Intervalley scattering potentials of Ge from direct exciton absorption under pressure

G. H. Li,* A. R. Goñi, K. Syassen, and M. Cardona
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany
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We have measured the dependence on pressure of the low-temperature (10 K) direct exciton optical absorption of Ge up to 12.3 GPa. The sharp exciton peak at the direct energy gap (E_0) of Ge is found to broaden significantly with increasing pressure. This effect, which is attributed to intervalley scattering via electron-phonon interaction, is most pronounced for pressures above ~0.6 GPa, where the X valley becomes the lowest conduction-band minimum. From the pressure-induced exciton broadening we determine the Γ to X point intervalley deformation-potential constant $D_{\Gamma X}$=2.2(3) eV/Å and an upper bound of $D_{\Gamma L}$=4.5 eV/Å for scattering from Γ to the L valleys. The deformation potential $D_{\Gamma X}$ of Ge is about 50% smaller compared to isoelectronic GaAs. This difference is attributed to the fact that interatomic matrix elements between s and d states of the Γ and X conduction-band minima as well as the d character of the X minimum are larger in GaAs.

I. INTRODUCTION

Phonon-assisted scattering processes play an important role in the electron kinetics of semiconductors. In view of the growing interest in Ge-Si alloys and superlattice heterostructures for device applications[1–3] knowledge about the fundamental scattering processes in high purity Ge becomes increasingly important. Of particular interest is the determination of the coupling constants for electron-phonon interaction, which mediates intervalley scattering processes of conduction-band electrons. Electron-phonon coupling also plays a major role for the temperature dependence of semiconductor band gaps[4,5] or the recently observed effects of the isotopic composition of Ge on the first-order phonon Raman line.[6] Information about the rates for phonon-assisted intervalley scattering are commonly obtained from transport measurements or hot-electron luminescence. In the case of Ge, however, these coupling constants are not well known. An alternative and powerful method, as previously demonstrated for GaAs,[7] is the measurement of the exciton absorption profile under pressure. Here, intervalley scattering rates are determined from the change of the exciton linewidth due to the pressure-induced reordering of different conduction-band minima.

Ge is an indirect-band-gap semiconductor with the lowest conduction-band minimum at the L point of the Brillouin zone (BZ) and a band gap energy of 0.74 eV at 10 K. The Γ valley is located only 0.15 eV above the L valleys.[8,9] Despite the fact that Γ-L intervalley scattering exists even at atmospheric pressure, a strong and sharp direct exciton peak can still be observed in the low-temperature absorption spectra.[9] The analysis of electron transport data indicates that the X valleys (the actual minima are along [100], slightly inside the BZ) are about 0.2 eV above the L valleys.[10–12] This value, however, is not accurately known.

The pressure-induced shifts of the relevant conduction-band minima in Ge (relative to the top of the valence band) are different in sign and magnitude (Γ: +0.13 eV/GPa, L: +0.05 eV/GPa, X: −0.01 eV/GPa; see Refs. 10, 13). Therefore, a Γ-X crossover occurs at a relatively low pressure of less than 1 GPa. Pressure tuning of the band structure of Ge is thus expected to result in changes of the direct exciton linewidth, which can be related to the opening of new channels for intervalley scattering processes. Previous measurements of the optical absorption in Ge under pressure were carried out at room temperature,[13–15] where the direct exciton peak in Ge cannot be observed and no information is obtained about the pressure dependence of exciton parameters.

In this work we report optical absorption measurements of the direct exciton in Ge at 10 K in the pressure range up to 12.3 GPa. The sharp exciton peak observed in the absorption spectra near atmospheric pressure is found to broaden significantly above an onset pressure of about 0.6 GPa corresponding to Γ-X crossing. An analysis of the pressure dependence (in the range from 0 to 3 GPa) of the exciton linewidth data in terms of electron-phonon interaction theory[16] yields an accurate value for the Γ-X and an upper bound for the Γ-L intervalley phonon-deformation potential. Since the investigation of intervalley scattering is the primary motivation of this work, we will discuss only briefly the results obtained for the pressure dependence of the E_0 gap, the related spin-orbit split transition, and other exciton parameters like binding energy and absorption strength.

II. EXPERIMENTAL DETAILS

Samples of high-purity Ge were mechanically thinned to thicknesses of 3.5, 6, and 11.5 μm and then cut into pieces of about 100×100 μm^2 in size. Optical absorption measurements were performed at 10 K using a diamond-anvil pressure cell in combination with a specially designed helium-flow cryostat. Condensed helium was used as the pressure-transmitting medium. Pressure was always changed at room temperature in order to ensure the best possible hydrostatic conditions. Pressure was

measured *in situ* using the ruby luminescence method[17] and temperature correction of the ruby calibration according to Ref. 18.

For the absorption measurements white light from a tungsten lamp was focused onto the sample, forming a spot of about 35 μm in diameter. The transmitted light was passed through a 0.6 m single-grating spectrometer and then detected by either a liquid-nitrogen cooled Ge detector (in the wavelength range 0.8–1.7 μm) or a cooled GaAs photomultiplier (0.5–0.86 μm). If necessary, the spectra measured with different detectors were adjusted slightly in order to join smoothly in the overlapping region. The absorption coefficient α was determined according to

$$\alpha(\omega) = (1/d)\ln[I_0(\omega)/I_s(\omega)] - c_0, \quad (1)$$

where I_s is the intensity transmitted through the sample, and I_0 is the reference intensity measured with light passing through the pressure cell next to the sample. The sample thickness d was determined from the interference pattern of light transmitted at photon energies below the direct absorption edge. The constant c_0 was adjusted for every spectrum to yield zero absorption at 0.7 eV (below the fundamental energy gap of Ge).

The pressure range for optical absorption measurements of semiconducting Ge is limited by the structural transition to the metallic β-Sn structure.[19] In a methanol-ethanol pressure medium the phase transition has been observed near 10.5±0.05 GPa (T = 300 K, increasing pressure),[15,20] which is close to the glass transition pressure in the alcohol mixture.[21] In the present experiments it was possible to measure absorption spectra up to a maximum pressure of 12.3 GPa where the semiconducting phase remained stable for several hours but eventually turned opaque. We believe that it is due to the low shear stress in the He pressure medium combined with the low temperature which allowed us to superpress the semiconducting phase well above the equilibrium phase transition pressure, which is estimated to be 8 GPa or less (see below).

III. RESULTS AND DISCUSSION

A. Experimental spectra

Figure 1 shows absorption spectra of the 3.5 μm-thick Ge sample at 10 K measured at different pressures. Similar results were obtained for the 6 and 11.5 μm-thick samples, but the maximum measurable absorption coefficients were limited to about 15 and 8 $\times 10^3$ cm^{-1}, respectively. At zero pressure a sharp absorption edge is observed near the energy of the E_0 band gap of Ge. The steplike structure apparent in the spectra of Fig. 1 at about 0.29 eV above E_0 is attributed to direct optical transitions from the spin-orbit split-off valence band to the conduction band at the Γ point (energy $E_0+\Delta_0$).

With increasing pressure the direct absorption edge and the spin-orbit split transition shift to higher energy. At the same time a slowly increasing tail becomes observable below the E_0 absorption edge. This tail is attributed to indirect absorption associated with transitions between the valence band at the Γ point and the L and X valleys in the conduction band. Absorption spectra were always measured over the full spectral range from 0.7 eV to the high energy limit determined by stray-light effects. Since the slowly increasing tail is similar in all spectra, we show in Fig. 1 only the indirect absorption of the spectrum taken at 12.3 GPa.

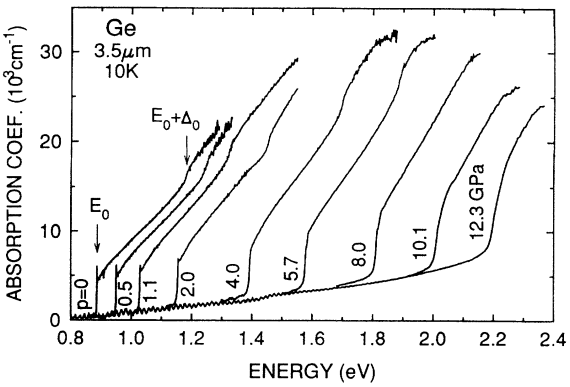

FIG. 1. Low-temperature optical absorption spectra of Ge (sample thickness 3.5 μm) at different pressures.

Figure 2 shows high-resolution spectra for the exciton absorption regime at different pressures. The sharp peak seen in the low pressure spectra is assigned to optical transitions into discrete exciton states. The absorption lines corresponding to different quantum numbers are not resolved, but the observed peak is dominated by the n=1 ground state of the exciton. With increasing pressure the exciton line broadens monotonically. At about 3 GPa the peak feature has almost disappeared and the absorption profile becomes edgelike. These spectral changes are fully reversible for decreasing pressure, provided that the maximum pressure has not exceeded 7 GPa.

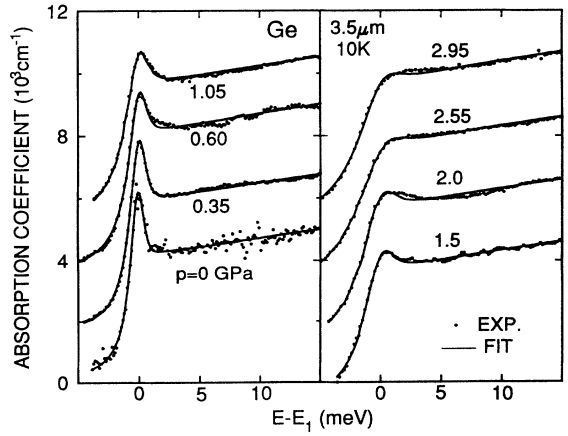

FIG. 2. Variation of the exciton absorption spectrum of Ge with pressure. Spectra are plotted relative to the peak energy E_1 of the exciton. The solid dots are the experimental data and the solid lines correspond to the results of least-squares fits (see text).

B. Exciton absorption model

In order to extract quantitative information about the pressure dependence of exciton parameters we performed a line-shape analysis of the absorption profile based on the three-dimensional exciton absorption model of Elliott.[22] The effects of a finite linewidth have been taken into account by introducing a Lorentzian broadening.[23] The absorption coefficient as a function of incident photon energy $\hbar\omega$ can be written as[7]

$$\alpha(\hbar\omega) = \frac{C_0 R^{1/2}}{\hbar\omega} \sum_{m=1}^{\infty} \frac{2R}{m^3} \frac{\Gamma_c}{(\hbar\omega - E_m)^2 + \Gamma_c^2} + \frac{C_0 R^{1/2}}{\hbar\omega} \int_{E_0}^{\infty} dE \frac{1}{1 - e^{-2\pi z}} \frac{\Gamma_c}{(\hbar\omega - E)^2 + \Gamma_c^2}, \quad (2)$$

with

$$C_0 = \frac{4\pi(2\mu)^{3/2} e^2 \mid M_R \mid^2}{nch^2 m_0^2}, \quad (3)$$

$$z^2 = \frac{R}{E - E_0}, \quad (4)$$

$$R = \frac{\mu e^4}{2\hbar^2 \epsilon^2}. \quad (5)$$

Here R is the effective Rydberg energy of the hydrogenlike exciton, E_0 the direct band gap, $E_m = E_0 - R/m^2$, m=1,2,3... are the energy levels of the bound exciton states (E_1 is the energy position of the ground state), μ is the exciton reduced mass, M_R the matrix element for the electron-photon interaction, Γ_c the half-width of the exciton line, m_0 the free electron mass, c the speed of light, n the low-frequency refractive index, and e the electronic charge. The first and second term in Eq. (2), denoted as α_1 and α_2 (see Fig. 3), represent the contribution of the discrete states and the exciton continuum, respectively. The integral in Eq. (2) has been calculated analytically.[7] Thus Eq. (2) can be evaluated directly.

The experimental spectra near the exciton peaks were fitted by using Eq. (2) with C_0, E_1, R, Γ_c as adjustable parameters. An additional constant term α_0 is introduced to include the contribution of the indirect absorption, i.e., $\alpha = \alpha_1 + \alpha_2 + \alpha_0$. An example of these fits is displayed in Fig. 3 (solid line) showing also the individual contributions α_1, α_2, and α_0 to the absorption profile (dashed lines). Obviously, Eq. (2) gives an excellent description of the exciton absorption spectra near the direct absorption edge.

C. Energies and absorption strength under pressure

In Fig. 4(a) we summarize the results of the pressure dependence of the direct energy gap E_0 and its spin-orbit split companion $E_0+\Delta_0$ for the 3.5 μm sample. The direct gap energy is obtained from fits of Eq. (2) to the exciton absorption spectra according to $E_0 = E_1 + R$. The energy $E_0+\Delta_0$, on the other hand, is taken from the zeros of the second derivative of the absorption coefficient with respect to photon energy.[13] The solid lines in Fig. 4(a) represent the results of least-squares fits to the experimental data for the whole pressure range using a quadratic relation. The corresponding parameters are

$$E_0 = 0.888(2) + 0.137(5)P - 0.0025(4)P^2, \quad (6)$$

$$E_0 + \Delta_0 = 1.179(2) + 0.143(6)P - 0.0031(8)P^2, \quad (7)$$

where pressure P is in GPa and energies in eV. The results are similar for samples with different thicknesses (the linear pressure coefficient determined for the 6 and 11.5 μm samples are 0.139(6) and 0.133(8) eV/GPa, respectively). Both the linear and quadratic pressure coefficients obtained here for E_0 are somewhat larger than the room temperature values (0.121 eV/GPa and −0.002

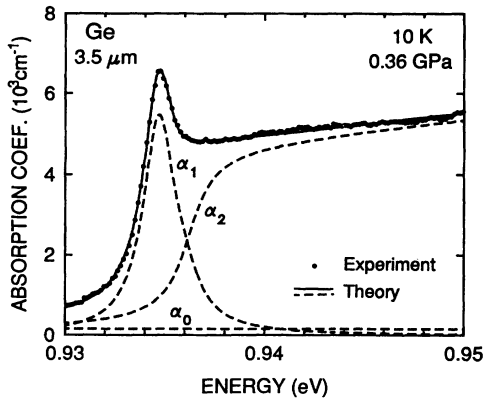

FIG. 3. A fitting example for the direct exciton absorption spectra of Ge at 0.36 GPa. The solid dots are experimental data. The solid line corresponds to the fitted exciton absorption model (see text). The dashed lines represent the contributions of the bound exciton states (α_1), the continuum exciton states (α_2), and the indirect(α_0) absorption, respectively.

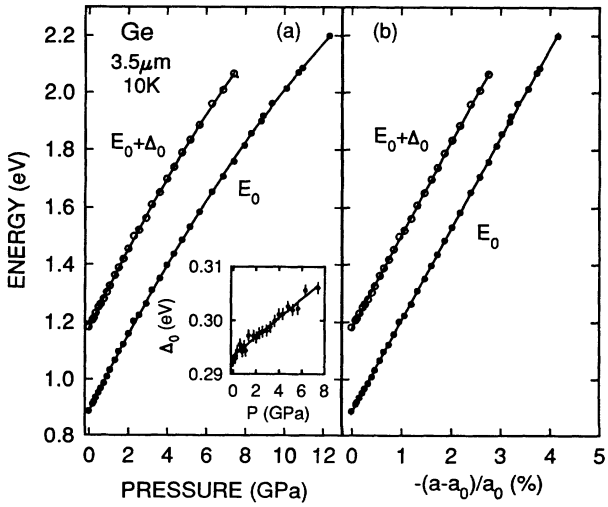

FIG. 4. (a) Pressure dependence of the direct gaps E_0 and $E_0 + \Delta_0$. The inset shows the pressure dependence of the spin-orbit splitting Δ_0. (b) The direct gaps E_0 and $E_0 + \Delta_0$ as a function of the relative variation of the lattice constant.

eV/GPa^2) reported by Goñi *et al.*[13] This difference arises in part from the correlation between linear and quadratic pressure coefficient. We have checked the pressure dependence at room temperature again by measuring absorption spectra of three different samples for pressures up to 8 GPa. The results are found to be consistent with the pressure coefficients from the low-temperature data. Thus within the experimental uncertainty there is no evidence for any temperature dependence of the linear pressure coefficient of the direct band gap in Ge.

The pressure dependences of the E_0 and $E_0+\Delta_0$ gaps show a significant sublinearity. Both gap energies when plotted as a function of the relative variation of lattice constant $\Delta a/a_0$ display an essentially linear dependence as shown in Fig. 4(b). Here, Δa is calculated by using the Murnaghan equation of state

$$P = (B_0/B_0')[(a_0/a(P))^{3B_0'} - 1], \tag{8}$$

with isothermal bulk modulus B_0=74.4 GPa and its pressure derivative B_0'=4.76.[24] A least-squares fit with a linear expression yields

$$E_0(\text{eV}) = 0.883(2) + 32.2(5)(-\Delta a/a_0), \tag{9}$$

$$E_0 + \Delta_0(\text{eV}) = 1.177(2) + 32.5(5)(-\Delta a/a_0). \tag{10}$$

The results of recent theoretical calculations within the local-density approximation (LDA) of the pressure dependence of band gaps in Ge are in good agreement with our data.[25–27] This is consistent with the notion that despite the well-known *gap problem* inherent to LDA (absolute values of semiconductor band gaps are too small within LDA due to incomplete treatment of exchange and correlation) the dependence on pressure or lattice parameter is well accounted for within these theories.

The pressure dependence of the spin-orbit splitting Δ_0 is obtained from the difference of the E_0 and $E_0+\Delta_0$ data measured at the same pressure. The results are shown in the inset of Fig. 4(a). We find that the spin-orbit splitting of Ge increases slowly with increasing pressure according to

$$\Delta_0(\text{eV}) = 0.294(5) + 0.0016(5)P(\text{GPa}). \tag{11}$$

This result, corresponding to $d\ln\Delta_0/d\ln V = -0.40(12)$, agrees quite well with the value of 2 meV/GPa predicted by relativistic band-structure calculations.[27,28] The small volume derivative of the spin-orbit splitting indicates a relative rigidity of the valence charge distribution in the core region due to Pauli's exclusion principle.[13]

From the line-shape analysis of the exciton absorption spectra we also determined the pressure dependence of the exciton binding energy R and the absorption strength parameter C_0. The results are plotted in Fig. 5 as a function of the direct gap E_0. The solid lines in this figure correspond to the relations

$$C_0 \propto E_0^{1.5(1)}, \quad R \propto E_0^{1.0(1)}. \tag{12}$$

According to Eqs. (3) and (5) we should have $C_0 \propto \mu^{3/2}$ and $R \propto \mu$. Within **k·p** theory the exciton reduced mass μ at the Γ point is proportional to the direct gap E_0.[29]

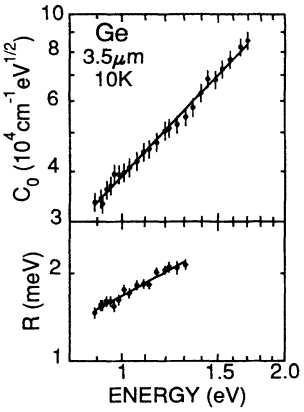

FIG. 5. The exciton binding energy R and the absorption strength parameter C_0 as a function of direct gap energy E_0. The solid lines represent fitted linear relations.

Thus the predictions of **k·p** theory are consistent with the present experimental results.

D. Broadening of the exciton line with pressure

Figure 6 shows the pressure dependence of the half-width of the exciton line for the 3.5 μm-thick Ge sample at 10 K. We distinguish three pressure regions with different behavior of the exciton linewidth. For pressures below ~0.6 GPa the half-width increases only slightly. In this range the pressure dependence of the exciton linewidth is determined by phonon-assisted intervalley scattering from Γ to the lower lying L minimum. There is also a pressure-independent contribution due to inhomogeneous broadening which depends on the quality of the sample. Above 0.6 GPa the X valley becomes the absolute conduction-band minimum, and Γ-X intervalley

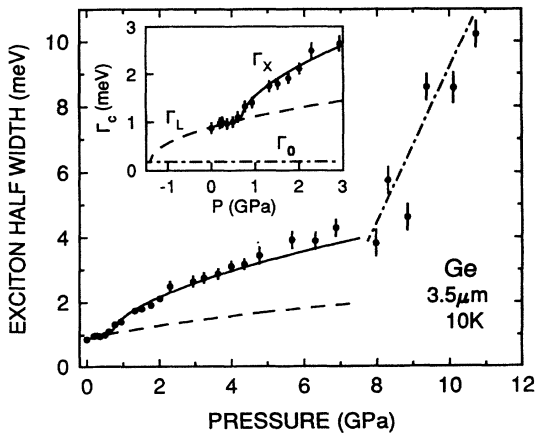

FIG. 6. Pressure dependence of the half-width Γ_c of the direct gap exciton line of Ge. The inset shows details in the 0–3 GPa pressure range. The solid (dashed) line corresponds to the fitted model (see text) including both the Γ-L and Γ-X intervalley scattering (only Γ-L intervalley scattering). The constant Γ_0 accounts for other scattering processes like impurity and defect scattering. The dash-dotted line in the main frame is a guide to the eye.

scattering sets in, giving rise to the strong broadening of the exciton line.

For pressures beyond 8 GPa the half-width rises sharply again. We attribute this behavior to an increase of scattering probability caused by the formation of defects while approaching the structural phase transition in Ge. In fact, the onset of defect-induced broadening of the exciton line indicates that the equilibrium stability range of the tetrahedral phase of Ge extends to a pressure of at most 8 GPa. Thus in the following we will restrict the discussion of the pressure dependence of the exciton linewidth to pressures below 7 GPa.

According to Heisenberg's uncertainty principle, the homogeneous half width of the exciton is related to its lifetime through $2\Gamma_c\tau = \hbar$. In a high-purity material, the electron-phonon interaction is the dominant scattering mechanism affecting the lifetime of the exciton. Ge is an indirect band gap material at atmospheric pressure and the Γ-X crossover takes place at a quite low pressure. Thus the main homogeneous broadening mechanism of the exciton line under pressure corresponds to phonon-assisted intervalley scattering. The half-width of the direct exciton can thus be expressed as

$$\Gamma_c = \frac{\hbar}{2}(P_{\Gamma L} + P_{\Gamma X} + P_0), \tag{13}$$

where $P_{\Gamma L}$ and $P_{\Gamma X}$ are the intervalley scattering probabilities from the Γ valley to the L and X valleys, respectively. P_0 includes additional contributions from inhomogeneous broadening and defect scattering. According to Conwell,[16] the intervalley scattering probability is given by

$$P_{\Gamma i} = \frac{N_i m_i^{3/2} D_{\Gamma i}^2}{\sqrt{2}\,\pi\hbar^2\rho E_q}[(N_q+1)(\Delta E_{\Gamma i} - E_q)^{1/2} + N_q(\Delta E_{\Gamma i} + E_q)^{1/2}] \tag{14}$$

where N_i ($i = L, X$) is the number of equivalent valleys, m_i the corresponding density-of-states effective mass, ρ the material density, E_q and N_q are energy and occupation number of the involved phonons, $\Delta E_{\Gamma i}$ is the energy difference between Γ and $L(X)$ valley, and $D_{\Gamma i}$ the phonon deformation potential constant for Γ-L (Γ-X) intervalley scattering. The first and second term in the square brackets correspond to phonon emission and absorption, respectively. At 10 K, however, only phonon emission processes need to be considered.

By symmetry only zone-edge LA phonons (energy $E_q{}^L$) can participate in Γ-L intervalley scattering processes in Ge.[31,32] On the other hand, the conduction-band minimum along the [100] direction is not exactly at the BZ boundary but somewhat shifted inwards along the Δ_1 line.[33] Therefore, LO phonons along the Δ line in the BZ (energy $E_q{}^X$) are allowed to participate in intervalley scattering from Γ to X.[31,32] In any case, experimentally one is dealing with energy-conserving scattering processes between electron states which are spread over a certain wave vector range around high-symmetry points of the BZ like Γ, X, or L. Therefore, for a comparison with theoretical results one should keep in mind that experimental intervalley scattering potentials are to be regarded as effective values averaged over wave vector regions around conduction valleys, which pick up different contributions from several phonon branches due to relaxation of the symmetry selection rules.

The energy position at ambient pressure of the Γ and L valleys relative to the top of the valence band has been determined accurately from absorption measurements. The low temperature values are 0.889(1) eV (Ref. 8 and this work) and 0.741(1) eV,[30] respectively. An analysis of the pressure dependence of electronic-transport data[10–12] indicates that at zero pressure the X valley is located about 0.18–0.20 eV above the L minimum. This energy is, however, not well known, and we keep it as an adjustable parameter in our analysis of the exciton line broadening. The pressure coefficients of the Γ, L, and X valleys are 0.137 (this work), 0.05,[10] and –0.01 eV/GPa,[10] respectively. We substitute for the energy differences between Γ and L, X in Eq. (13) the expressions $\Delta E_{\Gamma L}(P) = 0.148 + 0.087P$ and $\Delta E_{\Gamma X}(P) = 0.889 - E(X) + 0.147P$, where energy is in eV and pressure in GPa. From inelastic neutron scattering data[34] we have $E_q{}^L = 27.5$ meV and $E_q{}^X = 32.5$ meV. The pressure dependence of phonon frequencies can be neglected.

The half-width of the direct exciton line as a function of pressure can then be written as a sum of three terms:

$$\Gamma_c(P) = \frac{N_L m_L^{3/2} D_{\Gamma L}^2}{2\sqrt{2}\,\pi\rho\hbar E_q{}^L}[\Delta E_{\Gamma L}(P) - E_q{}^L]^{1/2} + \frac{N_X m_X^{3/2} D_{\Gamma X}^2}{2\sqrt{2}\,\pi\rho\hbar E_q^X}[\Delta E_{\Gamma X}(P) - E_q^X]^{1/2} + \Gamma_0. \tag{15}$$

The first and second term correspond to the intervalley scattering from Γ to L and X, respectively. The third term represents pressure-independent contributions from defect scattering and inhomogeneous broadening. The values of the other parameters in Eq. (15) are $N_L = 4$, $N_X = 6$, $m_L = 0.22m_0$, $m_X = 0.48m_0$,[10] and ρ=5.33 g/cm.[33]

The solid curve in Fig. 6 is obtained by fitting Eq. (15) to the measured exciton half-widths in the pressure range of 0–3 GPa. A more detailed representation of the half-width data for these pressures is shown in the inset to Fig. 6. The dashed curves in Fig. 6 represent the contribution of only the Γ-L intervalley scattering and the dashed-dotted line of the inset corresponds to Γ_0.

In evaluating the intervalley scattering deformation potential $D_{\Gamma L}$, only data points for P<0.6 GPa have been considered, i.e., below the Γ-X crossover pressure. Because it is not possible to separate intervalley scattering contributions from that of Γ_0, we can only give an upper bound for $D_{\Gamma L}$ of 4.5(3) eV/Å. This result is in very good agreement with the value of $D_{\Gamma L}$ =4.2(2) eV/Å obtained recently from time-resolved hot electron photoluminescence.[35]

The Γ-X scattering plays the main role in the broadening of the exciton as soon as the X valley becomes

the lowest conduction-band minimum. The intervalley scattering potential $D_{\Gamma X}$ can be determined with a high degree of accuracy from the observed pressure-induced broadening of the direct exciton. From a fit of Eq. (15) to the data points of Fig. 6 and using the measured value of $D_{\Gamma L}$ =4.2(2) eV/Å from Ref. 35 and Γ_0 =0.20 meV we find $D_{\Gamma X}$= 2.2(3) eV/Å and $E(X)$=0.96(2) eV. The same set of parameters also fits the experimental data obtained for the 6 and 11.5 μm-thick samples. We point out that the extrapolated energy position of the X valley at P=0 [0.22(2) eV above the L valley] determined from the exciton broadening is in good agreement with the results of electronic-transport experiments.[10] In our case part of the uncertainty in the determination of $E(X)$ comes from the pressure coefficient of the Γ-X indirect gap, which is not straightforward to obtain from transport experiments under pressure.[10,12]

There are only a few reports on the Γ-L intervalley scattering deformation potential constant in Ge. McLean[36] deduced from the shape of the indirect absorption edge a Γ-L intervalley deformation potential constant of 1.3 eV/Å. However, this author indicated that the calculated half-width of the direct absorption edge using his deformation potential is about a factor of 2 smaller than the observed one.[37] Using a pseudopotential method Herbert *et al.*[38] have calculated a value of 2.1 eV/Å. More recent self-consistent calculations[39] yield a larger value of 3.89 eV/Å, which agrees well with the upper bound reported here and the result deduced from time-resolved experiments.[35]

To our knowledge, experimental results for the $D_{\Gamma X}$ deformation potential of Ge have not been reported before. Krishnamurthy *et al.* have calculated this deformation potential self-consistently by using *ab initio* tight-binding methods.[39] They obtained a value of 2.27 eV/Å, which is in excellent agreement with our experimental results.

There is a striking difference between the intervalley deformation potentials of Ge and isoelectronic GaAs. The value of $D_{\Gamma X}$ determined here for Ge is about half of that measured for GaAs by the same method of pressure-induced exciton line broadening.[7] A similar observation has been recently reported regarding the much longer time constant for Γ-L scattering in Ge compared to GaAs, as deduced from subpicosecond time-resolved Raman spectroscopy.[40] Furthermore, the self-consistent calculations[39] for Ge and GaAs strongly support this result. In Ref. 40 this effect has been ascribed to the lack of Fröhlich interaction in nonpolar Ge. However, the Fröhlich coupling constant C_F depends strongly on the phonon wave vector $\mathbf{q}$ ($C_F \propto q^{-1}$) and thus should play an insignificant role in scattering processes involving phonons at the Brillouin zone edge.

The difference between the intervalley deformation potentials of Ge and GaAs can be easily understood in a tight-binding picture. The deformation potential constant for Γ-X intervalley scattering is proportional to the matrix element $M_{\Gamma X} = |\langle X|\Delta V|\Gamma\rangle|$, where ΔV stands for the change in the potential due to the atomic displacements obtained from the phonon eigenvector. The main contribution arises from the $V_{sd\sigma}$ interatomic potential[41] between the cation s orbital at Γ and the anion d_{3z^2-1} state at the X point. The increase in the cation s component due to the antisymmetric part of the potential in polar GaAs together with the much larger d-character of the wave function at the X-valley result in a strong enhancement of the matrix element of electron-phonon interaction and hence of the intervalley deformation potential of GaAs.

IV. SUMMARY

We have determined from the low-temperature direct optical absorption the pressure dependence of several exciton parameters in Ge. At low temperature the direct band gap energies E_0 and $E_0+\Delta_0$ exhibit a sublinear dependence on pressure, whereas as a function of the relative change in lattice constant this dependence is essentially linear. The spin-orbit splitting Δ_0 of Ge increases with pressure at a rate of 1.6(5) meV/GPa which is consistent with results of relativistic band-structure calculations. We find that the exciton binding energy R and strength of the exciton absorption also increase with pressure. This is explained within $\mathbf{k}\cdot\mathbf{p}$ theory in terms of the increase of the exciton reduced mass μ proportional to the direct gap E_0. The half-width of the exciton broadens significantly at pressures above ~0.6 GPa, a fact which is attributed to phonon-assisted Γ-X intervalley scattering processes. From the exciton line broadening we determine the phonon deformation potential $D_{\Gamma X}$ for Γ-X intervalley scattering. An upper bound is obtained for the deformation potential constants $D_{\Gamma L}$ in Ge.

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*On leave from Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China.

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