Pressure dependence of phonons and excitons in InSe films prepared by metal-organic chemical vapor deposition

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The pressure dependence of the Raman spectra of phase-pure InSe thin films prepared by the low-pressure metal-organic chemical vapor deposition technique has been studied using a diamond-anvil high-pressure cell. Enhancement in the intensities of the Raman modes has been observed as a result of pressure-induced ''tuning'' of the energy of the M_1-type hyperbolic exciton in InSe at ~ 2.54 eV through discrete incident laser photon energies. The pressure coefficients of the phonon modes and of the hyperbolic exciton in InSe have been determined.

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I. INTRODUCTION

Among III-VI semiconductors which crystallize with a layered structure InSe has been of particular interest because of its potential applications in photovoltaic devices[1] since it has a low density of dangling bonds on its surface. A number of methods for growing InSe thin films have been reported so far. Recently, we have succeeded in growing single-phase thin films of InSe by metal-organic chemical vapor deposition (MOCVD) using a single-source precursor: $[(\mathrm{Me})_2\mathrm{In}(\mu\text{-}\mathrm{SeMe})]_2$ (Ref. 2). Although these films are polycrystalline, their structural and optical properties have been found to be comparable to those of bulk single crystals of InSe. While InSe grown by the Bridgman method crystallizes in the γ-polytypes[3] with rhombohedral unit cells,[4] the MOCVD-grown InSe films were determined to belong to the β-polytype with hexagonal unit cells. In this paper we report a study of the pressure dependence of the Raman spectra in these films using a diamond-anvil high-pressure cell. We found that the splitting between the longitudinal and transverse optical phonons with the E' symmetry *decreases* as a function of pressure. In addition to measuring the pressure coefficients of the zone-center optical phonon modes, we have been able to determine the pressure coefficient of the M_1-type hyperbolic exciton in InSe (to be abbreviated as the M_1 exciton) using the technique of pressure-tuned resonant Raman scattering.

II. EXPERIMENTAL DETAILS

The InSe thin films used in this study were grown by low-pressure MOCVD on [100]-oriented GaAs substrates using a noble single-source precursor $[(\mathrm{Me})_2\mathrm{In}(\mu\text{-}\mathrm{SeMe})]_2$. The details of the growth and characterization of these films have been reported before[2] and will not be repeated in this paper. Since InSe form layers which are bonded to each other via weak van der Waals forces, the InSe film is not strongly bonded to the GaAs substrate. Thus the sample can be lifted easily from the substrate without further treatment and loaded into a gasketed diamond anvil cell (DAC). A mixture of methanol/ethanol was used as the pressure medium and the pressure was determined by the standard ruby fluorescence technique. The highest pressure reached in our experiment was ~ 7 GPa. The Raman scattering experiments were performed in the backscattering geometry at low temperature by loading the DAC into a closed-cycle He refrigerator. The Raman spectra were measured with a double monochromator and single-photon counting electronics. As noted by Ashokan *et al.*[5] and also reported by us earlier,[2] the intensities of several Raman modes in InSe are enhanced when excited by the discrete lines of an Ar ion laser as a result of a near-resonance between the laser photon energies and the M_1 exciton of InSe (energy $E_1 \sim 2.535$ eV at ambient pressure). However, unlike Ashokan *et al.*,[5] we have utilized pressure rather than temperature to tune the energy of the M_1 exciton. By tuning the energy of the M_1 exciton through the laser photon energy we have observed strong enhancement in both one-phonon and multiphonon Raman modes. The enhancement was so strong for the polar optical phonons that we observed easily their third harmonics at resonance.

III. EXPERIMENTAL RESULTS

Figure 1 shows the Raman spectra of our InSe films measured at the temperature (T) equal to 50 K as a function of pressure using the 476.5-nm (photon energy $= 2.602$ eV) line of the Ar ion laser as the excitation source. The identifications of the various peaks in the Raman spectra in terms of scattering from optical phonons have been discussed in Ref. 2 and are summarized again in Table I. As pressure is increased the Raman spectra exhibit two changes. First, the positions of all the peaks shift towards higher frequencies. Second, the intensity of the Raman peaks first increases with pressure, reaches a maximum, and then decreases upon further increase in pressure. However, the pressure at which each Raman mode attains its maximum intensity is different and depends on the laser wavelength. To obtain the pressure dependence of the frequency and intensity of the individual

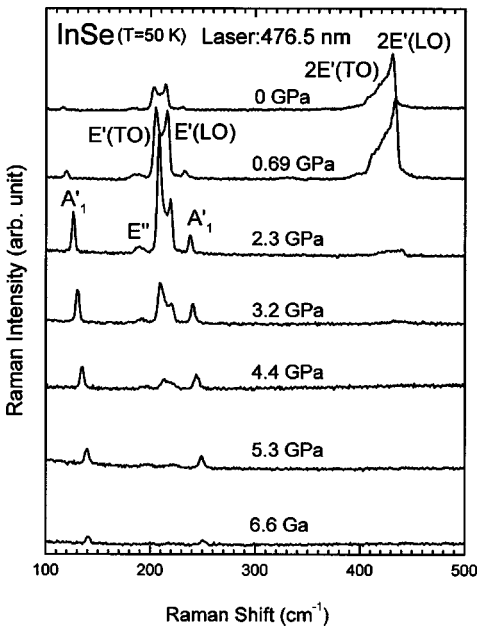

FIG. 1. Some Raman spectra of InSe thin films excited by the 476.5-nm (2.602-eV) line of an Ar ion laser at a fixed temperature of $T=50$ K at various pressures.

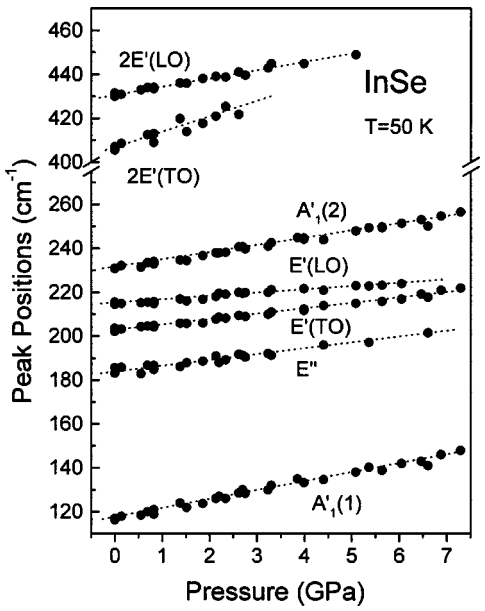

FIG. 2. The frequencies of the Raman peaks in InSe plotted as a function of pressure. The solid circles are the data points while the dashed curves represent linear fits to the experimental result. The data points for $P<4$ GPa were obtained with the 472.7-nm (2.622-eV) Ar laser line. The higher-pressure data points were obtained with the 457.9-nm (2.707-eV) laser line. The pressure coefficients of the Raman modes determined from these fits are given in Table I.

Raman peak, we have deconvolved each Raman spectrum into a sum of Gaussian peaks. The resultant pressure dependence of the Raman peak frequencies obtained by using several Ar laser lines is plotted as the data points in Fig. 2. The pressure coefficients of the Raman modes are then determined by making least-squares fits to the data points in Fig. 2 with straight lines. The pressure coefficients obtained in this way are presented in Table I. The pressure dependence of the intensities of the various Raman modes obtained at the laser wavelength of 476.5 nm (2.602 eV) is shown in Fig. 3(a). As a guide to the eyes we have fitted the data points with Lorentzian curves. These curves demonstrate that the different Raman peaks in InSe do not exhibit the same resonance behavior. There are at least two sets resonance peaks as a function of pressure in Fig. 3(a). One set of resonance occurs around 1.8–2.0 GPa for the polar E' longitudinal optical (LO) and transverse optical (TO) modes. A second and much weaker resonance occurs around 3 GPa for the nonpolar A_1' and E'' modes. By changing the excitation laser wavelength the pressures at which these resonance peaks occur also change. This shift in the resonance pressure with excitation laser wavelength is shown in Figs. 3(b) and 3(c) and can be easily explained by pressure-induced shifts of the M_1 exciton energy. Since the pressure at which the resonance in the Raman intensity peaks increases with the photon energy we conclude that the pressure coefficient (dE_1/dP) of the M_1 exciton energy is *positive*.

IV. DISCUSSION

A. Pressure dependence of Raman frequencies in InSe

We will first discuss the pressure dependence of the frequencies of the Raman modes in InSe thin films. From Table I we see that the pressure coefficient of the zone-center optical phonon modes can vary by as much as a factor of 3. The

TABLE I. Pressure coefficients of optical phonons in InSe.

Phonon modes (symmetry assignments based on Refs. 2 and 5)	Frequency ω (cm^{-1}) at $T=50$ K and $P=1$ bar	Pressure coefficient $d\omega/dP$ (cm^{-1}/GPa)	$(1/\omega)(d\omega/dP)$ (10^{-2} GPa^{-1})
$A_1'(1)$	117	4.0	3.4
E''	183	2.7	1.5
E'(TO)	205	2.2	1.1
E'(LO)	214	1.4	0.65
$A_1'(2)$	232	3.1	1.3
$2E'$(TO)	409		
$2E'$(LO)	432	3.3	0.76

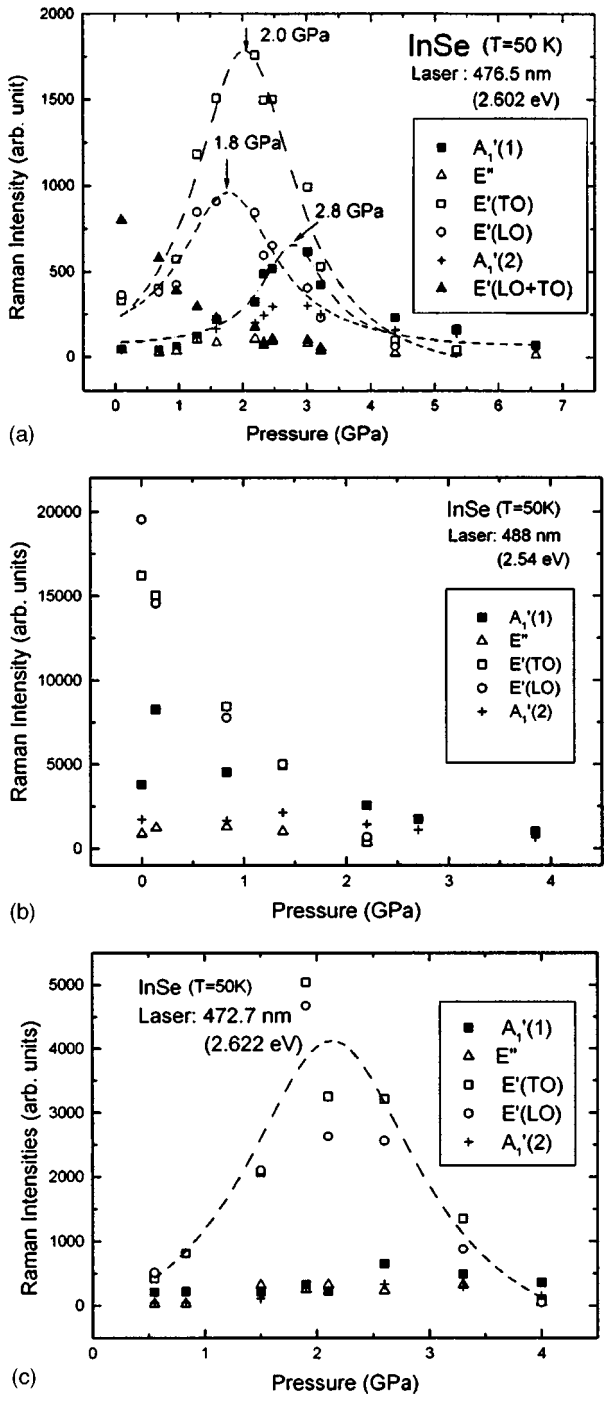

FIG. 3. The intensities of the Raman peaks in InSe plotted as a function of pressure for three different excitation photon wavelengths: (a) 476.5 nm (2.602 eV), (b) 488 nm (2.54 eV), and (c) 472.7 nm (2.622 eV). The dashed curves represent fits to the data points with Lorentzians. The pressures at which the intensity of some Raman modes reaches a peak value are indicated.

pressure coefficient is largest for the lowest-energy $A_1'(1)$ mode. In general, the pressure coefficient decreases with increasing phonon frequency modes. The only mode which does not obey this trend is the higher-frequency nonpolar $A_1'(2)$ mode. To further highlight this trend we have listed the normalized pressure coefficient $(1/\omega)(d\omega/dP)$ of the phonon modes in Table I.

The above trend in the pressure coefficients of InSe can be understood in terms of the crystal structure of InSe. It is now established that crystal structure of many III-VI semiconductors involves bilayers stacked on top of each other. Each bilayer consists of a double layer of group-III atoms sandwiched between two planes of group-VI atoms. A description plus pictures of the structure of the β-polytpe and of the bilayers in InSe can be found in Ref. 6. The bonding between the bilayers is due to a weak van der Waals interaction. As a result the bonding within a bilayer between adjacent atomic planes is much stronger than that between adjacent planes in neighboring bilayers. One consequence of this weak interbilayer bonding is that the crystal is much more compressible along the direction perpendicular to the bilayers (or parallel to the c axis) than parallel to the planes. Hence vibrations between the bilayers (sometimes referred to as interlayer modes) tend to have very low frequencies. These modes lie below the frequency range of our Raman modes. In case of the layered Ga chalcogenide compounds Besson[7] has reported a normalized pressure coefficient $(1/\omega)(d\omega/dP)$ of $\sim 20\times 10^{-2}$/GPa for these interlayer modes. We note that this pressure coefficient is about an order of magnitude larger than those listed in Table I. The modes we have observed are usually associated with intrabilayer vibrations (or intralayer modes). The low-frequency $A_1'(1)$ mode, for example, involves the displacement of the two InSe layers within the bilayer with respect to each other. This motion is expected to have a smaller spring constant since it involves bending of the weak In-In bond. On the other hand, the higher-frequency modes involve stretching of the strong In-Se bonds within the InSe layer. Based on the above argument we expect the higher-frequency modes to have smaller pressure coefficients. The normalized pressure coefficient $(1/\omega)(d\omega/dP)$ of these high-frequency modes in GaS and GaSe reported by Besson[7] was $\sim 1\times 10^{-2}$/GPa. We note that this value is quite comparable to the ones we obtained in InSe.

Another interesting result we found from Table I is that the pressure coefficient of the E'(TO) mode is larger than that of the E'(LO) mode. As a result, the TO-LO splitting *decreases* with pressure. This pressure coefficient difference amounts to $-0.8\ \mathrm{cm}^{-1}$/GPa while the TO and LO phonon splitting is $9\ \mathrm{cm}^{-1}$ (see Table I). Thus this splitting will disappear at a pressure of ~ 11 GPa. Since this splitting is a measure of the transverse or Born effective charge (e^*) of the InSe lattice,[8] this result implies that the InSe lattice becomes less ionic under pressure and its e^* will disappear around 11 GPa. Such a decrease of e^* with pressure is a rather common phenomenon among the group-III-V semiconductors with the zinc-blende structure.[9] In case of the zinc-blende-type semiconductors this decrease of e^* with compression has been explained in terms of a decrease in the bond polarity with pressure. Presumably a similar decrease in the In-Se bond polarity with compression accounts also for the result in InSe.

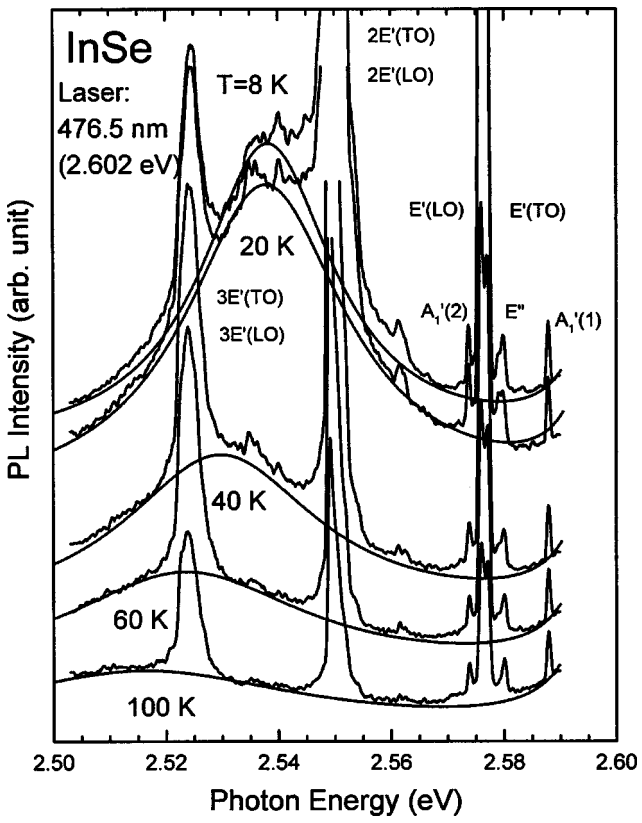

FIG. 4. Temperature dependence of the Raman modes in InSe on excitation laser photon energy. The dashed curves are least-squares fits with a Lorentzian to the broad photoluminescence background due to the M_1 exciton peak.

B. Pressure dependence of Raman intensities in InSe

The results in Figs. 3(a)–3(c) show that the intensity of the nonpolar A_1' modes tends to peak at a higher pressure than for the polar E'(LO) mode. To understand this difference we have measured the temperature dependence of the Raman spectra of InSe film when excited by the 476.5-nm laser line. The results are shown in Fig. 4. As the temperature is increased we find that some of the Raman peaks exhibit rather strong enhancement in agreement with the result of Ashokan *et al.*[5] These authors have explained this resonance solely based on the effect that the temperature tunes the energy of the M_1 exciton in bulk InSe (exciton energy $\sim$2.535 eV) through the incident laser photon energy. In our sample at low temperatures we found that the Raman peaks are superimposed on a broad photoluminescence (PL) peak centered around 2.54 eV as represented by the dotted curves in Fig. 4. We have identified this PL peak as due to radiative recombination from the M_1 exciton. As temperature is increased this peak redshifts while its intensity decreases. We note also that the intensity of some of the Raman peaks exhibits the strongest enhancement when they *overlap* with the M_1 exciton peak. Such resonance which occurs when the *scattered* photon energy coincides with that of the exciton has been referred to as an *outgoing resonance* in the literature.[10] Forbidden scattering by polar phonon modes has been known to exhibit especially strong outgoing resonances at excitons as a result of the Fröhlich electron-phonon interaction.[10] In the present case we found that this is true especially for the $3E'$(LO) mode. Resonance makes this mode in InSe even stronger than the E'(LO) at $T=40$ and 60 K. Similarly the $2E'$(LO) mode shows very strong enhancement as T is lowered to 8 K. From these temperature-dependent resonant Raman and PL spectra we deduce that (1) the energy of the M_1 exciton at $T=50$ K is 2.534 eV. This energy is in good agreement with the value of 2.535 eV at $T=77$ K obtained by Ashokan *et al.*[5] (2) The polar E'(TO) and E'(LO) modes exhibit mainly strong outgoing resonances. This result should be compared with the result reported by Ashokan *et al.*[5] who claimed that the incoming and outgoing resonance peaks in the Raman cross sections of the nonpolar modes are equally strong. (3) The PL spectra indicate that, with an increase in T, the *strength of the* M_1 *exciton decreases* while its *width increases* rapidly. As a result, we do not feel that *changing the sample temperature is a reliable way to determine the enhancement profile of the Raman cross section in InSe in the vicinity of the* M_1 *exciton*.

Unfortunately we found that when the sample was inside the DAC the intensity of the emission from the M_1 exciton was not easily observable. We have, instead, deduced the pressure dependence of the energy of the M_1 exciton from the resonance Raman scattering. To achieve this goal we first assume that the polar E'(TO) and E'(LO) modes exhibit only outgoing resonances with the M_1 exciton peak. At the incident photon energy of 2.602 eV (or 476.5 nm) these occur at pressures of 2.0 GPa and 1.8 GPa, respectively [see Fig. 3(a)]. Next we assume that when the incident laser photon energy is varied the *shape* of their resonance curves as a function of pressure remains unchanged although their peak heights and positions may change. To superimpose the resonance curves obtained at different incident photon energies as shown in Fig. 5, we translate the curves horizontally and scale their peak heights. From the horizontal translation of the curves we determine the adjustment in pressure ΔP (=peak pressure for 2.602 eV laser line-peak pressure for another laser line) necessary to bring the M_1 exciton into outgoing resonance with the incident photon energy. A plot of this change in the M_1 exciton energy ΔE *relative* to the 476.5-nm (2.602-eV) laser line as a function of ΔP is shown in Fig. 6. The pressure coefficient of the M_1 exciton (dE_1/dP) obtained from the slope of the straight line fit to the experimental points in Fig. 6 is equal to 35.3 meV/GPa.

As a consistency check of the pressure coefficient we have determined, we have translated the nonpolar A_1' mode resonance curves horizontally by the same amount of pressure ΔP as deduced from the E' polar modes when the incident photon energy is changed. After normalization of the peak heights we found that the resonance curves obtained for the different laser lines fall, more or less, on top of each other as shown in Fig. 5(b). The only exception is the sharp peak observed around 1.6 GPa at the incident laser wavelength of 488 nm (2.54 eV). The origin of this peak is not clear at this point. Finally, we use the results that (1) the outgoing resonance for the E'(LO) mode occurs at 1.8 GPa when the incident photon energy is 2.602 eV (476.5 nm) and (2) the pressure coefficient of the M_1 exciton is 35.3 meV/

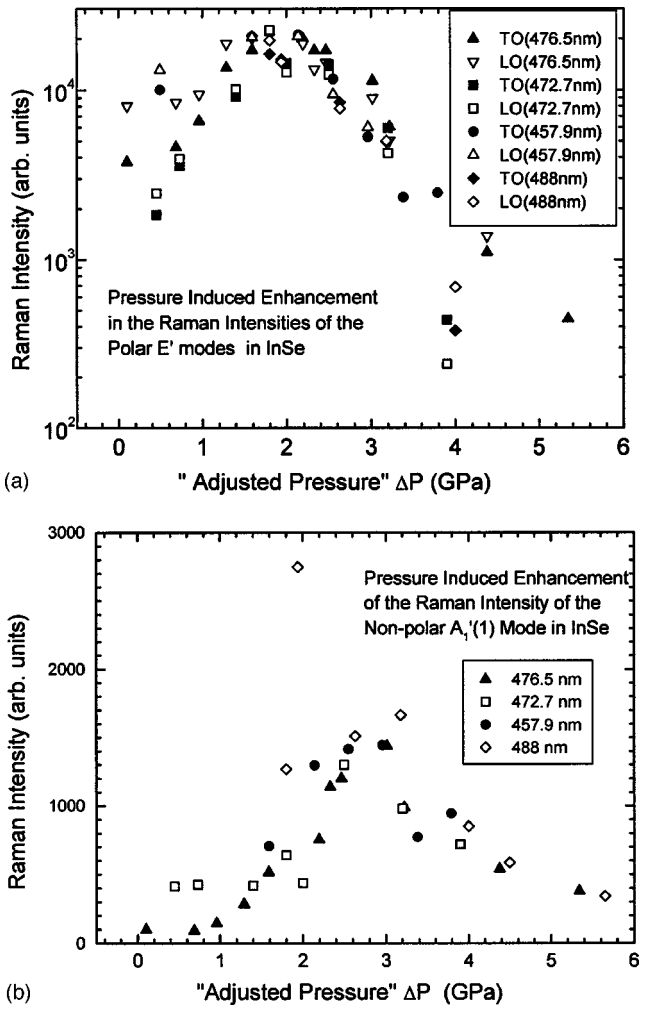

FIG. 5. Plots of the results in Fig. 3 for (a) the polar E'(LO) and (b) the nonpolar A_1' (1) mode by superimposing the results in Fig. 3(a) on those of Figs. 3(b) and 3(c) plus those for laser line at 457.9 nm (2.707 eV) and not shown in Fig. 3. This is achieved for the E'(LO) mode in (a) by (1) translating the curves horizontally by the ''adjusted pressure'' ΔP (which is defined as equal to peak pressure for 2.602 eV laser line *minus* the peak pressure for another laser line) and normalizing the peak heights so that the resultant peaks overlap with those of Fig. 3(a). The translation ΔP was obtained from the E'(LO) mode in (a) was then used without further adjustment in replotting the A_1' (1) mode in (b).

GPa to deduce that the outgoing resonance for this polar mode at atmospheric pressure will occur at an incident photon energy of 2.666 eV. Since this is the incident photon energy for an outgoing resonance, the energy of the M_1 exciton at atmospheric pressure is given by 2.666 eV minus the E'(LO) phonon energy (27 meV). This gives an energy of 2.539 eV for the M_1 exciton energy at $P=0$ GPa and $T=50$ K. As pointed out earlier, the energy of the M_1 exciton at $T=50$ K estimated from the PL peak (dashed curve) in Fig. 4 is ~ 2.534 eV. Thus by utilizing pressure-tuned resonant Raman scattering we have been able to determine the atmospheric pressure M_1 exciton energy, which is in good agreement with the value deduced directly from the temperature-dependent PL spectra. These consistency checks

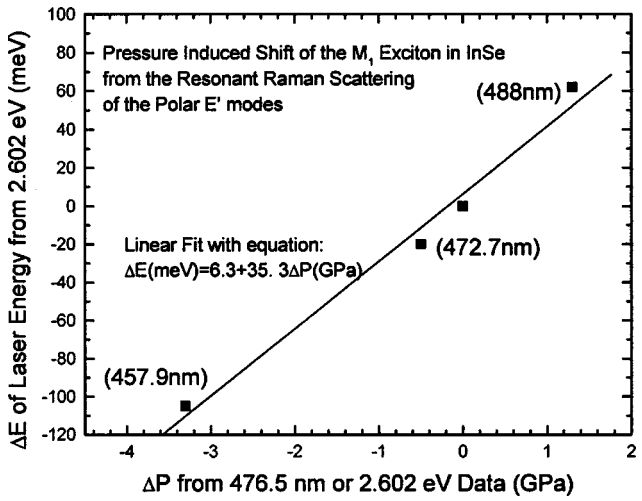

FIG. 6. A plot of the translation ΔP obtained by replotting the E'(LO) curves Figs. 3(b) and 3(c) so that the resultant peaks positions coincide with those measured at the incident photon energy of 2.602 eV (or 476.5 nm) vs the difference in energy ΔE between 2.602 eV and the photon energies of the laser lines used in Figs. 3(b) and 3(c). The plot also includes results for the laser line at 457.9 nm (2.707 eV) but not shown in Fig. 3.

demonstrate the validity of the technique we use to determine the pressure dependence of the M_1 exciton.

In addition to the shift of the resonance peak pressures we found also that the heights of the resonance peaks for the polar E' modes decrease significantly with laser excitation wavelength. This decrease does not occur for the nonpolar modes. Our explanation is that with an increase in laser photon energy the resonance occurs at higher pressures. But at higher pressures the effective charge of the E' modes decreases as discussed in Sec. IV A. As a result the strength of the Fröhlich interaction between the M_1 exciton and the polar optical phonons also decreases.[10] The net effect is that only the height of the resonance peaks for the polar modes decreases with pressure but not for the nonpolar modes. Thus the resonance Raman results are consistent with the decrease in the TO-LO splitting with pressure which is observed only for the polar E' modes as discussed in Sec. IV A.

C. Pressure coefficient of the M_1 exciton in InSe

To our knowledge the pressure coefficient of energy gaps in InSe has not been reported before. However, the pressure coefficients of the lowest-energy direct and indirect band gaps in the isostructural layered-type semiconductors GaS and GaSe have been measured. Besson[7] reported that these pressure coefficients are all *negative* with the direct band gap pressure coefficients ~ -40 meV/GPa and the indirect band gap coefficient ~ -110 meV/GPa. He also pointed out that the pressure coefficients are large in magnitude but negative in value because the band gap is caused by an *interlayer* interaction. On the other hand, he predicted the pressure coefficient to be positive but smaller in magnitude, if the band gap results from an *intralayer* interaction. Recently, Camara *et al.*[6] have performed a tight-binding calculation of the band structure of both GaSe and InSe. They found that the top of

the valence band in these materials is composed mainly of the bonding p orbitals arising from both the cation and anion (with a larger contribution from the p_z component) plus some hybridization with the s orbitals. The dominant interaction between these atomic orbitals is *intralayer* and results from the overlap of the In and Se orbitals. On the other hand, the conduction band edge is derived from several sources: s orbitals from the cation, s^* and p orbitals from both cation and anion. The next higher conduction band is derived mostly from the s^* orbital of the Se atoms. Thus the negative pressure coefficient of the fundamental band gap in GaSe (presumably this is also true for InSe) arises from the fact that the lowest-energy conduction band edge has a large contribution from the interlayer In-In interaction. In case of the M_1 exciton the conduction band is composed essentially of s^* orbitals from the Se atoms. The overlap integrals involving the s^* orbitals in the Se-Se bonds given in Ref. 6 are much smaller than the other overlap integrals and therefore we do not expect the conduction band in the M_1 exciton to be very sensitive to pressure. Thus the small but positive pressure coefficient of the M_1 exciton results mainly from the decrease in energy of the valence band edge with pressure.

V. CONCLUSIONS

We have studied the pressure dependence of the Raman modes in InSe grown by a single-source MOCVD technique. The pressure dependence of the Raman modes decreases with increase in their frequencies. This result is attributed to the fact that motions of the InSe layers relative to each other have lower frequencies but stronger dependence on layer separation. The modes due to stretching of the InSe bond have higher frequencies but smaller pressure dependence. The splitting between the TO and LO modes of E' symmetry was found to decrease with pressure. This result suggests that the Born effective charge in InSe decreases with pressure. By tuning the energy of the hyperbolic M_1 excition energy with pressure we have observed resonance enhancement in both the polar and nonpolar modes. The pressure coefficient of the M_1 excition was determined to be positive and equal to 35.3 meV/GPa. The strength of the enhancement in the polar E' modes was found to decrease rapidly as pressure is increased. This result is explained by the strong suppression of the Born effective charge by pressure. The positive pressure coefficient of the polar optical phonons and the pressure-induced suppression of the Born effective charge in InSe are quite similar to those found in zinc-blende-type semiconductors.

ACKNOWLEDGMENTS

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[1] A. Segura, A. Chevy, J. P. Guesdon, and J. M. Besson, Sol. Energy Mater. **2**, 159 (1980).

[2] In-Hwan Choi and P. Y. Yu, J. Appl. Phys. **93**, 4673 (2003).

[3] J. Rigoult, A. Rimsky, and A. Kuhn, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **36**, 916 (1980).

[4] Mahmoud Zolfaghari, K. P. Jain, H. S. Mavi, M. Balkanski, C. Julien, and A. Chevy, Mater. Sci. Eng., B **38**, 162 (1996).

[5] S. Ashokan, K. P. Jain, M. Balkanski, and C. Julien, Phys. Rev. B **44**, 11 133 (1991).

[6] M. O. D. Camara, A. Mauger, and I. Devos, Phys. Rev. B **65**, 125206 (2002).

[7] J. M. Besson, Nuovo Cimento Soc. Ital. Fis., B **38**, 478 (1977).

[8] See, for example, P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Material Properties*, 3rd ed. (Springer-Verlag, Berlin, 2001), Chap. 6.

[9] See, for example, the review article by B. A. Weinstein and R. Zallen, in *Light Scattering in Solids IV*, Topics in Applied Physics, Vol. 54, edited by M. Cardona and G. Gütherodt (Springer-Verlag, Berlin, 1984).

[10] See, for example, P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors: Physics and Material Properties*, 3rd ed. (Springer-Verlag, Berlin, 2001), Chap. 7.