the temperature dependence of the excitonic transitions and indirect band gaps of ReS_2 and $ReSe_2$.

Feature	Materials	E(0) (eV)	a (meV/K)	b (K)
E_1^{ex}	ReS_2[a]	1.554±0.005	0.36±0.05	175±75
	$ReSe_2$[a]	1.387±0.005	0.44±0.05	175±75
E_2^{ex}	ReS_2[a]	1.588±0.005	0.37±0.05	150±75
	$ReSe_2$[a]	1.415±0.005	0.50±0.05	150±75
E_{ind}	ReS_2[b]	1.52±0.02	0.62±0.05	115±50
	$ReSe_2$[b]	1.36±0.02	0.75±0.05	135±50

[a] This work.

[b] Reference 21.

The temperature dependence of the interband transition energies have also been fitted (dotted curves in Fig. 4) by an empirical expression proposed recently by O'Donnel and Chen,[14]

$$E_i(T)=E_{i0}-S_i\langle\hbar\Omega_i\rangle[(\coth\langle\hbar\Omega_i\rangle/2kT)-1], \qquad (4)$$

where $i=1$ or 2, E_{i0} is the transition energy 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 gap of n-type and p-type ReS_2,[9] and GaAs,[24] indirect gaps of ReS_2,[21] $ReSe_2$,[21] Si,[25] RuS_2,[26] and $RuSe_2$ (Ref. 26) are also included in Table II. As shown in Table II, our value of the electron (exciton)-phonon coupling parameter S_i is comparable to those of direct gaps of ReS_2,[9] and GaAs,[24] indirect gaps of Si,[25] RuS_2,[26] and $RuSe_2$.[26] However the value of S_i is much smaller than that for the indirect gap of ReS_2 and $ReSe_2$.[21] Usually the indirect gap of a semiconductor is determined from analyzing the absorption tail of the material. The results of the electron (exciton)-phonon coupling constants a_i in Eq. (2) and S_i in Eq. (4) which describes the temperature dependence of the excitonic transition energies for ReS_2 and $ReSe_2$ are smaller than that for the indirect band gaps are similar to the previous report on $2H$-MoS_2 and $2H$-$MoSe_2$ layer crystals.[27] Goldberg *et al.*[27] reported a detailed study of the low-energy absorption in layer crystals of MoS_2 and $MoSe_2$. The experimental results show that the temperature shift of the exciton is smaller than that of the absorption tail. The phenomena can be interpreted as when the temperature is lowered, the reduction in the thermal broadening of the exciton causes the faster shift of the absorption tail. From Eq. (4) for kT much larger than $\langle\hbar\Omega\rangle$, $dE_2^{ex}(T)/dT=-2kS_2$ (at higher temperature, the signal strength of E_1^{ex} is negligible). The calculated values of dE_2^{ex}/dT equal -0.34 (ReS_2) and -0.48 ($ReSe_2$) meV/K are in good agreement with the values of -0.33 (ReS_2) and -0.44 ($ReSe_2$) meV/K

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

Materials	E_0 (eV)	S	$\langle\hbar\Omega\rangle$ (meV)
$ReS_2(E_1^{ex})$[a]	1.551±0.005	2.0±0.1	19±3
$ReS_2(E_2^{ex})$[a]	1.584±0.005	2.0±0.1	20±3
$ReSe_2(E_1^{ex})$[a]	1.383±0.005	2.8±0.1	21±4
$ReSe_2(E_2^{ex})$[a]	1.408±0.005	2.8±0.1	21±4
p-$ReS_2(E_g^d)$[b]	1.56	2.56	19
n-$ReS_2(E_g^d)$[b]	1.53	2.24	16
$ReS_2(E_{ind})$[c]	1.51±0.02	4.05±0.50	20.0±2.0
$ReSe_2(E_{ind})$[c]	1.35±0.02	4.35±0.50	18.1±2.0
$GaAs(E_g^d)$[d]	1.521	3.00	26.7
$Si(E_{ind})$[e]	1.17	1.49	25.5
$RuS_2(E_{ind})$[f]	1.43	2.41	19.6
$RuSe_2(E_{ind})$[f]	0.89	1.94	12.5

[a] This work.

[b] Reference 9.

[c] Reference 21.

[d] Reference 24.

[e] Reference 25.

[f] Reference 26.

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

Feature	Materials	E_B (eV)	a_B (meV)	Θ_B (K)
E_1^{ex}	ReS_2[a]	1.583±0.008	32±10	200±50
	$ReSe_2$[a]	1.428±0.01	45±15	224±75
E_2^{ex}	ReS_2[a]	1.619±0.008	34±10	200±50
	$ReSe_2$[a]	1.462±0.010	53±20	225±75
E_g^d	GaAs[b]	1.512±0.005	57±29	240±102
E_g^d	ZnSe[c]	2.800±0.005	73±4	260±10

[a] This work.

[b] Reference 15.

[c] Reference 28.

as obtained from linear extrapolation of our $E_2^{ex}(T)$ data.

The temperature dependence of the interband excitonic transition energies can also be fitted (dashed curve) by an expression containing the Bose-Einstein occupation factor for phonon:[15,16]

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

where $i=1$ or 2, a_{iB} represents the strength of the electron (exciton)-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, GaAs (Ref. 15) and ZnSe (Ref. 28) are also listed for comparison.

The experimental values of $\Gamma_i^{ex}(T)$ (half width at half maximum) of the E_1^{ex} and E_2^{ex} transitions as obtained from the lineshape fit for ReS_2 and $ReSe_2$ are displayed in Fig. 5 with representative error bars. The temperature dependence of the broadening parameters of semiconductors can be expressed as[15,16]

$$\Gamma_i(T)=\Gamma_{i0}+\frac{\Gamma_{i\mathrm{LO}}}{[\exp(\Theta_{i\mathrm{LO}}/T)-1]}, \qquad (6)$$

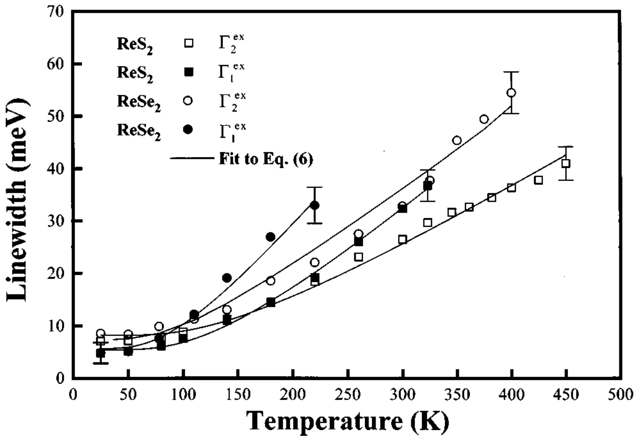

FIG. 5. The experimental temperature dependent linewidths of the E_1^{ex} and E_2^{ex} transitions of ReS_2 and $ReSe_2$. Representative error bars are shown. The full curves are least-squares fits to Eq. (6).

where $i=1$ or 2, the first term of Eq. (6) represents, the broadening invoked from temperature-independent mechanisms, such as impurity, dislocation, electron interaction, and Auger processes, whereas the second term is caused by the electron (exciton)-LO phonon (Fröhlich) interaction. The quantity $\Gamma_{i\mathrm{LO}}$ represents the strength of the electron (exciton)-LO phonon coupling while $\Theta_{i\mathrm{LO}}$ is the LO phonon temperature.[15,16] The solid curves in Fig. 5 are least-squares fit to Eq. (6), which made it possible to evaluate Γ_{i0}, $\Gamma_{i\mathrm{LO}}$, and $\Theta_{i\mathrm{LO}}$ for the excitonic transitions of ReS_2 and $ReSe_2$. The obtained values of these quantities are listed in Table IV together with the numbers for GaAs (Ref. 27) and ZnSe.[26]

The parameter a_i of Eq. (2) 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 that within error bars this relation is satisfied. The temperature variation of excitonic-transition energies are due to both the lattice-constant variations and interactions with relevant acoustic and optical phonons. According to the existing theory this leads to a value of Θ_{iB} significantly smaller than $\Theta_{i\mathrm{LO}}$. From Tables III and IV, it can be seen that our observations are in a good agreement with this theoretical consideration.

Our values of Γ_{10} and Γ_{20} for the excitonic transitions are about 5 and 7~8 meV, respectively, for ReS_2 and $ReSe_2$. This is an indication of the high quality of our single crystals. The values for the coupling constant $\Gamma_{1\mathrm{LO}}$ and $\Gamma_{2\mathrm{LO}}$ for ReS_2 and $ReSe_2$ are in the range of 40–70 meV, which are considerably larger than those reported for a number of semiconductors, such as GaAs (~20 meV) (Ref. 29) and ZnSe (~24 meV).[28] At this point we suspected that the large values of Γ_{LO} may be general characteristics of the crystals with layer structure. However, a more systematic experimentation should be carried out to verify this property.

IV. SUMMARY

In summary we have measured the temperature dependence of the energies and broadening parameters of the band-edge excitonic transitions of ReS_2 and $ReSe_2$ using PzR in the temperature range between 25 and 450 K. The temperature variation of the interband transition energies have been analyzed by Varshni, O'Donnel and Chen, and a Bose-Einstein type expression. The temperature dependence

TABLE IV. Values of the parameters which describe the temperature dependence of the broadening function of the excitonic transitions of ReS_2, $ReSe_2$, and direct band gaps of GaAs and ZnSe.

Feature	Materials	Γ_0 (meV)	Γ_{LO} (meV)	Θ_{LO} (K)
E_1^{ex}	ReS_2[a]	5.5 ± 1.0	74 ± 28	395 ± 100
	$ReSe_2$[a]	5.7 ± 1.4	67 ± 43	290 ± 100
E_2^{ex}	ReS_2[a]	7.8 ± 1.0	42 ± 8	363 ± 50
	$ReSe_2$[a]	8.4 ± 1.5	70 ± 24	385 ± 100
E_g^d	GaAs[c]	2	20 ± 1	417[b]
E_g^d	ZnSe[d]	6.5 ± 2.5	24 ± 8	360[b]

[a] This work.
[b] Parameter fixed.
[c] Reference 29.
[d] Reference 28.

of the broadening function also has been interpreted in terms of a Bose-Einstein equation that contains the electron (exciton)-LO phonon coupling constant Γ_{LO}. We find that Γ_{LO} in ReS_2 and $ReSe_2$ are considerably larger than that reported for a number of semiconductors.

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