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Resonant indirect optical absorption in germanium

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The optical absorption coefficient of pure Ge has been determined from high-accuracy, high-precision optical measurements at photon energies covering the spectral range between the indirect and direct gaps. The results are compared with a theoretical model that fully accounts for the resonant nature of the energy denominators that appear in perturbation-theory expansions of the absorption coefficient. The model generalizes the classic Elliott approach to indirect excitons, and leads to a predicted optical absorption that is in excellent agreement with the experimental values using just a single adjustable parameter: the average deformation potential $D_{\Gamma L}$ coupling electrons at the bottom of the direct and indirect valleys in the conduction band. Remarkably, the fitted value, $D_{\Gamma L} = 4.3 \times 10^8$ eV/cm, is in nearly perfect agreement with independent measurements and *ab initio* predictions of this parameter, confirming the validity of the proposed theory, which has general applicability.

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The distinction between direct-gap and indirect-gap band structures is a central concept in semiconductor physics [1]. A simple operational definition is based on the energy dependence of the optical absorption coefficient α . If α^2 is linear in energy near the absorption edge, the band gap is presumed to be direct, whereas a linear dependence of $\sqrt{\alpha}$ is considered the signature of an indirect gap. These predictions are justified theoretically under a number of common assumptions, including parabolic dispersions, constant matrix elements, neglect of excitonic effects, and neglect of factors that depend weakly on energy at the band edge [1,2]. While these assumptions are common to both direct and indirect absorption, in the latter case an additional approximation is made to deal with the second-order nature of the absorption process, which involves the electron-phonon coupling. When α is calculated using Fermi's golden rule to second order, it contains an energy denominator $\hbar\omega - E_m$, which is the difference between the incident photon energy and the intermediate-state energy. This denominator is often replaced by a constant $\hbar\omega - E_0$, where E_0 is the direct-gap energy, leading directly to the above-mentioned $\sqrt{\alpha}$ rule. However, as illustrated in Fig. 1, α is actually an integral over many possible transitions with changing values of E_m . If the changes in E_m are small compared to the average value of $\hbar\omega - E_m$, the constant-denominator assumption is a good one. This is the case in silicon [3], for which $E_m \sim 3.5$ eV and $\hbar\omega \sim 1.2$ eV, but it is a bad approximation for Ge because $E_m \sim 0.8$ eV and $\hbar\omega \sim 0.7$ eV. This important difference was first noted by Hartman [4], who showed that the integrals containing changing denominators could still be carried out analytically. Surprisingly, however, the Hartman solution does not appear to have ever been validated using published experimental data for Ge [5–7], and in fact these data are not entirely adequate for such validation, because they either do not cover the entire range between the indirect gap E_{ind} and E_0 , or assume a dispersionless reflectivity, or both. The Hartman formalism has been applied to III-V semiconductors [8], in some cases under hydrostatic pressure [9–11], but these have more complicated band structures in which several bands contribute to the absorption. This makes it extremely difficult to address an

additional consequence of the varying energy denominators: the possibility that they may affect excitonic enhancements. The basic theory of excitonic effects was formulated in a classic paper by Elliott [12], who treated indirect transitions within the constant-denominator approximation. Two key conclusions are that excitonic effects on the intermediate states can be neglected, and that the enhancement depends only on the value of the final-state excitonic wave function $F_{\lambda K}(\mathbf{r})$ at $\mathbf{r} = 0$. These conclusions, however, break down when the energy denominators are treated exactly. Recent work on the direct-gap absorption in Ge at room temperature has shown that good agreement between theory and experiment requires consideration of excitonic enhancements [13,14]. Since these enhancements are large (>2), one is led to the conclusion that any accurate theory of indirect absorption should go beyond the constant denominator approximation when including excitonic corrections.

In this Rapid Communication, we present determinations of α in Ge based on high-accuracy, high-precision optical measurements covering the entire range between E_{ind} and E_0 . The results are compared with expressions that generalize the Elliott exciton theory for the case of nonconstant denominators, and contain a deformation potential constant $D_{\Gamma L}$ as the only adjustable parameter. Excellent agreement with experiment is obtained using values of $D_{\Gamma L}$ that are identical, within experimental error, to values determined independently and validated by *ab initio* calculations. Thus the experimental results can essentially be modeled within this theoretical approach without any adjustable parameter.

High-accuracy optical measurements were performed on 170- μm -thick, double-side polished (roughness <1 nm rms) epi-ready undoped Ge substrates from UMICORE [15]. For each sample, the transmittance \mathcal{T} was measured at normal incidence with a PerkinElmer Lambda 1050 spectrophotometer, and the reflectance \mathcal{R} was obtained at near-normal incidence ($8.0^\circ \pm 0.25^\circ$) with a Lambda 900 spectrophotometer equipped with a VW directional reflectance accessory (PE L6310200). The measurements were carried out at an average temperature of 301 K, as recorded using a calibrated digital thermometer (Fluke model 1529-R; uncertainty is $\pm 0.0025^\circ\text{C}$ at 25°C)

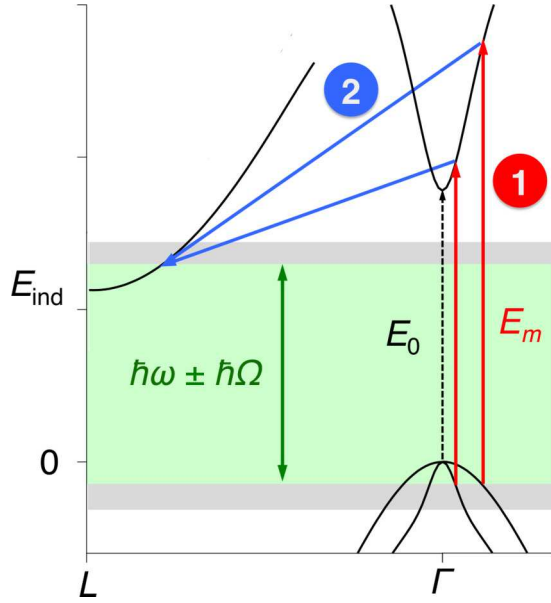


FIG. 1. Schematic illustration (energies not to scale) of the most resonant indirect absorption process in germanium. A virtual electron-hole pair is vertically excited across the direct gap near the Γ point of the Brillouin zone. The minimum direct-gap value E_0 at Γ is indicated with a dashed black arrow. The electron is transferred to the L -point valley at the fundamental indirect gap E_{ind} (blue arrows). For a given photon energy $\hbar\omega$, the absorption coefficient is obtained from a sum of transitions that satisfy energy and crystal momentum conservation, including the created or annihilated phonon of energy $\hbar\Omega$. The contributing transitions can be visualized as those that result from sliding the green band up and down within the limits of the gray band. As the green band slides, it selects intermediate states E_m with different energies.

mounted inside the sample compartment. The regular transmittance measurements are traceable to the well-characterized NRC Reference Spectrophotometer [16] and the accuracy of the absolute VW (Strong method) specular reflectance measurements was validated by comparison with a high-reflectance dielectric laser mirror optimized for 2037 nm. The absorption coefficient was extracted from the data by solving the pair of equations

$$z = \frac{\mathcal{A} - 1 + R}{\mathcal{A}R - 1 + R} \quad (2 - \mathcal{R})z^2 R^2 - (1 + z^2)R + \mathcal{R} = 0, \quad (1)$$

where $\mathcal{A} = 1 - \mathcal{R} - \mathcal{T}$, R is the (in principle unknown) reflectance at a single sample-air interface, and $z = \exp(-\alpha d)$, where d is the sample thickness. This system is best solved iteratively, starting with $R = \mathcal{R}$. Full convergence is typically achieved with only two iterations. Results for three different samples are virtually identical. Figure 2 shows the absorption coefficient for one of these samples.

The most resonant contribution to α corresponds to the process illustrated schematically in Fig. 1, involving the conduction band near the Γ point of the Brillouin zone (BZ) as an intermediate electron state, and the absolute minimum of the conduction band near the zone-edge L point as the final electron state. For this process, group theory shows that only

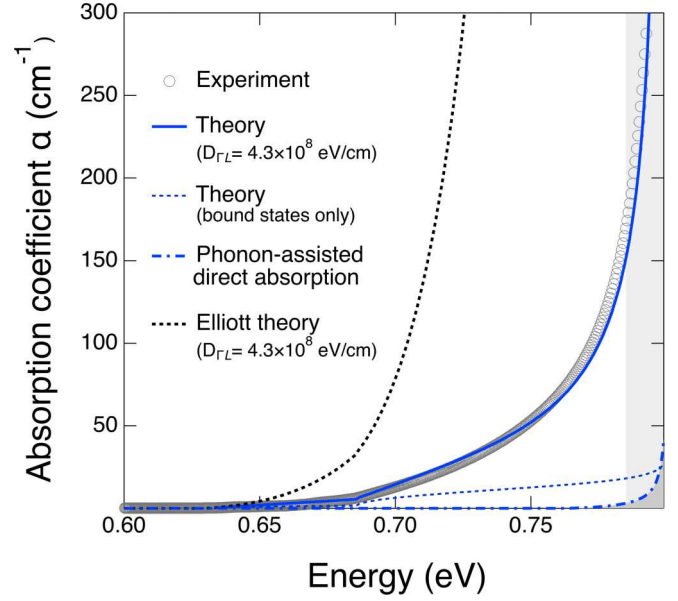


FIG. 2. Experimental room-temperature absorption coefficient of Ge compared with a calculation using the theory described in this paper (solid blue line). The kink at 685 meV in the theoretical curve represents the onset of phonon emission. The blue dotted line shows the partial contribution from the excitonic bound states, and the blue dashed-dotted line is the contribution from phonon-assisted direct transitions. The black-dotted line is a calculation using the standard Elliott theory.

zone-edge longitudinal acoustic (LA) phonons contribute to the absorption [17], and the results of Hartman can be written as $\alpha_{\text{free}} = \alpha_+ + \alpha_-$, with

$$\alpha_{\pm} = \frac{4e^2}{3\hbar^3 \pi c m} \left(\frac{1}{\hbar\omega} \right) \left(\frac{P^2}{m} \right) \left(\frac{1}{\rho n_{\text{op}}} \right) \times \left(\frac{D_{\Gamma L}^2}{\hbar\Omega} \right) \left(n_{\Omega} + \frac{1}{2} \pm \frac{1}{2} \right) (m_{\perp}^2 m_{\parallel})^{1/2} \sum_h f_h^{\pm}(\hbar\omega). \quad (2)$$

Here e , m , \hbar , and c are fundamental constants following the standard notation, $P^2/m = 12.61$ eV is the valence/conduction momentum matrix element at the Γ point of the BZ, which we obtain by fitting the experimental Γ -point conduction band effective mass m_c [18,19], $\rho = 5.323$ g/cm³ is the material's density, $n_{\text{op}} = 4.13$ is the index of refraction at the indirect gap, $\hbar\Omega = 0.027$ eV is the LA phonon energy [20], n_{Ω} is the Bose-Einstein occupation number, $m_{\parallel} = 1.58 m$ is the longitudinal electron mass at the L minimum, and $m_{\perp} = 0.078 m$ is the corresponding transverse mass [21–23]. Equation (2) is based on the standard assumptions of constant phonon energy and deformation potential, so these quantities should be viewed as averages. The functions $f_h^{\pm}(\hbar\omega)$ are given by

$$f_h^{\pm}(\hbar\omega) = \frac{m_h^{3/2}}{(1 + \beta_h)^2} \left\{ \frac{2 + \eta_h^{\pm}}{\sqrt{1 + \eta_h^{\pm}}} - 2 \right\}; \quad \eta_h^{\pm} = \frac{(1 + \beta_h)(\hbar\omega - E_{\text{ind}} \mp \hbar\Omega)}{(E_0 - \hbar\omega)}, \quad (3)$$

with $\beta_h = m_h/m_c$, and $m_c = 0.0338 m$ is computed from $k \cdot p$ theory using the above value of P and room-temperature band gaps. The summation in Eq. (2) is over $h = lh$ and $h = hh$, which correspond to the light- and heavy-hole bands, respectively. Since the model does not include nonparabolicity or warping, we use the averages $m_{hh} = 0.375m$ and $m_{lh} = 0.0385m$, which give the best fit of the valence-band density of states using the model of Ref. [24]. In the limit $\eta_h^\pm \rightarrow 0$ one can expand the square root in Eq. (3) and the expression becomes $f_h^\pm(\hbar\omega) = \frac{1}{4}m_h^{3/2}(\hbar\omega - E_{\text{ind}} \mp \hbar\Omega)^2/(E_0 - \hbar\omega)^2$, which leads to the standard textbook expression for indirect absorption [1,2]. This limit can be reached for $\beta_h \rightarrow -1$ (parallel conduction and valence bands near Γ) or, more realistically, when $\hbar\omega \sim E_{\text{ind}} \ll E_0$, which, as indicated above, is never a good approximation for Ge. Equation (3) diverges as $(E_0 - \hbar\omega)^{-1/2}$, whereas in the constant denominator limit one obtains a stronger divergence $(E_0 - \hbar\omega)^{-2}$. This is understandable, since the dispersion of the intermediate-state energies captured by the more realistic calculation should partially smear out the resonant enhancement.

For a comparison with experiment we must incorporate excitonic effects, which we do by expressing α as

$$\alpha(\hbar\omega) = \alpha_{\text{bound}}(\hbar\omega) + S(\hbar\omega)\alpha_{\text{free}}(\hbar\omega), \quad (4)$$

where α_{bound} represents the contribution from the bound indirect excitons and S is the excitonic enhancement arising from the continuum solutions. A rigorous treatment of indirect excitons is a formidable problem due to the degeneracy of light and heavy holes near the top of the valence band (Fig. 1) and the strong mass anisotropy of the conduction-band minimum. However, Lipari and Baldereschi [25] and Altarelli and Lipari [26,27] have shown that the excitonic Hamiltonian can be split into an s -like hydrogenic term and d -like perturbations. Since the exciton binding energy is reproduced very well by the hydrogenic term alone, we only consider this term in our calculations. This is a poor approximation if one is interested in describing the low-temperature fine structure at the onset of absorption [17,26], but we expect it to be accurate in the continuum region that is the focus of our work. We note, however, that the electron and hole effective masses in the s -like Hamiltonian are given by [25–27]

$$m_{e,\text{eff}} = \frac{3m_\perp m_\parallel}{2m_\parallel + m_\perp}; \quad m_{h,\text{eff}} = \frac{2m_{hh}m_{lh}}{m_{hh} + m_{lh}}, \quad (5)$$

and therefore the excitonic expressions *do not* approach α_{free} in the limit of vanishing electron-hole Coulomb interaction. We circumvent this problem by computing $S(\hbar\omega)$ as the ratio between our excitonic continuum calculation and α_{free} from Eq. (2) calculated using the Eq. (5) masses. For the bound component, we find that $\alpha_{\text{bound}} \propto (m_{e,\text{eff}}m_{h,\text{eff}})^{3/2}$, so that the correction factor is $[(m_\perp^2 m_\parallel m_{lh}^3)^{1/2} + (m_\perp^2 m_\parallel m_{hh}^3)^{1/2}]/(m_{e,\text{eff}}m_{h,\text{eff}})^{3/2}$.

The excitonic absorption coefficient is calculated as $\alpha_{\text{ex}} = R_{i \rightarrow f} n_{\text{op}}/c$, where $R_{i \rightarrow f}$ is the transition rate obtained from Fermi's golden rule. Since we allow for excitons not only in the final- but also in the intermediate states, we rewrite the perturbation expression in terms of the intermediate-state excitonic Green functions, and after some manipulations we

arrive at the expression

$$R_{i \rightarrow f}^\pm = \frac{4\pi}{\hbar} \left(n_\Omega + \frac{1}{2} \pm \frac{1}{2} \right) V |M|^2 |A|^2 \times \sum_{\mathbf{K}\lambda} \left| \int d\mathbf{r} F_{\lambda\mathbf{K}}^*(\mathbf{r}) e^{-is_h(\mathbf{K}+\mathbf{k}_L)\mathbf{r}} G_{\hbar\omega}(\mathbf{r}, 0) \right|^2 \times \delta(E_{\lambda,\mathbf{K}} \pm \hbar\Omega - \hbar\omega). \quad (6)$$

Here, V is the sample volume, $|M|^2$ and $|A|^2$ are the squares of the moduli of the electron-phonon and electron-radiation matrix elements, $s_h = m_{h,\text{eff}}/(m_{e,\text{eff}} + m_{h,\text{eff}})$, and \mathbf{k}_L is the electron wave vector at the conduction-band minimum. The excitonic wave functions $F_{\lambda\mathbf{K}}(\mathbf{r})$ with eigenenergies $E_{\lambda,\mathbf{K}}$ satisfy a hydrogenlike Schrödinger equation. The index λ represents the quantum numbers for the relative electron-hole motion, and \mathbf{K} is the wave vector for the center-of-mass motion. The Green function for the intermediate states is given by [28–30]

$$G_{\hbar\omega}(\mathbf{r}, 0) = \left(\frac{1}{2E_{B\Gamma}} \right) \left(\frac{1}{a_0^3} \right) \Gamma(1 - \kappa) \left(\frac{1}{\pi\kappa\rho} \right) W_{\kappa,1/2}(\rho), \quad (7)$$

where $E_{B\Gamma}$ is excitonic binding energy at the Γ point of the Brillouin zone, a_0 is the Bohr radius for this exciton, $\Gamma(z)$ is the Gamma function, and $W_{\kappa,1/2}$ is a Whittaker function of the first kind, with $\rho = 2r/(\kappa a_0)$, and $\kappa = [E_{B\Gamma}/(E_0 - \hbar\omega)]^{1/2}$. In the constant denominator limit we obtain

$$\lim_{E_0/\hbar\omega \rightarrow \infty} G_{\hbar\omega}(\mathbf{r}, 0) = \frac{\delta(\mathbf{r})}{E_0 - \hbar\omega}, \quad (8)$$

and inserting this back into Eq. (6) we recover Elliott's expression for α , in which the excitonic enhancement is proportional to $|F_{\lambda\mathbf{K}}(0)|^2$ [12]. Notice that Eq. (8) is *independent* of the excitonic parameters at the Γ point. This means that in this limit the absorption is not affected by the excitonic character of the intermediate states, which can be easily shown to be a consequence of the completeness of the excitonic wave-functions set.

The calculation of Eq. (6) proceeds numerically. Since Eq. (8) is not a good approximation for Ge, states with angular momentum $l \neq 0$ can in principle contribute. However, the weight of each bound state is proportional to n^{-3} , where n is the principal quantum number, so that the $1s$ state will still represent the dominant contribution. Furthermore, it turns out that the overall bound-state contribution is a small fraction of the continuum contribution, so we neglect $l \neq 0$ states. For the continuum states the index λ becomes a wave vector \mathbf{k} , and the wave function can be chosen as [31]

$$F_{\mathbf{k}\mathbf{K}}(\mathbf{r}) = \frac{1}{\sqrt{V}} \Gamma(1 + i\nu) e^{\pi\nu/2} e^{i\mathbf{k}\cdot\mathbf{r}} \times {}_1F_1(-i\nu, 1, -i\mathbf{k}\mathbf{r} - i\mathbf{k} \cdot \mathbf{r}), \quad (9)$$

with $\nu = \sqrt{E_{BL}/\varepsilon}$, $\varepsilon = \hbar^2 k^2/(2\mu)$, and $\mu^{-1} = m_{e,\text{eff}}^{-1} + m_{h,\text{eff}}^{-1}$. Here, E_{BL} is the binding energy of the indirect exciton and ${}_1F_1(a, b, z)$ is the Kummer confluent hypergeometric function. For $E_{BL} \rightarrow 0$, we obtain $F_{\mathbf{k}\mathbf{K}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}/\sqrt{V}$, as expected. The sums over \mathbf{k} and \mathbf{K} are converted to integrals over the density of states, and one of those integrals is eliminated by the delta

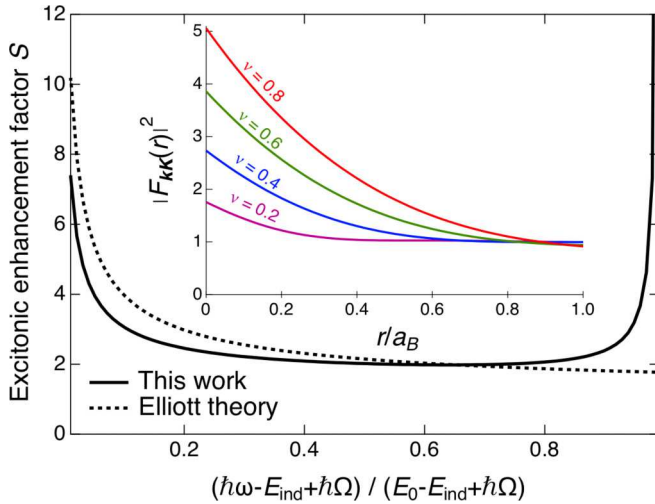


FIG. 3. Excitonic enhancement of the indirect absorption for the phonon-annihilation component. The phonon-creation part has a similar dependence. The solid line is the present calculation and the dotted line corresponds to Elliott’s theory. As the direct gap is approached, our theory predicts an enhancement due to the excitonic nature of the intermediate states, whereas Elliott’s enhancement does not depend on the excitonic character of these states. Near the indirect gap, Elliott’s enhancement is larger because it is proportional to $|F_{kK}(0)|^2$ and the excitonic function has a maximum precisely at $r = 0$, as seen in the inset, which shows the angular average of the wave function. By contrast, Eq. (6) averages over nonzero r values, and therefore the excitonic enhancement is reduced.

function. However, since the relative angles of \mathbf{r} , \mathbf{K} , and \mathbf{k} are arbitrary, Eq. (6) is effectively a four-dimensional integral over three spatial and one energy coordinate, which makes the calculation very time-consuming and impractical for fitting experimental data. A dramatic speedup in the calculation results from taking ${}_1F_1(-iv, 1, -ikr - i\mathbf{k} \cdot \mathbf{r}) \simeq {}_1F_1(-iv, 1, -ikr)$. This is consistent with the “sphericalization” of the excitonic problem. We have verified that the approximated form of the wave function is in excellent agreement with the angular average of the exact wave function, and that the normalization condition is unaffected by the approximation. Under these assumptions the integral over \mathbf{r} in Eq. (6) acquires cylindrical symmetry, and the overall calculation is reduced to a three-dimensional integral that can be easily carried out on a personal computer.

The calculated excitonic enhancement is shown in Fig. 3 and compared with the enhancement obtained using Elliott’s theory. At the onset of absorption near E_{ind} our theory predicts a smaller enhancement. This can be understood by examining the wave function in Eq. (9). In Elliott’s theory, Eq. (8) causes the excitonic enhancement to be proportional to $|F_{kK}(0)|^2$. As shown in the inset of Fig. 3, the square of the wave function has a maximum precisely at $r = 0$, and therefore the enhancement will be less in our calculation because our expression averages over values $r > 0$. On the other hand, as E_0 is approached the excitonic character of the intermediate states causes an increase in the indirect absorption, but this increase is not captured by the Elliott model, which is insensitive to the nature of the wave functions at the Γ point.

The final calculated absorption using Eq. (4) is shown as a solid line in Fig. 2. As the direct gap E_0 is approached, an additional contribution arises from optical-phonon assisted direct transitions. We have calculated this absorption using a similar formalism and $d_0 = 41$ eV for the optical-phonon deformation potential [32,33]. The contribution from this process is small, as seen in Fig. 2, but it has been added to the indirect-gap absorption for completeness. The best fit of the experimental data is obtained using $D_{\Gamma L} = (4.3 \pm 0.1) \times 10^8$ eV/cm. This is in excellent agreement with the value $D_{\Gamma L} = (4.2 \pm 0.2) \times 10^8$ eV/cm obtained from time-resolved transmission experiments [34] as well as with *ab initio* theoretical values of 4.0×10^8 eV/cm (Ref. [35]) and 4.1×10^8 eV/cm (Ref. [36]). On the other hand, the constant denominator Elliott model gives very poor agreement with experiment using $D_{\Gamma L} = 4.3 \times 10^8$ eV/cm, and there is no value that produces a good fit because the overall line shape is incorrect. If the excitonic enhancement is fully neglected, the overall fit is also worse, and the required deformation potential becomes $D_{\Gamma L} = 7.3 \times 10^8$ eV/cm, which not only disagrees with the values given above but exceeds the upper limit of 4.5×10^8 eV/cm derived by Li *et al.* [37].

It is important to note that as E_0 is approached, the direct-gap absorption cannot be ignored because the absorption edge is considerably broadened at room temperature. However, we have been able to obtain excellent fits of the direct absorption using Elliott’s model, and the results indicate that at 20 meV below the energy of the direct gap, the direct-gap absorption coefficient has been reduced to 10 cm^{-1} . This region is indicated as a gray band in Fig. 2, and we see that most of our spectral range is unaffected by direct transitions. Within the gray band, it becomes increasingly necessary to introduce broadening into our expressions. This cannot be simply accomplished by adding a constant imaginary part to the energies, because we find that a much better fit of the direct-gap absorption is obtained with Gaussian instead of Lorentzian broadening. Since the states involved in the direct absorption are the same as the intermediate states for the indirect process, a self-consistent treatment of broadening will require a nontrivial expansion of our theory.

Recently, *ab initio* results for the indirect-gap absorption of Si have appeared [3,38,39]. These calculations do not include excitonic effects but are in good agreement with experiment, except near the direct absorption edge. The reason for the apparent suppression of excitonic effects observed at low temperature [27]. The reduced excitonic enhancement shown in Fig. 3 for Ge should not apply to Si, because this material is much closer to the Elliott limit. *Ab initio* calculations for Ge could potentially resolve this issue. However, since the resonant absorption in Ge requires the difference $E_0 - E_{\text{ind}}$ to be known within ~ 0.01 eV, a full *ab initio* approach may be very challenging in this case.

In summary, we have presented high-accuracy, high-precision experimental data on the optical absorption of Ge between the indirect and direct gaps, and we have developed a model of excitonic indirect absorption that generalizes the

Elliott approach and leads to excellent agreement with the experimental data using independently measured deformation potential constants. A fundamental lesson from this model is that the excitonic enhancement of indirect transitions is qualitatively different from that of direct transitions in the resonant regime in which the energy of the intermediate states is comparable to the photon energy. The results presented here should find immediate applications in the emerging field of Ge optoelectronics, with particular emphasis on tensile-strained Ge. They are also extremely relevant to the study of the optical

properties of $\text{Ge}_{1-y}\text{Sn}_y$ alloys, in which the separation between the direct and indirect gaps can be continuously tuned and brought to zero at $y \sim 0.09$ [40], causing Eq. (3) to diverge and mandating the development of a self-consistent treatment of lifetime broadenings.

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