Temperature and Composition Dependence of Exciton Peak Positions and Band Gap Energies of \( \text{Zn}_{1-x}\text{Mg}_x(\leq 0.19)\text{Se} \) Epitaxial Films

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The temperature dependence of the 1s exciton energy has been measured in \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) epitaxial films at compositions \( x = 0, 0.07, 0.12, \) and 0.19 from 2 K up to 280 K. Detailed numerical fits of the individual temperature dependences are provided on the basis of an analytical four-parameter representation developed recently by one of the authors. These are compared with previously used three-parameter models of Viña et al. and Varshni. The \( x \)-dependence of the exciton energy, \( E_{1s}(T, x) \), and of the fundamental band gap energy, \( E_g(T, x) \), is given to very good approximation by linear functions of the composition \( x \) for any \( T \) from absolute zero up to room temperature. A comparison with recent room temperature band gap energy data by Jobst et al. shows that this linear dependence holds up to \( x \approx 0.7 \). The magnitudes of the model-dependent empirical parameters, which control the temperature dependence of the band gap energy in different compounds, are found to change significantly with increasing magnesium content. From the magnitude of the effective phonon temperature, particularly in the case of \( \text{ZnSe} \), we conclude that the main contributions to the band gap shrinkage effect are due to acoustic phonons.

1. Introduction

In recent years \( \text{ZnSe} \), as well as various \( \text{ZnSe} \)-based ternary compounds, have attracted considerable research activity due to their potential use in the fabrication of blue-green laser devices. For example, an increase of the magnesium content in \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) [1, 2] or the cadmium content in \( \text{Zn}_{1-x}\text{Cd}_x\text{Se} \) [3] leads to a monotonous increase or decrease of the fundamental band gap. In this way, by changing the content of the alternating group-II component in these ternary compounds, it is possible to tune the fundamental band gap within intervals of about 1 eV in both directions.

Of special interest are \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) compounds because of the presence of successive blue shifts in the emission spectra for increasing \( x \). Examining this effect in \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) mixed crystals, Firszt et al. [1] have found a nearly linear \( x \)-dependence of a certain near-band-edge emission line (at 40 K) from 0 up to \( x = 0.56 \). A similar behavior of the fundamental energy gap has been observed recently by Jobst et al. [2] in \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) epitaxial films at moderate magnesium contents (\( x \) up to about 0.7).

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On the other hand, it is generally known from experiments that in binary as well as in ternary II–VI compounds (with fundamental gaps larger than 1 eV, at least) an increase of the lattice temperature leads generally to a shrinkage of these gap values. Among other things, this means that the initial blue shift caused by a non-vanishing magnesium admixture, \( x > 0 \), tends to be gradually reduced by an increasing red shift associated with an elevation of the lattice temperature \( T \). Therefore, for exact control of the actual emission line position under variable operating conditions, it is necessary to know the detailed dependence of the energy gap, \( E_g(T, x) \), both on the composition parameter \( x \) and the lattice temperature \( T \). Concerning the temperature dependence of the fundamental energy gap, exciton peak positions, or other near-edge emission lines, one can find a series of experimental data sets for the case of the binary compound ZnSe [4 to 11]. However, there is, so far, almost no information on such temperature dependences for ternary \( \text{Zn}_1-x\text{Mg}_x\text{Se} \) compounds (except for a rough determination of the temperature dependence of a photoluminescence spectrum in \( \text{Zn}_{0.44}\text{Mg}_{0.56}\text{Se}:\text{Al} \) [1]).

The main purpose of this paper is to provide detailed experimental information as well as careful numerical fits of the temperature dependence of exciton energies for several \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) epitaxial films within the composition range \( x < 0.2 \) (where the corresponding exciton absorption features could be properly observed from 2 K up to about 280 K). In Section 2 we give a brief description of the experimental setup used for our measurements. This enables the determination of the \( x \)-dependence of the exciton binding energy based on the measured separations between the 2s and 1s exciton peaks, which could be clearly monitored at low temperatures \( (T < 80 \text{ K}, \text{ at least}; \text{ cf. Figs. 1 and 2a}) \). The temperature dependence of the positions of the 1s exciton peaks, \( E_{1s}(T, x) \), is measured from about 2 K up to about 280 K for the compositions \( x = 0, 0.07, 0.12, \text{ and } 0.19 \). The numerical analysis of these data in Section 3 is based on a model developed recently by one of the authors [12 to 14]. In Section 4, we derive the composition dependence both of the 1s exciton energies, \( E_{1s}(T, x) \), and of the associated band gap energies, \( E_g(T, x) \). These results are discussed in Section 5. We give in Section 6 an illustration of significant qualitative and quantitative differences between our more elaborate four-parameter representation [12 to 14] for such temperature dependences and previous three-parameter models [15 to 18] used predominantly in experimental literature published up till now.

2. Sample Preparation and Experimental Set-Up

In this work we have prepared and investigated a sequence of thin \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) epitaxial films \((x = 0, 0.07, 0.12, \text{ and } 0.19) \) in order to obtain information on both the temperature and composition shift of the excitonic absorption at the fundamental energy gap. All samples were grown on (001)-GaAs substrates by MBE and have zincblende structure with a good structural quality. This was proved by high resolution X-ray diffraction, by means of which we have also found the actual Mg content for the individual ternary systems to be 0.072 (±0.003), 0.117 (±0.003), and 0.189 (±0.005). The sample quality was found to decrease with increasing Mg-content. Thus, it was not possible to obtain sufficiently accurate experimental data for Mg-compositions \( x > 0.19 \).

The film thickness \( d \) of all films ranged between 500 and 800 nm. In order to carry out absorption measurements, the substrates were selectively etched off by a mixture of 82% 1N-NaOH and 18% H\(_2\)O\(_2\) (30% solution in water). These freestanding films were pre-
pared on fine copper nets in order to avoid strain effects. The samples were placed in a He cryostat operating between 2 and 300 K. The possible inaccuracies of the sample temperature as measured by a Si diode are confined to $0.3 \text{ K} \leq T < 30 \text{ K}$, $0.25 \text{ K}$ up to 77 K, and $0.15 \text{ K} < T > 77 \text{ K}$. The transmitted light was analyzed by a 1 m double-grating monochromator and detected by a multichannel diode array with an energy resolution of about 0.08 meV. The detector covers an energy region of more than 50 meV. Thus we were able to do measurements up to 60 K without moving the grating of the monochromator. Deviations due to the tuning mechanism are avoided.

The absorption coefficient $\alpha(h\nu)$ was determined according to Lambert-Beer’s rule [19],

$$
\alpha(h\nu) = -\frac{1}{d} \ln \left( \frac{I(h\nu)}{I_0(h\nu)} \right) - \alpha_c,
$$

Fig. 1. Absorption spectra of ZnSe and Zn$_{0.93}$Mg$_{0.07}$Se at 2 K (solid lines). Energies of 1s and 2s exciton transitions were obtained by fittings according to Goñi et al. [19] and Toyozawa [20]. The transition labeled I$_2$ is due to a chlorine-bound exciton. Deviations at the highly absorbing 1s exciton peak are due to dark noise of the detector.

Fig. 2. Absorption spectra near the fundamental band gap of ZnSe at a) low and b) higher temperatures. Note that the 2s exciton peak is visible up to 100 K, while the 1s absorption can be monitored even up to room temperature. The 2s to 1s exciton peak energy separation was found to be independent of temperature within the error bars (indicated in Table 1).
where \( I(h\nu) \) and \( I_0(h\nu) \) are the intensity of light transmitted through the sample and the reference intensity measured in absence of the sample, respectively, and \( \alpha_c \) accounts for the losses at the surface of the sample. This is a good approximation in regions of high absorption. The 1s exciton energy was obtained from the absorption spectra by a fitting scheme developed by Toyozawa [20] and Goñi et al. [19] (cf. Fig. 1). Within this description, Elliot’s excitonic model [21] is used and Lorentz broadening is also taken into account. In all samples the 1s exciton peak is clearly visible at low temperatures and could be recorded up to about 280 K (Fig. 2b). The fits obtained are, as a rule, very satisfactory. (Note that deviations at the highly absorbing 1s exciton peak are due to dark noise of the diode array.) The possible errors for exciton peak energy positions in ternary compounds are < 0.5 meV at \( T < 60 \) K, < 1.0 meV up to 100 K, < 1.5 meV up to 150 K, and < 3 meV up to 300 K. In the case of ZnSe the corresponding errors are smaller by factors of about 2. By comparing these experimental error bars with the full widths at half maximum (FWHM) of the excitonic parts of the absorption spectra measured at different temperatures, we have found an approximate proportionality between both quantities, whereby the errors are an order of magnitude smaller than the FWHMs. We have represented these uncertainties, ± 0.1 FWHM(\( T \)), by corresponding error bars in Fig. 3. (The relatively small magnitudes of these error bars at \( T < 60 \) K are properly visualized within the narrow-scale representations in Figs. 6a to 6d.)

The 2s exciton peak is visible in ZnSe and in the compositions Zn\(_{1-x}\)Mg\(_x\)Se, \( x \leq 0.12 \), up to temperatures of about 80 K (see Fig. 2), and no change of the \( E_{2s} \) versus \( E_{1s} \) energy separation is observed (within the error bars indicated in Table 1). Therefore we may assume, as usual, a temperature independent exciton binding energy given approximately by

\[
R(x) \cong \frac{4}{3} (E_{2s}(T, x) - E_{1s}(T, x))
\]

(according to the hydrogen model [21]).

A small difference between the magnitudes of the exciton binding energies at room versus low temperature could eventually occur due to their dependence, \( R \propto \mu/e^2 \) [22, 23], on the reduced mass \( \mu \) [23] and the static dielectric constant \( \varepsilon \) [24] (which are weakly dependent on \( T \)). We have estimated the total change (reduction) of the magnitude of \( R \) from 0 up to 300 K for the case of ZnSe to be

Fig. 3. Temperature dependence of the experimental 1s exciton energies \( E_{1s}(T, x) \), observed in Zn\(_{1-x}\)Mg\(_x\)Se epitaxial films at different temperatures (2 K < \( T < 280 \) K). Solid curves represent the numerical fits using eqn. (5)
of the measured 1s exciton energies, $E_{1s}$, the exciton binding energies, $R(x)$, are obtained from the $E_{2s}$ versus $E_{1s}$ separation using the hydrogen model (eqn. (2); cf. Fig. 2). The absolute zero and room temperature values, $E_{1s}(0)$ and $E_{1s}(300 \, \text{K})$, of the 1s exciton peak positions follow readily from $T \rightarrow 0$ and $T \rightarrow 300 \, \text{K}$ extrapolations of the experimental $E_{1s}(T)$ data (see Fig. 3) in accordance with eqn. (5). The corresponding energy gaps $E_g(T, x)$ are given by $E_{1s}(T, x) + R(x)$ (eqn. (3), where the increase of the error bar by 2 meV for 300 K is due to a possible slight $T$-dependence of $R$). In the last column we have listed the first derivatives $dE_g(T)/dT$ at 300 K that follow from the fine numerical fits of our experimental data (Fig. 3) on the basis of equation (5)

| Sample          | $R$ (meV) | $E_{1s}(0)$ (meV) | $E_{1s}(300 \, \text{K})$ (meV) | $E_g(0)$ (meV) | $E_g(300 \, \text{K})$ (meV) | $dE_g(T)/dT |_{T=300 \, \text{K}}$ (meV/K) |
|-----------------|----------|------------------|-------------------------------|---------------|-----------------|-----------------------------|
| ZnSe            | 20.0 ± 0.3 | 2805.1           | 2701.6 ± 1.0                  | 2825.1 ± 0.3  | 2722 ± 3        | −0.479 ± 0.003              |
| Zn$_{0.93}$Mg$_{0.07}$Se | 22.3 ± 0.5 | 2875.0           | 2769.0 ± 1.2                  | 2897.3 ± 0.5  | 2791 ± 4        | −0.489 ± 0.003              |
| Zn$_{0.88}$Mg$_{0.12}$Se | 24.5 ± 0.6 | 2922.7           | 2811.7 ± 1.2                  | 2947.2 ± 0.6  | 2836 ± 4        | −0.515 ± 0.003              |
| Zn$_{0.81}$Mg$_{0.19}$Se | 27.0 ± 1.0 | 2990.8           | 2876.3 ± 1.5                  | 3017.8 ± 1.0  | 2903 ± 5        | −0.543 ± 0.005              |

smaller than 2 meV. (This additional uncertainty is indicated by increased error bars for all $E_g(300 \, \text{K}, x)$ values in Table 1 and in the corresponding $E_g(T, x)$ equations in Section 4.)

Within this approximation, the energy gaps, $E_g(T, x)$, of the ternary compounds in consideration are given by the combinations

$$E_g(T, x) \simeq E_{1s}(T, x) + R(x)$$

(3)

of the measured 1s exciton energies, $E_{1s}(T, x)$ (see Fig. 3), and the associated exciton binding energies, $R(x)$ (which are listed for the samples studied in Table 1). The $x$-dependence of the latter is easily seen to be described to a very good approximation (within a maximum deviation of only 0.2 meV) by the linear function

$$R(x) \simeq R(0) + \left. \frac{dR(x)}{dx} \right|_{x=0} \cdot x = (20.0 + 37.3x) \, \text{meV}.$$  

(4)

3. Temperature Dependence

The temperature dependences of the 1s exciton peak positions of the Zn$_{1-x}$Mg$_x$Se samples studied are presented in Fig. 3. Note the high density of measurements undertaken in the low-temperature region. (More than 25 experimental points have been obtained within the region 0 K < $T$ < 80 K for all of the four investigated compositions.) Such a high density of experimental data is an essential prerequisite for an accurate determination of basic empirical parameters (cf. Table 2).

In a series of recent publications [12 to 14] one of us has studied, in some detail, the analytical description of the temperature dependence of fundamental energy gaps in semiconductors. Within the analytical treatise [14], the electron–phonon interaction mechanism has been considered to be as usually the dominating one. The corresponding electron–phonon spectral function, $f(\hbar \omega)$, has been taken within a certain interval of phonon energies, $0 \leq \hbar \omega \leq \hbar \omega_0$, to be described approximately by a power dependence, $f(\hbar \omega) = C(\hbar \omega)^n$ (where the exponent $n$, the proportionality factor $C$, and the cut-off energy $\hbar \omega_0$ are empirical quantities). The fundamental parameters which are directly

| Sample          | $R$ (meV) | $E_{1s}(0)$ (meV) | $E_{1s}(300 \, \text{K})$ (meV) | $E_g(0)$ (meV) | $E_g(300 \, \text{K})$ (meV) | $dE_g(T)/dT |_{T=300 \, \text{K}}$ (meV/K) |
|-----------------|----------|------------------|-------------------------------|---------------|-----------------|-----------------------------|
| ZnSe            | 20.0 ± 0.3 | 2805.1           | 2701.6 ± 1.0                  | 2825.1 ± 0.3  | 2722 ± 3        | −0.479 ± 0.003              |
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| Zn$_{0.81}$Mg$_{0.19}$Se | 27.0 ± 1.0 | 2990.8           | 2876.3 ± 1.5                  | 3017.8 ± 1.0  | 2903 ± 5        | −0.543 ± 0.005              |
related to the observable temperature dependence of the energy gap are given in terms of the lowest-order moments [14] of the spectral function \( f(\hbar \omega) \) as

\[
S \equiv k_B \int_0^{\hbar \omega_0} d(\hbar \omega) f(\hbar \omega) (\hbar \omega)\^{-1} \quad \text{and} \quad \Theta \equiv S^{-1} \int_0^{\hbar \omega_0} d(\hbar \omega) f(\hbar \omega).
\]

(Note that the quantity \( S \) had been denoted in [12 to 14] by \( a \).) Combining both definitions we see that \( k_B \Theta \) represents a certain average (harmonic mean) of phonon energies, \( (k_B \Theta)^{-1} \equiv (\hbar \omega_{\text{eff}})^{-1} \equiv (\hbar \omega)^{-1} \), whereby the spectral function \( f(\hbar \omega) \) plays the role of the weighting factor. This effective phonon energy, \( \hbar \omega_{\text{eff}} \equiv k_B \Theta \), is represented for convenience on the temperature scale by a corresponding phonon temperature \( \Theta \). A detailed analytical and numerical study of this model [14] has shown that the observable temperature dependence of the energy gap in question is given to good approximation by an analytical expression of the form [14]

\[
E_{1s}(T, x) = E_{1s}(0, x) - \frac{S \Theta}{2} \left[ \sqrt{1 + \left( \frac{2T}{\Theta} \right)^p} - 1 \right],
\]

where \( p = v + 1 \). In the range of very low temperatures, \( T \ll \Theta \), we see that the temperature dependence of (5) reduces to a power dependence [12 to 14],

\[
E_{1s}(T, x) \to E_{1s}(0, x) - S \frac{2^{p-1}T^p}{p \Theta^{p-1}},
\]

where the characteristic exponent \( p \) is higher by unity (see above) than the exponent \( v \) controlling the shape of the underlying spectral function, \( f(\hbar \omega) \propto (\hbar \omega)^v \). This empirical parameter \( p \) has been estimated for a large number of semiconductor materials to be usually significantly higher than 2 [12 to 14]. (Note that this apparent restriction, \( p > 2 \),

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**Table 2**

Parameter value sets deduced from the temperature dependence of the 1s exciton energy position, \( E_{1s}(T) \), in Zn_{1-x}Mg_xSe epitaxial films (Fig. 3) using the four-parameter expression (5) and earlier three-parameter models (eqns. (12) and (13)). In the last column are listed the corresponding reduced chi-square values, \( \chi^2/\nu \) [28] (for \( w_i \propto (\sigma_i)^{-1} \)). Characteristic uncertainties of parameter values are quoted and discussed in Section 6.

<table>
<thead>
<tr>
<th>equation</th>
<th>( x )</th>
<th>( E_{1s}(0) ) [meV]</th>
<th>( S ) or ( \alpha ) [meV/K]</th>
<th>( \Theta ) or ( \beta ) [K]</th>
<th>( p )</th>
<th>( \chi^2/\nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>eqn. (5) (Pässler [12 to 14])</td>
<td>0.07</td>
<td>2875.0</td>
<td>0.506</td>
<td>193</td>
<td>2.60</td>
<td>2.60</td>
</tr>
<tr>
<td>eqn. (5) (Viña et al. [17], O’Donnel and Shen [18])</td>
<td>0.12</td>
<td>2922.7</td>
<td>0.533</td>
<td>195</td>
<td>2.62</td>
<td>1.6</td>
</tr>
<tr>
<td>eqn. (5) (Varshni [15], Thurmond [16])</td>
<td>0.19</td>
<td>2990.8</td>
<td>0.564</td>
<td>213</td>
<td>2.48</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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Where: 
- \( E_{1s}(0, x) \) is the 1s exciton energy at zero temperature and \( x \) is the material parameter.
- \( \chi^2/\nu \) is the reduced chi-square.
- The values are given with uncertainties.
can be theoretically understood as a consequence of predominantly concave shapes of the underlying electron–phonon spectral function [14] in combination with non-vanishing contributions of the thermal expansion mechanism [3, 11, 18, 25 to 27] to the total gap shrinkage effect in the given material.) At very high temperatures, \( T \gg \Theta \), eqn. (5) goes to the universal asymptotic form [14],

\[
E_{1s}(T, x) \to E_{1s}(0, x) - S \left( T - \frac{\Theta}{2} \right).
\]

(5b)

From the latter we see that the parameter \( S \) represents the high-temperature limiting value of the corresponding gap entropy [13, 16],

\[
S = S_{1s}(T \to \infty, x) \equiv -\frac{\partial E_{1s}(T, x)}{\partial T} \bigg|_{T \to \infty}.
\]

(6)

The empirical parameter values \( E_{1s}(0, x), S(x), \Theta(x), \) and \( p(x) \) obtained by careful numerical fittings with eqn. (5) from the temperature dependence of the \( E_{1s}(T, x) \) energy positions (Fig. 3) are listed in the upper part of Table 2 (and discussed below in Sections 5 and 6). The full curves in Fig. 3 give the corresponding theoretical \( E_{1s}(T, x) \) dependences. Particular values for these recalculated exciton peak energy positions in the \( T \to 0 \) limit and near room temperature (\( T = 300 \) K) are collected in Table 1.

4. Composition Dependence

By examining the \( x \)-dependence of the zero temperature limits (listed in Table 1) of the 1s-exciton peak position, \( E_{1s}(0, x) \), and the associated band gap energy, \( E_g(0, x) \), we can readily see that they are described to good approximation by the linear expressions

\[
E_{1s}(0, x) \simeq (2.805 + 0.976x) \text{ eV} \pm 0.001 \text{ eV}
\]

(7a)

and

\[
E_g(0, x) \simeq (2.826 + 1.013x) \text{ eV} \pm 0.002 \text{ eV}
\]

(7b)

(in accordance with eqns. (3) and (4)). The \( x \)-dependences of both quantities at \( T = 300 \) K (Table 1), which result from fits of the experimental data with eqn. (5) (in combination with eqns. (3) and (4)), are given by the analogous linear expressions

\[
E_{1s}(300 \text{ K}, x) \simeq (2.703 + 0.913x) \text{ eV} \pm 0.002 \text{ eV}
\]

(8a)

and

\[
E_g(300 \text{ K}, x) \simeq (2.723 + 0.951x) \text{ eV} \pm 0.005 \text{ eV}.
\]

(8b)

Both sets of linear approximations (eqns. (7a, b) and (8a, b)) are plotted in Fig. 4 by full lines up to \( x \leq 0.2 \). The dashed lines in Fig. 4 are linear extrapolations for exciton peak energy positions \( E_{1s}(0, x) \) (7a) and band gap energies \( E_g(300 \text{ K}, x) \) (8b) up to \( x \leq 0.7 \).

By examining in more detail the temperature and composition dependence of the exciton energies, \( E_{1s}(T, x) \), which we have fitted and recalculated using eqn. (5) (shown by the curves in Fig. 3), we find an approximately linear \( x \)-dependence at any temperature from 0 up to 300 K (within an accuracy of better than \( \pm 2 \) meV). At the same time we see by comparing the \( E_{1s}(T, x) \) or \( E_g(T, x) \) curves for \( T = 0 \) and 300 K in Fig. 4 that
their slopes are slightly different (due to the different magnitudes of the linear expansion coefficients in (8a, b) versus (7a, b)). This means that we have to take into account, in general, a certain temperature dependence of the corresponding expansion coefficient.

Generally, we can represent the $x$-dependence of exciton peak positions within the composition regime of $0 < x < 0.2$ (at least) by a linear approximation like

$$E_{1s}(T, x) \approx E_{1s}(T, 0) + \frac{\partial E_{1s}(T, x)}{\partial x} \bigg|_{x = 0} \cdot x \equiv E_{1s}^{\text{ZnSe}}(T) + a_{1s}(T) \cdot x,$$

where the linear expansion coefficient is given by the corresponding partial derivative, $a_{1s}(T) \equiv \frac{\partial E_{1s}(T, x)}{\partial x} \bigg|_{x = 0}$. To enable a numerical determination of the temperature dependence of this expansion coefficient we have calculated the $E_{1s}(T, x)$ positions (from eqn. (5)) for a series of five additional equidistant points ($\Delta T = 50$ K, at the four $x$-values in consideration) and we have determined the corresponding expansion coefficients $a_{1s}(T)$ in eqn. (9) by linear fittings of these five additional series of $E_{1s}(T, x)$ positions (in analogy to eqns. (7a) and (8a); cf. Fig. 4). The total set of the discrete $a_{1s}(T)$ values (given by 0.976 eV at 0 K, 0.973 eV at 50 K, 0.967 eV at 100 K, 0.960 eV at 150 K, 0.947 eV at 200 K, 0.931 eV at 250 K, and 0.913 eV at 300 K) can be very well approximated by the second-order Taylor expansion

$$a_{1s}(T) \approx 0.976 \text{ eV} - 1.358 \times 10^{-5} \text{ eV K}^{-1} T - 6.52 \times 10^{-7} \text{ eV K}^{-2} T^2(\pm 0.001 \text{ eV}).$$

In analogy to approximation (9) we can represent the composition dependence of the band gap energy, $E_g(T, x)$ (eqn. (3)), within a maximum error of $\pm 0.005$ eV, by the linear expression

$$E_g(T, x) \approx E_g^{\text{ZnSe}}(T) + a_g(T) \cdot x,$$
where \( E_g(ZnSe)(T) = E_{1s}(ZnSe)(T) + 0.020 \) eV (according to Table 1 and eqn. (4)) and the linear expansion coefficient is given, on the basis of eqn. (10), by \( a_g(T) = a_{1s}(T) + 0.037 \) eV (in accordance with eqns. (3) and (4)). Thus the slopes \( a_g(T) \) for the \( x \)-dependence of the gap widths, \( E_g(T,x) \) (eqn. (11)), are slightly higher than the slopes \( a_{1s}(T) \) for the \( x \)-dependence of the associated exciton peak positions, \( E_{1s}(T,x) \) (eqn. (9)). This slight enhancement (cf. Fig. 4) is due to the additional \( x \)-dependence of the exciton binding energy, \( R(x) \) (eqn. (4)).

5. Discussion

The changes in the empirical parameters \( S(x), \Theta(x), \) and \( p(x) \) from one sample to another (see the upper part of Table 1) indicate a general tendency to a non-linear dependence for increasing \( x \). However, it is obvious that the parameter sets available now, for only four different composition values \( x \), are not sufficient for a trustworthy analytical simulation of the actual \( x \)-dependence of these parameters from 0 up to 0.19. From Table 2 we see that the characteristic curve-shape parameter (low temperature exponent) \( p \) occurring in eqn. (5) is, in analogy to many other semiconductor materials [12 to 14], significantly higher than 2 for all the \( Zn_{1-x}Mg_xSe \) samples \((x = 0.0, 0.07, 0.12, \) and 0.19). We also see from Table 2 that this parameter \( p(x) \) tends to decrease significantly with increasing \( x \). This is the first obvious indication of a strong variability in this curve shape adjustment parameter \( p(x) \) within a given sequence of ternary compounds.

We were able to construct in Section 4 a simple analytical framework that is capable of predicting exciton energies, \( E_{1s}(T,x) \), and fundamental gap energies, \( E_g(T,x) \), with an accuracy of better than \( \pm 2 \) meV or \( \pm 5 \) meV, respectively, for any composition within the range \( 0 \leq x < 0.2 \) and any temperature from zero up to room temperature (at least). This simple computational scheme is based on the observation that the exciton energies \( E_{1s}(T,x) \) (Fig. 3) as well as the associated energy gap \( E_g(T,x) \) (eqn. (3)), which are of primary interest in practice, are given to very good approximation by expressions \textit{linear} in \( x \) (eqns. (7) to (9); cf. Fig. 4). In this way, the problem of numerical calculations of the temperature dependence of \( E_{1s}(T,x) \) (9) and \( E_g(T,x) \) (11) for the ternary com-

\[ \text{Fig. 5. The temperature dependence of the experimental 1s exciton energy in ZnSe, } E_{1s}(T,x=0), \text{ fitted by eqn. (5) [12 to 14] and by previous models [17, 18] and [15, 16] (with weighting factors } w_i \propto (\sigma_i)^{-2} \propto (\text{FWHM}(T_i))^{-2} \text{ (29)). } \]

\[ \text{eqn. (5) (Plassler [12 to 14]), } \]
\[ \text{eqn. (12) (Vina et al. [17], O’Donnell and Chen [18]), } \]
\[ \text{eqn. (13) (Varshini [15], Thurmond [16])} \]
pounds Zn$_{1-x}$Mg$_x$Se ($0 < x < 0.2$) is essentially reduced to that of calculating the exciton energies $E_{1s}(ZnSe)(T)$ (via eqn. (5)) of the binary compound ZnSe (cf. Fig. 3 and 5).

For practical purposes it may be of interest to consider whether the linear $x$-dependence of the exciton energy, $E_{1s}(T, x)$ (9), and that of the associated band gap energy, $E_g(T, x)$ (11), which has been determined here exclusively on the basis of experimental data for Zn$_{1-x}$Mg$_x$Se compounds with low magnesium content ($x < 0.2$), might also be valid beyond this range of $x$. To this end we have included in Fig. 4 the approximate results [28] of some rougher estimations of $E_{1s}(2 K, x)$ positions in several compounds with higher magnesium contents ($x = 0.21, 0.28, 0.36$; cf. the crosses in Fig. 4). Their comparison with theoretical $E_{1s}(T \to 0, x)$ values derived by extrapolating the linear dependence (7a) (represented by the upper dashed line in Fig. 4) shows that within uncertainties of up to $\pm 20$ meV [28] eqn. (7a) holds up to $x \approx 0.4$ (at least).

This finding is strongly supported by a comparison of the extrapolation of the linear $E_g(300 K, x)$ dependence (8b) (represented by the lower dashed line in Fig. 4) with corresponding experimental band gap energy data recently published by Jobst et al. (see Fig. 1 in [2]). The experimental $E_g(300 K, x)$ data [2], for compositions $x = 0.28, 0.32, 0.36, 0.46, 0.57,$ and $0.68$, are represented by filled triangles in Fig. 4. Their comparison with estimated values (dashed line calculated via eqn. (8b)) shows no systematic deviations. (The sporadic deviations of about 20 meV are due to experimental uncertainties.) This comparison shows that the linear $x$-dependences (eqns. (7) to (11)), which were determined in Section 4 exclusively from experimental data for $0 \leq x \leq 0.19$, are obviously valid, within reasonable approximation, for any composition up to $x \approx 0.7$ (cf. Fig. 4).

6. Comparison with Previous Models

One usually has a good chance of accurately predicting energy gaps in parameter ranges not comprised by previous experiments by carefully fitting and extrapolating the available temperature dependence. This applies in particular to calculations basing on a properly devised four-parameter model [12 to 14] (cf. Section 3). The actual accuracy of such predictions and extrapolations naturally depends on details of the analytical model used. In this section we examine the reliability of previous three-parameter models [15 to 18] using the present experimental results.

Consider first the single-phonon energy model of Viña et al. [17] which, after a suitable transformation [13, 14] of the original parameter set [17], can be written in the form [13, 14, 18],

$$E_{1s}(T, x) \approx E_{1s}(0, x) - \frac{S\Theta}{2} \left( \coth\left(\frac{\Theta}{2T}\right) - 1\right).$$

For $T \gg \Theta$ this tends to the same high temperature asymptote (5b) as eqn. (5). However, at very low temperatures, $T \ll \Theta$, eqn. (12) tends to a plateau in contrast to the more realistic power law dependence [12 to 14], $\propto T^p$ (5a), predicted by eqn. (5). This functional difference is responsible for the apparent differences of theoretically calculated $E_{1s}(T, x)$ curves at low temperatures, $T < 80 K$ (as illustrated for the individual Zn$_{1-x}$Mg$_x$Se samples in Figs. 6a to d).

Another well-known simple model for the temperature dependence of fundamental energy gaps or exciton energies in semiconductors is given by Varshni’s formula [15],

$$E_{1s}(T, x) \approx E_{1s}(0, x) - \frac{dT^2}{T + \beta}.$$
Here, the empirical parameter \( a \) plays the role of the \( T \rightarrow \infty \) limit (6) of the gap entropy \([13, 16]\), and should thus be directly comparable with the parameter \( S \) in eqns. (5) and (12); cf. Table 2. Varshni’s empirical temperature parameter \( b \) \([15]\), however, is factually undefined from general analytical points of view \([14]\). Pronounced differences (cf. Table 2) between \( b \) in (13) and \( Q \) in (5) or (12) must thus be anticipated.

A careful comparison of the characteristic experimental uncertainties at different temperatures \( T \) and compositions \( x \) has shown that the square roots of the variances \([29]\) for the individual experimental \( E_{1s}(T) \) values are nearly proportional to the squares of the experimentally measured FWHMs (cf. Section 2), i.e. \( \sigma_i \propto \text{FWHM}(T) \). The corresponding proportionality factors are about 0.04 for ZnSe and 0.03, 0.02, or 0.015 for \( x = 0.07, 0.12, \) and 0.19, respectively. The least square fits of our experimental \( E_{1s}(T \rightarrow 0, x) \) data (given in Fig.3) were performed, accordingly, with weighting factors \( s_i/\text{FWHM}(T_i) \) \([29]\) by using alternately the analytical model expressions (5), (12), and (13). The quality of the different fits is characterized by the corresponding reduced chi-square values, \( \chi^2/\nu \) \([29]\), listed in the last column of Table 2. It is found that the \( \chi^2/\nu \) values pertaining to eqn. (5) are on the order of unity throughout. This means that our new analytical model \([12 \text{ to } 14]\) adequately represents the temperature dependence of the exciton peak positions, \( E_{1s}(T, x) \), both in ZnSe \((x = 0; \text{cf. Figs. 3, 5, and 6a}) \) and ternary compounds \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) \((0 < x < 0.2; \text{cf. Figs. 3 and 6b to 6d}) \). In contrast, we see from Table 2 that the \( \chi^2/\nu \) values characterizing the fits by means of eqns. (12) \([17, 18]\) and (13) \([15, 16]\) range from 10 to 30. This is a clear indication \([29]\) of an insufficient degree of adequacy of these three-parameter models for numerical representations of the \( E_{1s}(T, x) \) dependence in the \( \text{Zn}_{1-x}\text{Mg}_x\text{Se} \) compounds studied. The inadequacy of the previous models \([15 \text{ to } 18]\) is apparent in particular for the case of ZnSe (Fig. 5 and 6a). The curves calculated from eqns. (12) and (13) run predominantly outside the experimentally relevant error bars. The deviations between experimental points and estimated values are especially pronounced for Varshni’s formula (13) where they reach 5 to 10 meV at temperatures of 260 to 300 K (see Fig. 5).
In addition to modeling a measured temperature dependence, it is usually desired that the analytical model be able to yield reasonable numerical values for the empirical parameters in connection with estimations of $E_{1s}(T)$ or $E_g(T)$ values for higher temperatures. Again we compare the results of eqn. (5) with those given by the three-parameter models [15 to 18] (eqns. (12) and (13)) using the experimental exciton peak position data for ZnSe.

The magnitude of the effective phonon temperature $\Theta$ of 193 K ($\pm$5 K) in ZnSe (Table 2) corresponds to an effective phonon energy [14] of $h\omega_{\text{eff}} \equiv k_B\Theta = 16.6$ meV ($\pm$0.4 meV). Comparing the latter with the cut-off energy $h\omega_{\text{LA}} = 23.6$ meV [24] of the LA-phonon branch we see that $h\omega_{\text{eff}}$ lies within the acoustic phonon energy spectrum. The main contribution to the total energy gap shrinkage effect in ZnSe is thus obviously due to acoustic phonons (in analogy to CdS [12], Si [13], and GaAs [14]). Moreover, we see that this effective phonon energy is located 4.8 meV above the middle, $(1/2) h\omega_{\text{LA}} = 11.8$ meV, of the acoustic part of the phonon spectrum. This is in qualitative agreement with a magnitude of $p = 2.66$ ($\pm$0.03) of the characteristic shape parameter in eqn. (5), which indicates (according to [14]) a pronounced concave shape of the underlying electron–phonon spectral function (in analogy again to CdS [12], Si [13], and GaAs [14]). Comparing further the fitted $\Theta$ value of about 193 K with the limiting Debye temperature for ZnSe, $\Theta_D = 339$ K [24], we obtain a ratio $\Theta/\Theta_D$ of about 0.57. This is of the same order of magnitude as the average value ($\approx 0.63$ [14]) for a large number of semiconductor materials. In contrast, the $\beta$ value of about 971 K is almost three times larger than $\Theta_D$. This shows once more that Varshni’s temperature parameter $\beta$ is only a fictive quantity [30, 31] that cannot be associated in a reasonable way with the actual phonon energy spectrum in ZnSe [24].

According to eqn. (5), the magnitude $S = 0.496$ meV/K ($\pm 0.007$ meV/K) (Table 2) of the limiting entropy, $S \equiv S(\infty)$ (eqn. (6)), is only about 3.5% higher than the room temperature entropy value, $S(300 \text{ K}) = 0.479$ meV ($\pm 0.003$ meV/K) (cf. Table 1 and Fig. 7b). Such small differences between entropy values, $S_g(T) \equiv -dE_g(T)/dT$ [13, 16], at room temperature versus the $T \to \infty$ limit are a characteristic feature of the electron–phonon interaction mechanism (see Section 2 in [14] and papers cited there) in medium-gap semiconductor materials ($1 \text{ eV} < E_g < 3 \text{ eV}$ [14]). In striking contrast to this, we see that the parameter value $\alpha \approx 1.62$ meV/K (Table 2) following from eqn. (13) is larger than the limiting entropy, $S(\infty)$, by a factor of about 3.3. This large difference shows that even the parameter $\alpha$ in Varshni’s formula [15, 16] (eqn. (13)) is also only a fictive quantity [30, 31] that cannot be assigned to the actual slope (6) of the $E_g(T)$ curve at $T \gg 300 \text{ K}$ (cf. Figs. 7a and 7b).

It is important to note that least square fittings of measured $E_{1s}(T)$ or $E_g(T)$ curves are usually performed by choosing constant weights, $w_i \to 1$, instead of properly varying weighting factors, $w_i \propto (\sigma_i)^{-2}$ [29, 32]. In order to estimate the influence of this common simplification we have performed a series of corresponding alternative fittings. In this way we could satisfy ourselves that the empirical parameter values $S$, $\Theta$, and $p$ calculated from eqn. (5) are rather insensitive to this simplification. The shifts of these parameters, e.g., in the case of ZnSe, amount to only 0.007 meV/K, 4 K, and 0.03, respectively. Thus they still range within the uncertainties quoted above. On the other hand, the parameters derived for ZnSe using Varshni’s formula (13) within this simplified fitting method, $w_i \to 1$, are $\alpha \approx 0.76$ meV/K and $\beta \approx 340$ K (comparable with those quoted in [11]). These values are quite different (by factors of 2 to 3) from the param-
eter values $\alpha \approx 1.62$ meV/K and $\beta \approx 971$ K (Table 2) determined above within the more appropriate $w_i \propto (\alpha_i)^{-2}$ fitting regime [29, 32]. This dramatic dependence of Varshni’s $\alpha$ and $\beta$ parameters on the choice of weighting factors $w_i$ at low versus room temperature (which seems to have been observed and reported here for the first time) might eventually be considered as an even more serious flaw of this conventional model [15, 16] than the pseudo-fittings (cf. Figs. 5 and 6) characterized by excessively large $\chi^2/\nu$ values (cf. Table 2). Moreover, such changes of magnitudes of weighting factors for different temperature regions are equivalent to changing the densities of experimental points in these regions. Thus Varshni’s parameter values are also strongly dependent on the actual constellation of experimental data densities in different temperature regions, i.e. in particular on the actual extensions of different experimental curves for the same material. A high degree of arbitrariness in empirical parameter values estimated by different authors on the basis of different experimental data constellations is thus practically anticipated by the ad-hoc nature of Varshni’s model [15, 16] (cf. the parameter sets $\alpha = 0.859$ meV/K and $\beta = 405$ K [8], $\alpha = 0.73$ meV/K and $\beta = 295$ K [11], and $\alpha = 1.3$ meV/K and $\beta = 500$ K [31] for ZnSe, whose region of variability is comparable to that for $\alpha$ and $\beta$ values in the case of GaAs [14 to 16, 32 to 34]).

An extrapolation up to 1000 K of the $E_g(ZnSe)(T)$ curve (3) using eqn. (5) gives a fundamental band gap energy of $E_g(1000 \text{ K}) \cong 2.38$ eV. The comparable $E_g$ value calcu-
lated from eqn. (12) is 2.41 eV. Thus we can safely assume a value of about 2.4 eV for $E_g(1000 \text{ K})$. In contrast, the estimation of $E_g(1000 \text{ K})$ via eqn. (13) with the parameter values $\alpha = 1.62 \text{ meV/K}$ and $\beta = 971 \text{ K}$ (Table 2) yields about 2.00 eV (cf. Fig. 7a). This is a huge deviation that shows the unreliability of Varshni’s ad-hoc model [15, 16] in extrapolations of measured $E_g(T)$ data.

7. Summary

Present results show that the novel analytical representation (eqn. (5)) developed in [12 to 14] for the temperature dependence of fundamental band gap energies (or the associated exciton energies) is well suited for physically adequate and numerically accurate fittings and extrapolations of experimental data and reasonable determinations of the magnitudes of the underlying empirical parameters both in binary and ternary compounds. On the basis of an approximately linear composition dependence of exciton energies in Zn$_{1-x}$Mg$_x$Se epitaxial films we were able to develop a relatively simple analytical framework for calculations of fundamental band gap energies giving adequate results both within and beyond the limits of the experimentally realized intervals of compositions, $0 \leq x < 0.2$, and temperatures, $2 \text{ K} < T < 280 \text{ K}$. Furthermore, we can conclude from the significant (apparently non-linear) $x$-dependence of the basic empirical parameters $S(x)$, $\Theta(x)$, and $p(x)$ in eqn. (5), which determine the temperature dependence of the corresponding band gap energies, that an eventual analytical description of such an $x$-dependence requires much more comprehensive and denser sequences of experimental data for ternary compounds.

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