Direct-band-gap absorption in germanium under pressure

A. R. Goñi, K. Syassen, and M. Cardona
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, Federal Republic of Germany
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The optical absorption of Ge near the direct band gap E_0 ($\Gamma_{8v}^+ \rightarrow \Gamma_{7c}^-$) has been investigated at pressures up to 9 GPa with use of thin samples of 3 and 11 μm thickness. We find a linear blue shift of the gap energy ($dE_0/dP = 0.121$ eV/GPa) and an indication for a small increase of the corresponding spin-orbit splitting Δ_0 by 2.4 meV/GPa. The pressure dependence of the band gap E_0 predicted by recent *ab initio* band-structure calculations is in good agreement with the present experimental results. The strength of the absorption at the direct edge is found to increase by a factor of 3 in the pressure range from 0 to 9 GPa.

I. INTRODUCTION

The high-pressure behavior of energy-band gaps in tetrahedrally bonded semiconductors is well established through early optical measurements at pressures below 1 GPa (Refs. 1–3) and through more recent studies at higher pressures using diamond-anvil-cell (DAC) techniques (Ref. 3; see also Refs. 4–6 for GaAs and Ref. 7 for other III-V compounds). In general, the experimental results obtained by using various optical methods are in good agreement. A notable exception is the direct band gap E_0 ($\Gamma_{8v} \rightarrow \Gamma_{7c}$) of Ge. The absorption-edge measurements of Welber *et al.*[8] in the range 0–10 GPa yield an initial pressure coefficient which is about 25% larger compared with that obtained from piezoreflectance data below 1 GPa.[9] A similar discrepancy exists between the experimental data of Ref. 8 and theoretical results calculated within *ab initio* band-structure schemes.[10–13] Furthermore, a sublinear dependence of E_0 on lattice parameter has been reported,[8] whereas Rodriguez *et al.*[12] calculate a supralinear dependence. In view of the overall success of recent *ab initio* calculations to predict the pressure dependence of band gaps in semiconductors, the origin of the discrepancy between theoretical results for Ge (Refs. 11–13) and the experimental data[8] from DAC absorption studies needs clarification.

In this paper we report on the pressure dependence of the direct band gaps E_0 and $E_0+\Delta_0$ of Ge (Δ_0 is the valence-band spin-orbit splitting at the Brillouin-zone center) as determined from optical absorption in very thin samples of 3 and 11 μm thickness. With these thin samples it was possible to measure absorption spectra up to energies beyond the $E_0+\Delta_0$ structure. In this respect the present experiments differ from the previous DAC absorption studies[8] of Ge, where thicker samples were used resulting in a lower limit for the maximum detectable absorption level. In the present study, the E_0 and $E_0+\Delta_0$ features remained well defined up to a pressure of 9 GPa, which is close to the phase transition of Ge from the diamond to the β-Sn structure.[14] In addition to the pressure effect on band-gap energies, we have also investigated the magnitude of the absorption coefficient $\alpha(E_0)$ at the direct edge as a function of pressure.

II. EXPERIMENTAL DETAILS

High-purity Ge crystals were mechanically thinned to thicknesses of 3, 11, and 17 μm and then cut to dimensions of about 100×100 μm^2. Samples were loaded into a gasketed DAC using a 4:1 methanol-ethanol pressure medium. The ruby-luminescence method with calibration according to Ref. 15 was used to measure pressure. Absorption measurements were performed with a microoptical setup. White light from a tungsten-halogen source was focused onto the sample, forming a focal spot of about 35 μm diameter. The transmitted light intensity $I(\omega)$ was measured with various combinations of double-grating spectrometers and detectors (PbS cell, Si photodiode, liquid-nitrogen–cooled Ge photodiode, and cooled GaAs photomultiplier) which allowed us to cover the relevant spectral range from 0.6 to 2 eV as well as a wide range of optical densities. The absorption coefficient $\alpha(\omega)$ was determined according to

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

where I_s and I_0 are the intensity transmitted through the sample and the reference intensity measured with light passing through the cell next to the sample, respectively. The sample thickness d was obtained from the interference pattern in transmitted light at photon energies below the absorption edge. Equation (1) neglects reflection losses at sample surfaces, which are of no importance here.

III. RESULTS AND DISCUSSION

Absorption spectra of a 3-μm-thick Ge sample at different pressures above 5.7 GPa are shown in Fig. 1(a). These spectra were recorded with the photomultiplier detector. The low-energy edge in the spectra of Fig. 1(a) corresponds to absorption across the direct band gap E_0 ($\Gamma_{8v}^+ \rightarrow \Gamma_{7c}^-$) which shifts to higher energies with increasing pressure. The second structure in the absorption spectra at about 0.28 eV above E_0 is attributed to the $\Gamma_{7v}^+ \rightarrow \Gamma_{7c}^-$ valence- to conduction-band transition at energy $E_0+\Delta_0$. The energies E_0 and $E_0+\Delta_0$ have been determined by taking the second derivative of the spectra with respect to photon energy, as illustrated in Fig. 1(b) for a spectrum at 6.6 GPa. The gap energies are assigned

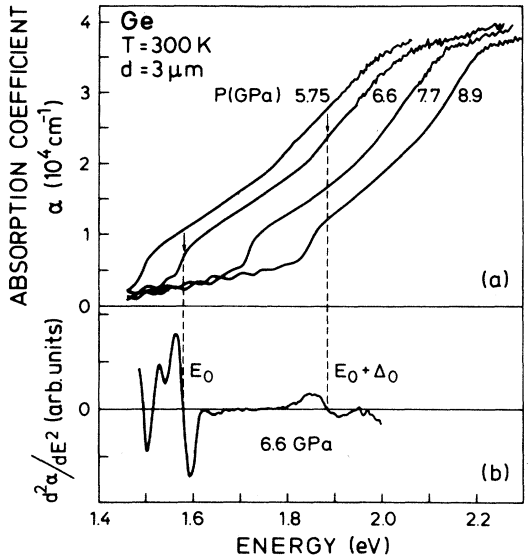

FIG. 1. (a) Absorption spectra of Ge at different pressures ($T=300$ K) for a sample of 3 μm thickness. (b) Second derivative with respect to photon energy of the spectrum at 6.6 GPa. The gap energies indicated by arrows in (a) are taken from the zeros of the derivative spectra in (b).

to the zeros of the second-derivative spectra.

For 3-μm-thick samples the amplitude of the interference pattern in the infrared (ir) spectral range was comparable with the absorption step at E_0, thus introducing uncertainties in the determination of this gap position. Therefore, thicker samples were also used and spectra for 11-μm samples measured with a Ge detector or photomultiplier are shown in Fig. 2. The same horizontal ticks on the absorption curves in Fig. 2 correspond to the gap energies as determined from the derivative spectra for samples of either 3 or 11 μm thickness.

Since absorption measurements have been taken with various spectrometer-detector combinations, the uncorrected optical-density spectra do not usually refer to the same zero-absorption reference level in the transparent region of the samples, i.e., below the indirect-absorption edge of Ge at $\hbar\omega < 0.7$ eV. In order to determine the absolute absorption coefficients given in Figs. 1 and 2 and to relate the measurements in the Ge-detector range ($0.8 < \hbar\omega < 1.25$ eV) to those in the photomultiplier range ($\hbar\omega > 1.4$ eV), we have referred all spectra to a common background attributed to indirect transitions as indicated by the solid line in Fig. 2. This background is obtained from a series of pressure measurements for a sample of 17 μm thickness, using detectors with overlapping spectral ranges (PbS cell for $0.6 < \hbar\omega < 1.35$ eV and Si diode for $\hbar\omega > 1.1$ eV).

Figure 3 shows the E_0 and $E_0+\Delta_0$ gap energies as a function of pressure. The data reveal an essentially linear dependence of the two energy gaps on pressure. The solid lines in Fig. 3 represent the result of least-squares fits to the data. The pressure coefficients so obtained are listed in Table I. We find good agreement with the linear pressure coefficient obtained from piezoreflectance measurements,[9] but our results differ significantly from those of Welber *et al.*[8] A possible reason for this discrepancy

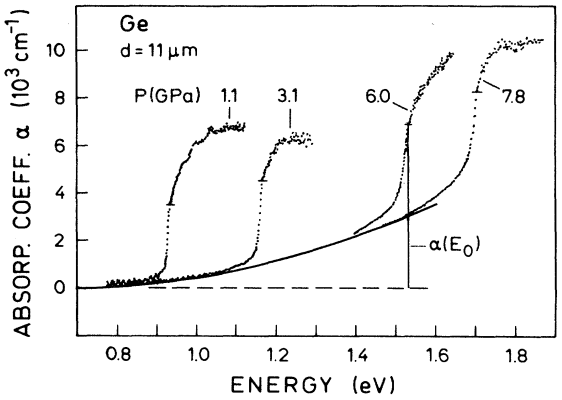

FIG. 2. Absorption spectra of Ge at different pressures for a sample of 11 μm thickness. Horizontal ticks on the absorption curves mark the direct E_0 energy gap at the corresponding pressure. The solid line is the background absorption due to indirect transitions determined from a set of spectra obtained with a thicker sample (see text for details). The quantity $\alpha(E_0)$ refers the absorption coefficient at the E_0 direct-gap energy.

may be that, due to the larger optical density of their samples, they assigned the position of the direct band edge to an absorption level on the raising part of the absorption edge, i.e., to an energy below the optical gap.

The results of recent theoretical calculations of the pressure dependence of E_0 (Refs. 11–13) are in good agreement with the experimental pressure coefficients (see Table I). The dashed line in Fig. 3 represents the calculated E_0-versus-pressure relation of Ref. 12, which predicts a small nonlinearity.

Table I also gives first- and second-order coefficients of the energy-gap–versus–lattice-parameter relation. For the conversion from pressure to lattice parameter we have used a Murnaghan equation of state[16] with isothermal bulk modulus $B_0=74.4$ GPa and its pressure derivative $B'=4.76$ taken from Ref. 17. The gap defor-

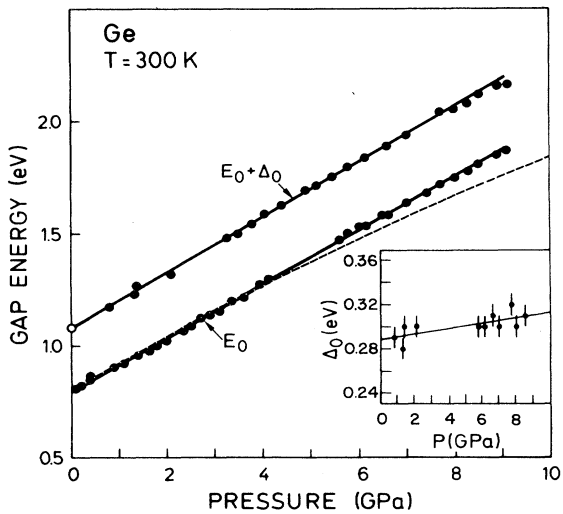

FIG. 3. Direct-absorption edges E_0 and $E_0+\Delta_0$ of Ge as a function of pressure. The solid lines represent the results of least-squares fits to the experimental data using linear functions. The dashed line represents the theoretical result of Ref. 12. The inset shows spin-orbit splitting Δ_0 as a function of pressure.

TABLE I. First- and second-order coefficients describing the dependence of the direct gaps E_0 and $E_0+\Delta_0$ of Ge on pressure $[E(P)=E_{P=0}+bP+cP^2]$ and relative change in lattice parameter $[E(P)=E_{P=0}+b^*(-\Delta a/a_0)+c^*(-\Delta a/a_0)^2]$. Experimental results for GaAs are also listed for comparison.

	$E_{P=0}$ (eV)	b (meV/GPa)	c (meV/GPa^2)	b^* (eV)	c^* (eV)
Ge					
E_0	0.795(7)[a]	121(2)[a]	−0.2(3)[a]	26.7(6)[a]	236(20)[a]
	0.82(1)[b]	153(5)[b]	−4.5(1)[b]	37.5[b]	−52[b]
		125(5)[c]			
		123[d]		27.3[d]	
		124.7[e]	−2.04[e]	27.79[e]	55[e]
		128[f]			
				31.2[g]	−80[g]
$E_0+\Delta_0$	1.08(1)[a]	123(2)[a]		26.8(9)[a]	280(30)[a]
		125[d]		27.9[d]	
GaAs					
E_0	1.43(1)[h]	108(3)[h]	−1.4(2)[h]	26.0(8)[h]	46(20)[h]

[a]Present work.
[b]Reference 8, absorption DAC.
[c]Reference 9 piezoreflectance, uniaxial.
[d]Reference 13, linear muffin-tin orbitals (LMTO) calculation.
[e]Reference 12, pseudopotential calculation.
[f]Reference 11, pseudopotential calculation.
[g]Reference 10, LMTO calculation.
[h]Reference 16, absorption DAC.

mation potential for the gap E_0 is $dE_0/d\ln V = -9.0(3)$ eV. For the dependence of experimental gap energies on relative change in lattice parameter $(-\Delta a/a_0)$, we find a positive second-order coefficient c^* (See Table I) in qualitative agreement with the prediction of Ref. 12.

GaAs is isoelectronic to Ge, and has almost the same zero-pressure lattice parameter and pressure-volume relation[4,17] as Ge, but the gap E_0 of GaAs is less pressure dependent compared to Ge (see Refs. 4–6 and Table I). A qualitative explanation for this difference may be given in terms of the Phillips–Van Vechten theory,[2,18] where energy gaps in covalent materials are written in terms of a covalent or homopolar (E_h) and an ionic (C) component:

$$E_{\text{gap}}=E_h(1+C^2/E_h^2)^{1/2} . \quad (2)$$

Effects arising from filled d shells are neglected in Eq. (2). The quantity E_h represents the energy separation between states with different bonding and antibonding character and therefore depends strongly on a change in bond length. GaAs is supposed to have the same covalent contribution E_h to the E_0 gap as Ge. For Ge we have $C=0$, while $C=2.9$ eV for GaAs represents the Coulomb interaction of charge distributions centered around Ga and As atoms. The quantity C is hardly affected by volume changes. Consequently, the E_0 gap of GaAs should be less pressure dependent compared to Ge, as is experimentally observed.

The extrapolation of the fitted lines in Fig. 3 to ambient pressure gives a spin-orbit splitting of the valence band of Ge of $\Delta_0=0.289(5)$ eV, in agreement with values reported in the literature.[3] The inset in Fig. 3 shows data for the spin-orbit splitting Δ_0 as a function of pressure. We show only those data points where the energies E_0 and $E_0+\Delta_0$ were available from the same absorption spectrum. The solid line represents the result of a fit and corresponds to a linear pressure coefficient of

$$d\Delta_0/dP=2.4(1.5)\ \text{meV/GPa} .$$

Thus, we find a small increase of Δ_0 with pressure, but the experimental uncertainty is quite large. In first-order perturbation theory, the spin-orbit splitting is proportional to the momentum operator $\mathcal{P}\sim V^{-1/3}$ and to the valence charge density ρ_c in the core region.[19] One expects that ρ_c is not simply inversely proportional to volume, because the exclusion principle acts against an increase of ρ_c. The pressure coefficient of the spin-orbit splitting Δ_0 given above corresponds to a volume scaling parameter $d\ln\Delta_0/d\ln V=-0.7(4)$, which is roughly consistent with the expected behavior. For comparison, relativistic band-structure calculations[13,19] predict $d\ln\Delta_0/d\ln V=-0.59$ and -0.6, respectively. We note that a small pressure coefficient of Δ_0 implies a weak pressure dependence of the ionic contribution C in a polar material like GaAs.

Electronic transitions to excitonic states are responsible for the step in the absorption edge at E_0. According to Elliott,[20] the absorption coefficient at a direct excitonic edge is given by (in atomic units)

$$\alpha_{\text{dir}}=2.72\pi E_0/3c\mathcal{P}^3\epsilon^{3/2} , \quad (3)$$

where c is the speed of light, $\mathcal{P}$ the interband momentum matrix element ($\mathcal{P}\sim 2\pi/a$, a is the lattice parameter), and ϵ is the static dielectric constant. Figure 4 shows $\alpha(E_0)$ as a function of gap energy E_0. Within the pressure

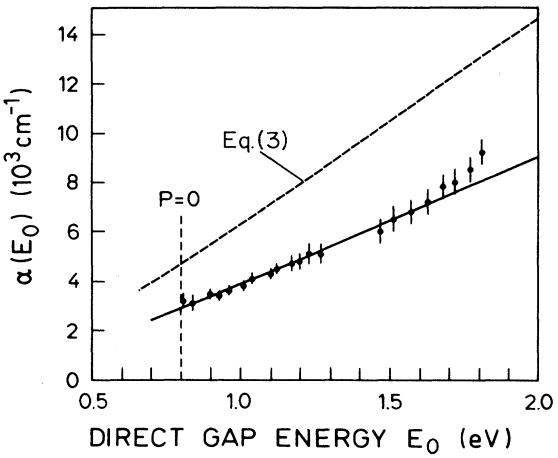

FIG. 4. Absorption coefficient $\alpha(E_0)$ at the E_0 direct-absorption edge of Ge as a function of E_0 band gap. The theoretical curve (dashed line) results from the direct evaluation of Eq. (3), while the solid line represents the scaling of Eq. (3) by a factor fitting the experiment at ambient pressure.

range up to 9 GPa, $\alpha(E_0)$ increases monotonically by a factor of 3. The dotted line in Fig. 4 results from the direct evaluation of Eq. (3) for Ge, with $d\epsilon/dP = -0.36$ GPa^{-1} taken from Ref. 21. The significant difference between theoretical estimate and experimental data is not unexpected because simplifying assumptions (e.g., effective-mass approximation and the value taken for $\mathcal{P}$) enter into the derivation of Eq. (3). The solid line in Fig. 4 is obtained by scaling Eq. (3) by a constant factor in order to match the experimental value at ambient pressure which is $\alpha(E_0)=3.1(3)\times 10^3$ cm^{-1}, in close agreement with results given elsewhere.[3] The scaled $\alpha_{\text{dir}}(E_0)$ fits the experimental data rather well. This does not mean, however, that the increase of $\alpha(E_0)$ with increasing E_0 is entirely due to excitonic effects in the direct-absorption process. At pressures above ~ 5 GPa indirect absorption below E_0 becomes quite strong compared to the total absorption at E_0 (see Fig. 2). Thus, a significant part of the absorption at E_0 may be due to indirect transitions. A separation of $\alpha(E_0)$ into a direct and indirect contribution is not a straightforward procedure, because possible resonance effects in the indirect-absorption process have to be taken into account when the photon energy approaches the direct gap.

We summarize the results of optical-absorption measurements of Ge under pressure as follows. (1) The direct-gap energies E_0 and $E_0+\Delta_0$ of Ge obtained from absorption measurements show an essentially linear dependence on hydrostatic pressure. This corresponds to a pronounced supralinearity of the energy-gap–versus–lattice-parameter relation. (2) Linear pressure coefficients calculated recently with *ab initio* band-structure methods[11–13] agree to within 3% with present experimental results. (3) We find a stronger dependence on pressure of the direct gap in Ge compared to isoelectronic GaAs in agreement with the semiquantitative prediction of the Phillips–Van Vechten dielectric theory. (4) Within experimental uncertainty, the magnitude of the change in spin-orbit splitting Δ_0 of Ge under pressure is consistent with theoretical predictions.[13,19] (5) The optical-absorption coefficient $\alpha(E_0)$ at the direct-absorption edge in Ge is found to increase with increasing energy gap E_0. This behavior is in part attributed to excitonic effects. In addition, indirect (phonon-assisted) processes are expected to contribute to the increase of $\alpha(E_0)$.

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