Lattice dynamics of CdS/ZnSe strained layer superlattices studied by Raman scattering

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We report on the lattice dynamical properties of cubic CdS/ZnSe strained-layer superlattices, investigated by means of Raman scattering. Folded acoustic phonons, confined optical phonons and a Zn-S interface vibration, which is a result of the AB/CD structure of the investigated heterostructure, are observed. The interpretation of the observed modes as an interface mode and confined ZnSe and CdS optical vibrations is supported by the behavior of multiple (two) LO-phonon scattering. The experimental results are compared with model calculations. Here the Rytov model is applied for the folded acoustic phonons. The frequencies of the confined optical phonons are described by the linear-chain model, while their intensities are compared with the bond-polarizability model. The agreement between these model calculations and the experimental observations is very good.

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I. INTRODUCTION

Lattice-dynamical properties of superlattices differ from those of the bulk materials constituting a superlattice (SL). Due to the back-folding of acoustic-phonon dispersions into the SL mini-Brillouin zone, folded acoustic phonons are observed. If there is no spectral overlap between the opticalphonon dispersions of the two constituent materials, optical phonons become confined in their respective materials, i.e., in the individual superlattice layers. Raman spectroscopy proved to be a powerful tool to study these specific phonon properties. This has been demonstrated for many III-V superlattices, particularly in the GaAs/(Ga,Al)As system, where, e.g., strong confinement of optical phonons was observed (see, e.g., Ref. 1 and references therein). II-VI superlattices are, in general, more difficult to grow and often highly strained. In spite of these difficulties, folded acoustic phonons have been observed by means of Raman scattering, in CdS/ZnS e.g., and ZnS/ZnSe strained-layer superlattices,^{2,3} and recently by means of infrared spectroscopy in CdS/CdSe superlattices due to piezoelectric coupling.^{4,5} In these systems, strain-induced shifts of the phonon frequencies become important.2,4,6

The CdS/ZnSe superlattices discussed in this paper are of special interest: They are composed of two materials which share no common anion or cation, so called AB/CD SL's. Besides the lattice vibrations of SL's discussed above, additional eigenmodes occur in these AB/CD SL's which are related to the bonds at the interfaces, in our case to Cd-Se and Zn-S bonds. These additional eigenmodes are a two-dimensional analog to the vibration modes of point defects in bulk semiconductors. They have to be distinguished from such interface modes, which result from different dielectric functions of both materials forming the SL, as observed, e.g., for GaAs/AlAs SL's.⁷ The interface vibrations occurring in AB/CD SL's were first predicted in 1986 by Fasolino *et al.*, who calculated the phonon spectrum of InAs/GaSb SL's using a linear-chain model with interplanar force constants.⁸ In

the following years, interface vibrations were observed by means of Raman scattering for InAs/(Al,Ga)Sb SL's (see, e.g., Refs. 9-12, and references therein) and for CdSe/ZnTe SL's.¹³⁻¹⁶

In this work we report on an observation of folded longitudinal acoustic phonons, confined longitudinal optical phonons, and longitudinal interface phonons in CdS/ZnSe AB/CD SL's. Due to the lattice mismatch of about -2.7%between CdS and ZnSe, strain-induced shifts of the phonon frequencies become important. The experimental data are compared with calculations based on models like the Rytov model, the linear-chain model, the photoelastic model and the bond polarizability model.

II. EXPERIMENTAL DETAILS

The investigated superlattices were grown by molecularbeam epitaxy using CdS and ZnSe compound sources. The samples consist of a 200-period SL on top of a 300-nm-thick ZnSe buffer layer, and are grown on a GaAs(001) substrate. Some SL's are covered by a 30-nm ZnSe cap layer. The substrate temperature was lowered to $170 \,^{\circ}$ C just before the superlattice growth, in order to stabilize the cubic modification of the CdS in the SL layers. More details are given in Ref. 17. The SL period lengths are short, below 20 ML. They were determined by x-ray diffraction, and were usually in excellent agreement with those deduced from growth rates. The thickness of the individual layers was evaluated from growth rate data as monitored by beam flux pressures.

The Raman scattering experiments were performed in the quasibackscattering geometry along the [001] growth direction using the 476.5-nm line of an Ar^+ laser. All spectra were recorded at a sample temperature of 80 K in the diagonal 001(100,100)00 $\overline{1}$ or off-diagonal 001(100,010)00 $\overline{1}$ scattering configuration. The scattered light was dispersed by a Dilor XY spectrometer and detected by a liquid-nitrogencooled charge-coupled-device detector. The spectral resolution was about 2 cm⁻¹.



FIG. 1. Raman spectra of a $200 \times (1.7 \text{ nm}/1.4 \text{ nm}) \text{ CdS/ZnSe}$ superlattice, recorded in the diagonal and off-diagonal scattering configurations. The dotted arrows mark the wave numbers of the LO phonons in ZnSe and CdS bulk material at 256 and 305 cm⁻¹, respectively.

III. RESULTS AND DISCUSSION

When performing Raman spectroscopy from the CdS/ ZnSe superlattices, a special challenge is to prevent the ZnSe buffer or capping layer from obscuring or interfering with the optical phonon signal from the ZnSe SL layers. Here this problem is overcome by exploiting the resonant enhancement of the phonon signal when the incident and/or scattered photon energy is close to an electronic gap energy. Selectivity between the SL and the buffer and cap is easily achieved, because the SL band gap is between 2.2 and 2.4 eV, whereas for the buffer it amounts to 2.7 eV. However, when choosing an incident photon energy too close to the SL gap, the Raman spectrum would be superimposed by a strong photoluminescence structure. Therefore our spectra were recorded with the 476 nm line of the Ar⁺-laser (2.6 eV).

Figure 1 shows typical Raman spectra of a (1.7 nm/1.4 nm) CdS/ZnSe superlattice recorded in diagonal and offdiagonal scattering configurations. The vertical dotted arrows indicate the frequencies of the LO phonons of the bulk materials ZnSe and CdS at 256 and 305 cm⁻¹, respectively.^{18,2} In the wave number range below 150 cm⁻¹, Raman signals from folded longitudinal acoustic phonons (FLAP's) are observed, mainly in the diagonal scattering configuration. The signals arising from scattering with LO phonons are situated approximately between 220 and 330 cm⁻¹. The multiple (two) LO-phonon signals are observed approximately between 450 and 650 cm⁻¹. In the following the signals observed in these three wave number ranges will be discussed in more detail.

A. Folded longitudinal acoustic phonons

Because of the very similar sound velocities of the different materials (about 4000 m/s), the propagation dynamics of acoustic phonons through SL's show a bulklike behavior. The enhanced periodicity of SL's with respect to homogeneous bulk materials is described formally by a reduction of the Brillouin zone, which results in a folding of the acousticphonon branch. The dispersion relation of folded acoustic phonons is usually calculated by using the Rytov model.¹ In this model, the SL is assumed to be an elastic continuum, and the sound velocity v of the propagating acoustic modes is calculated along the growth direction by

$$v = \frac{d}{d_{ZnSe} / v_{ZnSe} + d_{CdS} / v_{CdS}}.$$
 (1)

Here d_{ZnSe} (d_{CdS}) is the thickness of the ZnSe (CdS) layers, and $d = d_{ZnSe} + d_{CdS}$ is the period length. The sound velocity of ZnSe (CdS) along the [001] growth direction is 4030 m/s (4000 m/s).^{18,2} Within the Rytov model, the wave numbers of the twofold-degenerate folded acoustic modes at the Γ point can be approximated very well by

$$\Omega_{\nu} \approx \frac{2\,\nu\,\pi\upsilon}{d},\tag{2}$$

where $\nu = 1, 2, ...$ describes the order of the folded mode. Taking into account the difference of the acoustic impedances of the two SL materials lifts the degeneracy, leading to the formation of minigaps. The size of these minigaps depends on the layer thicknesses, but is usually very small. The largest possible value for CdS/ZnSe SL's is below 1 cm⁻¹ (Ref. 19).

In a Raman experiment with quasibackscattering geometry, the transfer of the quasi-momentum $\hbar q_{ph}$ to the phonon system can be approximated by

$$\hbar q_{ph} \approx \frac{\hbar 4 \pi n}{\lambda},\tag{3}$$

where λ is the laser wavelength used for the experiment, and *n* the refractive index of the SL at this wavelength. Unlike in bulk materials, the phonon wave vector length is usually not negligible in comparison to the mini-Brillouin-zone length, and can be tuned, e.g., by changing the laser wavelength.

In Fig. 2(a), Raman spectra are shown for a 200 $\times (1.9 \text{ nm}/1.9 \text{ nm})$ CdS/ZnSe SL and а 200 \times (1.7 nm/1.4 nm) CdS/ZnSe SL. For both SL's, Raman signals due to the scattering with FLAP's up to the third order are observed. In case of the first-order modes, a splitting is resolved, indicated by 1- and 1+, which results from the non-negligible phonon wave-vector length in comparison to that of the edge of the mini-Brillouin-zone. The intensity of the higher-order modes, indicated by 2-/2+ and 3-/3+, is strongly reduced in comparison to that of the first-order modes. This observation is in qualitative agreement with predictions based on the photoelastic model.^{1,19} For symmetrical superlattices $(d_{ZnSe} = d_{CdS})$, e.g., the signal of the second-order modes should vanish and the intensity of the third-order modes should be one-third of that of the firstorder modes. The experimentally observed third- to firstorder intensity ratios amount to 0.07 for the (1.9 nm/1.9 nm) SL, and to 0.38 for the (1.7 nm/1.4 nm) SL. It is expected, especially for short-period superlattices, that the intensity ratio predicted from a continuum approximation (i.e., a photoelastic model) fail to some extent since interfacial layers (i.e., interface bonds) and the atomic structure are neglected.



FIG. 2. (a) Raman spectra of a (1.7 nm/1.4 nm) CdS/ZnSe superlattice and a (1.9 nm/1.9 nm) CdS/ZnSe superlattice in the wave number range of the folded longitudinal acoustic phonons (FLAP's). Spectra are recorded in diagonal scattering configuration. (b) Calculated dispersion relations of the FLAP's for the two superlattices of (a) with period lengths $d_1=3.8$ nm and $d_2=3.1$ nm. Data points are the experimental FLAP wave numbers from spectra (a), plotted at $q = q_{ph}$, the FLAP phonon wave vector length given by Eq. (3).

In order to evaluate the FLAP positions, the folded dispersion curves were calculated for both superlattices according to the Rytov model, using the x-ray period lengths of $d_1=3.8$ nm and $d_2=3.1$ nm, respectively. Note that the longer-period SL has a smaller Brillouin zone $(q_{max} = \pi/d)$, which implies a reduced folding period on the wave number scale.

Figure 2(b) shows the calculated FLAP dispersion curves for both SL's. The formation of minigaps has been neglected. The dotted vertical line at $q = 0.066 \text{ nm}^{-1}$ corresponds to the phonon wave vector q_{ph} of Eq. (3), using an average refractive index of 2.5. The open and full circles correspond to the observed Raman shifts from the spectra of Fig. 2(a). Obviously, the agreement of the experimental data with the calculated dispersion curves is very good. Furthermore, the observation of the folded acoustic modes indicates a good lateral and in-depth homogeneity of the SL period length and layer thicknesses.

In evaluating the FLAP dispersion relations, strain has not been taken into account. A compressive (tensile) in-plane strain increases (decreases) the sound velocity along the growth direction.^{2,3,20} Because we are dealing with (nearly) symmetrical superlattices, and due to the fact that the sound velocities of CdS and ZnSe are very similar, the strain has little effect on the sound velocity and hence the wave numbers calculated from Eqs. (1) and (2). Therefore, the neglect of strain effects in the calculation is justified. Such an action is supported by results of Refs. 3 and 20, where it was shown that taking strain into account does not improve the agreement between the experimental data and the calculations.

B. Confined optical phonons, strain effects, and interface phonons

Unlike in the case of FLAP's, strain has to be taken into account in the case of optical phonons in order to understand

TABLE I. Elastic constants and elastic compliances of ZnSe and cubic CdS (Ref. 34).

Material parameter	Unit	ZnSe	CdS
<i>C</i> ₁₁	GPa	85.0	77.9
<i>C</i> ₁₂	GPa	50.2	52.7
<i>S</i> ₁₁	$(TPa)^{-1}$	21.1	28.3
S ₁₂	$(TPa)^{-1}$	-7.8	-11.4

their properties. As shown below, by analyzing the Raman spectra in the wave number range of the longitudinal optical phonons, the CdS/ZnSe SL's discussed here adopt a strain state which corresponds to that of a (nearly) free-standing SL. In this case, the in-plane lattice parameter a_{\parallel} is given by²¹

$$a_{\parallel} = \frac{a_{ZnSe}G_{ZnSe}d_{ZnSe} + a_{CdS}G_{CdS}d_{CdS}}{G_{ZnSe}d_{ZnSe} + G_{CdS}d_{CdS}}.$$
 (4)

Here *d* denotes the layer thicknesses, *a* the bulk lattice constants [$a_{ZnSe} = 0.567$ nm (Ref. 18) and $a_{CdS} = 0.582$ nm (Ref. 22), and

$$G = 2(C_{11} + C_{12} - 2(C_{12})^2 / C_{11})$$
(5)

is the shear modulus. The elastic constants C_{ij} of ZnSe and CdS are listed in Table I. The in-plane strain ϵ_{\parallel} of the individual ZnSe and CdS layers is given by

$$\epsilon_{\parallel} = \frac{a_{\parallel} - a}{a},\tag{6}$$

with a_{\parallel} the superlattice in-plane lattice parameter. The straininduced shift of the LO-phonon wave number $\Delta \Omega_{LO}$ is obtained by²³

$$\Delta\Omega_{LO} = \frac{pS_{12} + q(S_{11} + S_{12})}{S_{11} + S_{12}} \frac{\epsilon_{\parallel}}{\Omega_{LO}}.$$
 (7)

 S_{11} and S_{12} are the elastic compliances also listed in Table I, p and q are the phonon deformation potentials, and Ω_{LO} is the LO phonon wave number of the bulk material. The phonon deformation potentials of ZnSe are given by p $= 0.93 \ \Omega_{LO}^2$ and $q = 2.27 \ \Omega_{LO}^2$ (Ref. 1). In the case of cubic CdS these values are not known so far. As a first approximation we used the same values as for ZnSe. This approximation is justified because in II-VI materials usually p $\approx 1 \ \Omega_{LO}^2$ and $q \approx 2 \ \Omega_{LO}^2$ hold.^{2,23} By using Eqs. (4)–(7) the strain-induced shift of the LO phonon wave number for symmetrical superlattices is calculated to be $\Delta \Omega_{LO} =$ $-4.4 \ \text{cm}^{-1}$ for ZnSe and $\Delta \Omega_{LO} = +6.9 \ \text{cm}^{-1}$ for CdS. These values constitute the basis for the force constants in our linear-chain model.

To interpret the experimental observations of the LOphonon scattering in detail, calculations based on a linearchain model have been performed.^{1,8} Only the interaction between nearest neighbors has been taken into account. The force constants necessary to describe the interaction between Cd and S atoms and Zn and Se atoms have been chosen in



FIG. 3. Linear-chain model calculation applied to a CdS/ZnSe superlattice with 6-ML CdS and 5-ML ZnSe. Left-hand side: dispersion relation of longitudinal phonons. The arrows indicate the strain-shifted bulklike wave numbers of the CdS and ZnSe LO phonons. Right hand side: atomic displacement patterns (q=0) for some selected modes across one period length *d*. For clarity, the calculated longitudinal atomic displacements are plotted as transverse ones. (E)IFM stands for (extended) interface mode. The displacement patterns shown in (b) and (c) [(d) and (e)] describe confined CdS (ZnSe) phonons.

such a way as to fit the bulk LO-phonon frequencies at the Γ point of ZnSe and CdS, modified by the strain-induced shifts calculated above. At the interfaces, formed by Cd-Se and Zn-S bonds, continuum strain theory is inadequate. Therefore, to a first approximation, the force constants describing the interaction between Cd and Se atoms and Zn and S atoms, respectively, were obtained by fitting the Γ -point bulk CdSe and ZnS LO phonon wave numbers of 210 and 351 cm⁻¹, respectively.^{2,14}

The left-hand side of Fig. 3 shows the dispersion relation calculated from the linear-chain model for a SL with a period length of 6-ML CdS plus 5-ML ZnSe. These numbers correspond to a very good approximation to the (1.7 nm/1.4 nm) CdS/ZnSe SL sample. The arrows indicate the strain shifted bulk LO-phonon wave numbers of ZnSe and CdS. At wave numbers below 150 cm⁻¹, the dispersion relation describes the FLAP's. In the wave number range between 310 and 275 cm⁻¹ (250 and 200 cm⁻¹), the dispersion relation reflects the confinement of the CdS (ZnSe) LO phonons. The most important result is that the linear-chain model predicts a vibration mode, the eigenwave number of which exceeds the calculated wave number of the first-order-confined CdS LO phonon.

The atomic displacement patterns of some selected vibration modes at q=0 are shown on the right-hand side of Fig. 3. For clarity, the longitudinal displacements are plotted as transverse ones. Patterns (b) and (c) describe the first- and second-order-confined CdS LO phonons, and patterns (d) and (e) the corresponding ZnSe phonons. The vibration mode with the highest eigenwave number is clearly correlated with the Zn-S interface, and therefore is assigned to a Zn-S longitudinal interface mode (IFM). Further simulations show that the modes with the eigen displacements (f) and (g) are also related to interface bonds. Because there is at least



FIG. 4. Calculated wave numbers of some selected vibration modes (q=0) as functions of the period length of symmetrical CdS/ZnSe superlattices. (E)IFM stands for (extended) interface modes, LO 1 and LO 2 for the first- and second-order-confined longitudinal optical phonons, and FLAP's for folded longitudinal acoustic phonons.

partial overlap of four bulk dispersion relations in the wave number range between 150 and 200 cm⁻¹ (LA ZnS, LA ZnSe, LO CdSe, and LO ZnSe), however, the interpretation of these two modes is much more complicated. Their displacement patterns extend into the CdS and ZnSe layers, showing a behavior more or less similar to acoustic vibrations. In the following, the two vibrations (f) and (g) are therefore called extended interface modes, (E)IFM 1 and (E)FIM 2, respectively.

Figure 4 shows the eigenwave number of various modes calculated within the linear-chain model as function of the number of CdS and ZnSe monolayers assuming a symmetrical SL. The wave numbers of the first- and second-orderconfined modes (LO 1 and LO 2) and of the first- and second-order FLAP's clearly depend on the number of monolayers. This is not the case for the Zn-S IFM, where the eigenwave number becomes independent on thickness for thicknesses exceeding one monolayer. The calculated eigenwave number of this mode is 317 cm^{-1} for all thicknesses, except the smallest thickness, where it is 315 cm^{-1} . Because the displacement patterns of the (E)IFM 1 and (E)IFM 2 extend into the CdS and ZnSe layers, the eigenwave number of these modes also depends on the layer thickness. Similar results are obtained for asymmetric SL's $(d_{ZnSe} \neq d_{CdS})$. In particular, the robustness of the wave number of the Zn-S IFM upon thickness variation is confirmed.

In Fig. 5, the Raman spectra of the 200 \times (1.7 nm/1.4 nm) CdS/ZnSe SL in a wave number range between 170 and 350 cm⁻¹ are shown, recorded in the off-diagonal (diagonal) scattering configuration. The dotted lines indicate the calculated wave numbers of the confined LO modes (the numbers indicate the mode order), and the dashed line marks the calculated wave number of the Zn-S IFM. According to the selection rules,¹ scattering with a first-order-confined ZnSe LO phonon is mainly observed in the off-diagonal scattering configuration, and with the second-order mode in the diagonal configuration. Obviously, the Raman shifts observed in the experiment are in very good



FIG. 5. Raman spectra of a (1.7 nm/1.4 nm) CdS/ZnSe superlattice in the wave number range of confined optical phonons and interface modes (IFM), recorded in the diagonal and off-diagonal scattering configuration. Vertical lines indicate the wave numbers calculated from the linear-chain model for a (6 ML/5 ML) CdS/ ZnSe superlattice (the numbers give the order of confined LOphonon modes).

agreement with the calculated wave numbers. In addition, the wave number of the peak maximum around 316 cm⁻¹ is 6 cm⁻¹ above the calculated wave number of the firstorder-confined CdS mode. However, the wave number of the peak maximum agrees almost exactly with the calculated wave number of the Zn-S interface mode of 317 cm⁻¹. Therefore, we attribute this signal around 316 cm⁻¹ to light scattering with the Zn-S interface mode. This interpretation is supported by the fact that the signal is observed in both diagonal and off-diagonal scattering configurations, in agreement with the selection rules for such interface modes.⁹ In comparison to the confined ZnSe modes, the CdS modes appear broadened. This finding is attributed to a reduced quality of the CdS layers in the SL owing to the metastability of the cubic crystal phase in CdS.²

In order to estimate the scattering intensities of the different modes, we used the bond polarizability model.^{1,24} In this model, the intensity of a specific mode is proportional to the square of the sum of all relative atomic displacements, multiplied by the corresponding bond Raman polarizabilities α . The summation extends over one period length. The bond Raman polarizabilities of superlattices are often taken as adjustable parameters.^{13,14,24} If we assume, to a first approximation, the polarizabilities to be the same for both materials, $\alpha_{ZnS} = \alpha_{CdS}$, the ratio of the scattering intensity between the Zn-S IFM and the CdS LO 1 mode is 0.6 in the off-diagonal scattering configuration. The contributions of the Zn-Se and Cd-Se bonds have been ignored in this estimation, which appears reasonable considering the displacement patterns (a) and (b) in Fig. 3. If we assume, e.g., $\alpha_{ZnS} = 2 \times \alpha_{CdS}$, the intensity ratio is enhanced to 1.1. Similar results are obtained for the scattering intensity between the Zn-S IFM and the CdS LO 2 mode in the diagonal scattering configuration. These estimations indicate that the scattering intensity of the IFM is comparable to that of the confined modes, due to the strong atomic displacement of the Zn-S interface vibration,



FIG. 6. Raman spectra of three superlattices with different layer thicknesses in the wave number range of the confined optical and interface modes (diagonal scattering configuration).

and because of the short period of the SL's. Furthermore, the type-II electronic band alignment of the CdS/ZnSe heterostructure²⁵ enhances the scattering probability of the virtually excited electron-hole pairs with the interface phonons in a Raman process.

The Raman spectra of three SL's with different periods are compared in Fig. 6, recorded in the diagonal scattering configuration. The Raman shift of the second-order-confined ZnSe LO mode is seen to decrease clearly with decreasing thickness of the ZnSe SL layers. In contrast, the Raman shift of the Zn-S interface mode appears insensitive to the layer thickness, which varies by nearly a factor of 2. Both observations agree well with the calculated thickness dependence of these modes within the linear-chain model. (The calculation is shown in Fig. 4.) This agreement further supports the interpretation of the 316 cm⁻¹ signal as an IFM.

Figure 7 shows the wave numbers of the confined ZnSe LO modes of the three SL's against the effective wave number $q = m\pi/d_{ZnSe}$, where *m* is the order of the confined mode.¹ The solid line represents a fit using the expression²⁶

$$\omega^{2}(q) = A + \{A^{2} - B[1 - \cos(a_{ZnSe}q/2)]\}^{1/2}, \qquad (8)$$

where *q* is in units of $2\pi/a_{ZnSe}$. The experimental data points can be fitted well using $A = 3.175 \times 10^4$ cm⁻² and $B = 4.11 \times 10^8$ cm⁻⁴ which are reasonable values,^{26,27} leading to a LO-phonon wave number at the Γ point of 251.8 cm⁻¹. The LO-phonon wave number of the unstrained bulk material is 256 cm⁻¹, hence there is a difference of $\Delta \Omega_{LO} =$ -4.2 cm⁻¹. This difference is attributed to the tensile inplane strain of the ZnSe layers. Its value is very near to the strain shift of -4.4 cm⁻¹ calculated for a symmetric freestanding SL using Eqs. (4)–(7) (see the beginning of this section). From this coincidence we conclude²⁸ that the investigated SL's have a strain state corresponding to that of (nearly) free-standing SL's.

For the calculation of the effective wave vector $q = m\pi/d_{ZnSe}$ of the confined modes, the nominal layer thickness d_{ZnSe} has been used. In case of AB/AC-type SL's such as, e.g., GaAs/AlAs (As common to both constituents), often half a monolayer or an entire monolayer is added to the



FIG. 7. Wave numbers of the confined optical modes from Raman spectra of three different superlattices (see Fig. 6), plotted against the effective wave vector $q = m \pi/d_{ZnSe}$. The solid line is a fit of Eq. (8). The arrow indicates the position of the LO phonon of unstrained bulk ZnSe.

nominal layer thickness for the calculation of the effective wave vector.¹ This procedure takes into account that the As atoms at the interfaces vibrate in case of both the GaAs and AlAs confined modes. Applying the same procedure to the CdS/ZnSe SL's resulted in a ZnSe dispersion relation which



FIG. 8. (a) Raman spectrum of a (1.7 nm/1.4 nm) CdS/ZnSe superlattice in the wave number range of the confined LO phonons and interface modes. (b) Raman spectrum of the same superlattice in the wave number range of the two-LO-phonon scattering. To make easier a comparison, the *x* axis of spectrum (b) has been divided by a factor of 2. Dotted lines indicate the calculated confined LO modes of a (6 ML/5 ML) CdS/ZnSe superlattice. The dashed line marks the IFM.

showed a clear deviation from that known from neutronscattering data.²⁶ In particular, the curvature became too large. This finding reflects the AB/CD type nature of CdS/ ZnSe SL's, where no atom plane common to both constituents exists which could add to the effective thickness of the vibrating layers.

Concerning the (E)IFM's, clear Raman signals arising from light scattering with these modes were not observed. Similar experimental results were already reported for the CdSe/ZnTe system.^{13–16} By applying the bond polarizability model to the CdS/ZnSe system, we found that the scattering intensity of the (E)IFM is much less pronounced compared to that of the Zn-S IFM.^{5,19} Basically, this result comes from the fact that the atomic displacement pattern of the Zn-S IFM corresponds to an optical vibration, while that of the (E)IFM's rather corresponds to an acoustic vibration.

C. Multiple LO-phonon scattering

Further support to assign the signal observed around 316 cm⁻¹ to the Zn-S IFM is furnished from multiple (two) LO-phonon scattering. Very strong two-LO-phonon signals have been reported in CdS and ZnSe bulk materials using appropriate laser lines.^{29–31} As shown in Refs. 32 and 33, the two-LO-phonon signal of GaAs/AlAs SL's is dominated by combinations of even-order-confined LO modes (with decreasing intensity LO 2 + LO 2, LO 2 + LO 4, LO 4 + LO 4, ...). These observations let us expect at least two LO-phonon modes in CdS/ZnSe SL's with energies twice that of the CdS and ZnSe LO 2 modes.

Figure 8 shows Raman spectra of the (1.7 nm/1.4 nm)



FIG. 9. Raman spectra in the wave number range of the two-LO-phonon scattering of three different superlattices, recorded in the diagonal scattering configuration. Dotted lines are guides to the eye to stress the wave number dependence of the two LO 2 signals on the superlattice layer thicknesses.

CdS/ZnSe SL in the diagonal scattering configuration. Figure 8(a) shows the one-LO-phonon scattering, and Fig. 8(b) the two-LO-phonon scattering. To make easier visual comparison of the two spectra, the Raman shift of the two-LOphonon spectrum (b) has been divided by a factor of 2. The dotted vertical lines indicate the calculated wave numbers of the LO 2 and LO 4 modes, while the single dashed line marks the Zn-S IFM. The two-LO-phonon spectrum (b) shows signals exactly twice the frequency of the ZnSe and CdS LO 2 modes of spectrum (a). The additional signal around 270 cm^{-1} in between of these maxima is attributed to scattering with combinations of these modes (summation modes). In contrast, the two-LO-phonon scattering of the Zn-S IFM appears to be strongly suppressed. The reason for this finding is presently not understood in detail, but it is in qualitative agreement with results of others.¹⁵ Nevertheless, the data shown in Fig. 8 exclude the interpretation that the signal at 316 $\,\mathrm{cm}^{-1}$ arises from light scattering with the CdS LO 2 mode, and again favor the assignment of this signal the Zn-S IFM.

Figure 9 shows the Raman spectra of three different SL's in the wave number range of two-LO-phonon scattering, recorded in the diagonal scattering configuration. The signals attributed to the ZnSe $2 \times LO$ 2 mode are observed clearly to shift to lower wave numbers with decreasing ZnSe thickness. A similar trend holds for the $2 \times LO$ 2 CdS signals. This behavior is expected from the second-order scattering of confined modes, and thus confirms the assignment of these signals to the two-LO-phonon scattering.

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IV. SUMMARY

We reported on the lattice-dynamical properties of cubic CdS/ZnSe superlattices which have been investigated by means of Raman scattering. Preparation by molecular-beam epitaxy allowed for a stabilization of the cubic CdS phase, producing superlattice structures good enough to observe various phenomena associated with superlattice phonons. Folded longitudinal acoustic phonons up to the third order were detected. The wave numbers of the modes deduced from the experiment are in very good agreement with the theoretical values calculated within the Rytov model. Strong phonon confinement and strain-induced shifts of the phonon wave numbers were observed in case of longitudinal ZnSe vibrations. In addition, as a result of the AB/CD structure of the investigated superlattices, a Raman signal of a Zn-S interface vibration was observed. The spectral positions of the Raman signals of the longitudinal optical phonons are in very good agreement with those calculated from the linearchain model. Furthermore, by using the bond-polarizability model, it was shown that the scattering intensity of the Zn-S IFM is comparable to the ones of the confined longitudinal modes. The multiple (two) LO-phonon Raman spectra demonstrate the confinement of the ZnSe modes, and support the interpretation that a Raman signal of the Zn-S interface vibration has been observed.

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