

## Band structure of semiconductors under high stress

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(Received 22 November 1976)

We pursue a nonperturbative approach to the calculation of the electronic structure of crystals under high strain, in which all input parameters are determined from just selected properties of the unstrained crystal. The method is applied to calculate the band structure of diamond- and zinc-blende-type semiconductors under strain, with particular application to Ge, Si, and GaAs. The strain dependence in the absence of spin-orbit interactions of the energies and matrix elements of selected transitions are presented for the three crystals. Although most of the calculated quantities display linear variations with strain, there are a number of notable exceptions as well, where nonlinear behavior is predicted.

PACS numbers: 71.25.Rk, 71.25.Tn

### I. INTRODUCTION

It has long been recognized that the application of appropriate stresses to a crystal can provide information about the properties of the unstressed crystal.<sup>1</sup> For example, uniaxial stress experiments were instrumental in demonstrating the indirect nature of the minimum band gaps in Si and Ge.<sup>1</sup> Stress effects have also been utilized for device applications; stress-tuned lasers and stress modulation are examples. Calculations of band structure under stress should contribute to the understanding of these as well as more fundamental phenomena such as stress-induced semiconductor to semimetal transitions. The present work is aimed at developing an approach capable in principle of providing a reasonably complete picture of the electronic structure of diamond and zinc-blende semiconductors under high stress, and illustrating progress in this direction via calculations for Ge, Si, and GaAs. We will speak interchangeably of either "stress"- or "strain"-induced effects, depending on which is more appropriate in a given instance.

The early studies of effects of uniaxial strains on crystals were mostly phenomenological in nature, with the shifts and splittings of various high-symmetry states characterized in terms of deformation-potential constants (DPC).<sup>2</sup> The number of independent DPC were determined by symmetry considerations and the results of a variety of experiments, including stress-optical ones, were utilized to determine their values. As methods for calculating energy bands progressed, attention was directed at theoretical prediction of DPC. For example, Kleinman<sup>3</sup> calculated the strain splitting of the top valence states in Si using the orthogonalized-plane-wave (OPW) method. Later, Goroff and Kleinman<sup>4</sup> extended this work to other valence and conduction states as well. The OPW calculations appear to be rather cumbersome for uniaxial

strain configurations. Saravia and Brust<sup>5</sup> demonstrated that pseudopotential methods could be utilized to predict strain splittings of energy levels in Ge; the results were in good agreement with experiment. The shortcoming of the latter approach, however, is that the wave-vector dependence of the pseudopotential form factors of the strained crystal need to be determined empirically. One thus requires at least a partial knowledge of quantities which the theory purports to predict.

All the above-mentioned calculations are perturbative in nature, namely, the strain-induced changes of both the kinetic- and potential-energy terms of the Hamiltonian are treated as perturbations to the undistorted Hamiltonian. The calculation therefore is carried out in the unstrained space. The electronic wave function and energy of the unstrained crystals are calculated first and a subsequent perturbation calculation is performed to take account of the effects of strain. However, it has been realized<sup>6</sup> that a crystal under a uniaxial strain can alternatively be regarded as a new crystal with a different Bravais lattice and/or point-group symmetry. Melz<sup>7</sup> was the first to partially exploit this point of view, by expressing the kinetic energy of the strained Hamiltonian utilizing the strained reciprocal space. This avoided the untidy expansion of the same quantity with respect to the unstrained space. However, the potential energy was treated as a perturbation on the unstrained crystal, and the calculations were limited to just a few critical-point band gaps (for which reasonably good agreement with experiment was achieved). The wave-vector dependence of the pseudopotential in Melz's calculation was determined from the Heine-Abarenkov model potential.<sup>8</sup>

The objective of the present work is to develop a nonperturbative approach which, in principle, need not be limited to small values of stress, and to apply the method under restricted conditions to predict electronic structure and transition matrix ele-

ments throughout the entire Brillouin zone. We also desire an approach which will be computationally feasible, and will contain no adjustable parameters beyond those for the unstrained crystal. The principal element of the approach chosen here to realize these goals is the consideration of the strained crystal as a new one possessing a Bravais lattice, and/or point-group symmetry different from that of the undeformed crystal. The band-structure calculation is implemented utilizing a variant of the empirical pseudopotential method which we outline in some detail in Sec. II. Preliminary accounts of aspects of the present treatment and some results of calculations have been given elsewhere.<sup>9,10</sup> The application of our method to the small-stress regime (calculation of DPC) has been given in Ref. 9. In Sec. III, we describe results of sample calculations of electronic structure under strain for Ge, Si, and GaAs when spin-orbit coupling has been omitted. In contrast to previous work, we also obtain the dependence of the full band structure of the crystals under strain rather than just a few critical-point band gaps.

## II. BAND-STRUCTURE FORMALISM FOR CRYSTALS UNDER UNIAXIAL STRAIN

Adopting the view that the strained crystal is a new crystal with a different Bravais lattice and/or point-group symmetry, we first define the primitive translation vectors  $\vec{a}'_i$ , of the strained crystal as

$$\vec{a}'_i = (\vec{1} + \vec{\tau}) \cdot \vec{a}_i, \quad i = 1, 2, 3, \quad (1)$$

where  $\vec{a}_i$  is the corresponding vector in the undistorted crystal;  $\vec{1}$  is the unit matrix and  $\vec{\tau}$  is the strain tensor, assumed to be uniform throughout the crystal. Equation (1) specifies the Bravais lattice of the strained crystal, from which its reciprocal lattice can be straightforwardly determined. Under certain strain configurations, the macroscopic strain  $\vec{\tau}$  does not completely specify the relative positions of the atoms in the primitive cell. One requires, in addition, the internal strain parameter, which specifies the relative extent of bond stretching and bond bending when the crystal is subject to certain strains, such as a [111] uniaxial strain. This parameter is discussed at considerable length in the literature<sup>11</sup>; theoretical as well as experimental values of the parameter for a number of tetrahedrally bonded semiconductors are available. In the present work, experimental values of the parameters will be used whenever they are available.

We next determine the pseudopotential form factor required for the strained crystal calculations. We shall here utilize an empirical pseudopotential, and assume transferability of the ionic pseudo-

potentials. The latter principle, i.e., that the pseudopotential of an ion determined from the band-structure calculation of a particular crystal can be transferred for use in another crystal containing the same ion, has been demonstrated convincingly by Cohen and co-workers.<sup>12</sup> The transferability is expected to be even more suitable if the environments in which the ion is embedded are similar in both crystals. In the present calculation, even though we view the strained crystal as having a different structure, the difference is in fact small, at least when compared with the difference between, say, the zinc-blende and wurtzite structures (which are even regarded as very similar). Furthermore, we expect that since we are concerned with uniaxial strains which, to the first order in the strains, do not change the crystal volume, the screening effect of the valence electrons will have a negligible influence on the pseudopotential.

We determine the pseudopotential form factor  $V_i(\vec{Q})$  (where  $\vec{Q}$  is a reciprocal-lattice vector) of the  $i$ th constituent atom from

$$V_i(\vec{Q}) \equiv \frac{1}{\Omega \epsilon(\vec{Q})} \int v_i(\vec{r}) e^{-i\vec{Q} \cdot \vec{r}} d\vec{r}, \quad (2)$$

where  $\Omega$  is the volume of the unit cell;  $\epsilon(\vec{Q})$  is the wave-vector-dependent dielectric function, which accounts for the screening effect of the valence electrons; and  $V_i(\vec{r})$  is the pseudopotential of the  $i$ th ion. The transferability of pseudopotentials consists of the assumption that  $V_i(\vec{r})$  is characteristic of the isolated ion, but independent of the embedding environment. Thus the function

$$U_i(\vec{Q}) \equiv V_i(\vec{Q}) \Omega \epsilon(\vec{Q}) \quad (3)$$

as a function of  $\vec{Q}$  should be independent of "small" changes in crystal structure if the pseudopotential of the ions is exactly transferable. To determine  $U_i(\vec{Q})$  for an ion, it is only necessary to know  $V_i(\vec{Q})$  and  $\epsilon(\vec{Q})$  for one particular crystal containing the ion. For cubic Si and Ge, numerical calculations<sup>13</sup> of  $\epsilon(\vec{Q})$  based on realistic band structures are available. Unfortunately, they are often given in numerical form, which is not convenient to work with. On the other hand, there are analytic expressions<sup>12</sup> for  $\epsilon(\vec{Q})$  derived for a free electron gas, which have been used as an approximation in semiconductors. We choose to utilize the model dielectric function first proposed by Penn<sup>14</sup> and subsequently modified by Brust<sup>15</sup>; namely,

$$\epsilon(\vec{Q}) = 1 + 0.65 [Q(\vec{Q}) - 1] [1 - f_H(\vec{Q})], \quad (4)$$

where

$$Q(\vec{Q}) = 1 + \left( \frac{\hbar \omega_p}{E_g} \right)^2 F \left[ 1 + \left( \frac{E_F}{E_g} \right) \left( \frac{q}{K_F} \right)^2 F^{1/2} \right]^{-2}$$

and

$$F = 1 - 0.25(E_g/E_F) .$$

$\omega_p$ ,  $E_F$ , and  $K_F$  are, respectively, the plasma frequency, Fermi energy, and Fermi wave vector corresponding to appropriate valence-electron density.  $E_g$  is the Penn gap, and

$$f_H(\vec{q}) = 0.5 / (1 + K_s^2/q^2 + K_F^2/q^2) ,$$

$$K_s^2 = 2K_F/\pi \quad (\text{in atomic units}),$$

is the Hubbard exchange and correlation function.

$U_i(\vec{q})$  is, by definition, the Fourier transform of the ionic pseudopotential  $v_i(\vec{r})$ . In principle,  $v_i$  can be determined by using appropriate model potentials. However, since most model potentials are based on a drastic simplification of the real situation, it is felt that  $V_i(\vec{q})$  obtained in this manner may not be adequate. We note that there are very few satisfactory band-structure calculations for semiconductors derived from model potentials without further adjustments. This is also partially reflected in the results of Melz's<sup>7</sup> calculation, where one of the most carefully constructed model potentials, i.e., the Heine-Abarenkov model potential, was employed, yet the agreement with experiment was not satisfactory in various instances. In the present work, instead of using a model potential, we implement the following procedure based on empirical pseudopotentials: We first determine  $V_i(\vec{q})$  by fitting a polynomial (in  $\vec{q}$ ) through the original pseudopotential form factors of Cohen and Bergstresser<sup>16</sup> for undeformed crystals. Along with the dielectric function prescribed above,  $U_i(\vec{q})$  is established. Employing the transferability ansatz, the latter quantity is assumed to remain unchanged when the crystal is distorted. Thus one need just account for the change of the dielectric function  $\epsilon(\vec{q})$  when the crystal is deformed, in order to determine the Fourier component  $V_i(\vec{q})$ , and thus the needed pseudopotential form factors, for the strained crystal.

In principal, it would be desirable to obtain  $\epsilon(\vec{q})$  self-consistently but, in practice, such a procedure turns out to be very cumbersome. The strain-induced change in  $\epsilon(\vec{q})$  depends, in general, on the unit cell volume, as well as the strain configuration. Since we will be concerned with pure shear strains, the volume change of  $\epsilon(\vec{q})$  need not be considered. Due to the complexity of including strain effects on  $\epsilon(\vec{q})$ , we have decided to omit them as a first approximation, although their inclusion may be appropriate for more accurate calculations. It should be pointed out that it is a common approximation in the literature to account for the change in  $\epsilon(\vec{q})$  only through the change in electron density (or unit cell vol-

ume), when pressure or strain-dependent band structure is calculated. For tetrahedrally bonded semiconductors and their slight modifications a partial justification for this approximation is that for the reciprocal-lattice vectors  $\vec{G}$  at which one needs the values of the pseudopotential,  $\epsilon(\vec{G})$  is sufficiently close to unity<sup>13</sup> (i.e., no screening), that an approximate treatment of the change in  $\epsilon(\vec{q})$  which is restricted to volume-related effects may perhaps be sufficient.

The spin-orbit (SO) interaction is omitted in the initial calculations presented here, for a variety of reasons. First of all, to our knowledge, no adequate first-principles treatment of the strain dependence of the SO interaction is available, and all previous calculations assume SO interactions to be independent of strain. Thus, so far as the strain dependence of energy levels is concerned, inclusion of SO interactions does not necessarily provide additional information. Furthermore it is a good rule of thumb that the effects of external perturbations on two SO split levels, when an appropriate weighted average is taken, tends to be very close to that arising from the single level which exists in the absence of SO interactions. Secondly, in certain instances (such as Si, e.g.) for the higher values of strains that are of prime interest for the present approach, the spin-orbit interaction has a relatively smaller effect compared to strain-induced splittings (changes in gaps may be two to three times smaller than those induced by strain). Thirdly, the amount of computer time required to include SO interactions with the same level of accuracy is substantially greater. Nevertheless, it will certainly be worthwhile (especially when accurate calculations are required or for small values of strain) and, in certain cases, necessary, to extend the present calculations to include SO effects. We choose to defer the more extensive computations required to do so to future work, but nevertheless take note of their importance here.

### III. CALCULATED RESULTS FOR BAND STRUCTURE UNDER STRESS

In carrying out the calculations we follow standard procedure by expanding the wave function in terms of about 100 plane waves. Among them approximately 20 are treated exactly, with the remaining ones taken into account by the Löwdin perturbation scheme. The real (Si, Ge) and Hermitian (GaAs) matrices that are actually diagonalized are of the order of  $20 \times 20$ . The computations were performed on a CDC 6600 computer using matrix diagonalization subroutines developed by Argonne National Laboratory.<sup>17</sup> We found that the accuracy of the computations is

such that a change in eigenvalue of  $10^{-4}$  eV, and a change of optical-transition matrix element of one part in a thousand can be reliably determined. This is accurate enough to determine unambiguously the real effects of strain on band gaps and optical-transition matrix elements for the cases investigated.

A. Energy-band structure

In our preliminary communication on this work, we presented calculations of the band structure of

Ge under both [001] and [111] strains. However, Ge can be regarded as a prototype crystal for the present case and much of the notation, as well as the general nature of the calculated results, remains the same for Si and GaAs. We therefore here repeat the results for Ge under strain for purposes of completeness and to enable comparison with the results for Si and GaAs.

Figure 1(a) shows the  $E$ - $\vec{k}$  diagram of Ge under a [001] uniaxial strain for  $\vec{k}$  along several high-symmetry directions. None of the directions

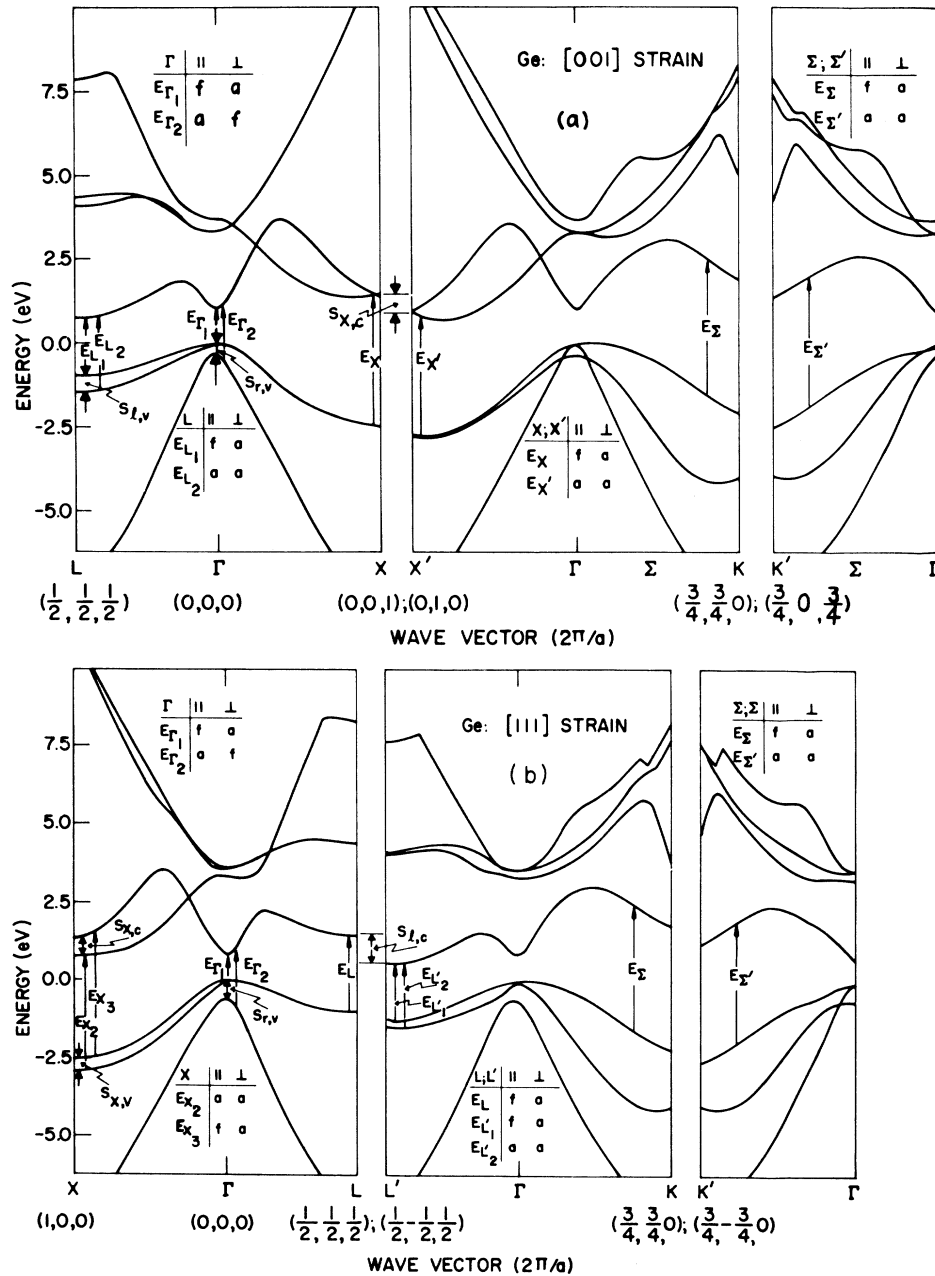


FIG. 1. Band structure of Ge under strain with  $\delta = 0.02$ . None of the high-symmetry  $\vec{k}$  directions plotted are equivalent, although coordinates of  $\vec{k}$ 's appropriate for the case of zero strain are used in the labelings. Several important interband transitions are indicated by thin arrows, with the corresponding selection rules shown as inserts, where  $\parallel$  stands for parallel polarization,  $\perp$  for perpendicular polarization,  $a$  for allowed transition, and  $f$  for forbidden transition. Strain-induced intra-band or interband splittings, such as  $S_{r,v}$ ,  $S_{l,v}$ , and  $S_{X,c}$  are indicated by thick arrows.

plotted are equivalent, although labels appropriate for the case of zero strain are used. Under such a strain, the eight  $[111]$   $\vec{k}$  directions remain equivalent, and only one of the directions need be plotted. The major effect of strain on the band structure for  $\vec{k}$  along this direction is the splitting (as indicated by thick arrows) of the energy bands, which are originally doubly degenerate. For  $\vec{k}$  along the direction of the applied strain, i.e.,  $[00\pm 1]$  direction, the symmetry of the wave function is not lowered by the strain, and the de-

generacy is therefore not lifted, although the corresponding band gaps do change. For  $\vec{k}$  perpendicular to the strain direction, the symmetry of the wave functions is reduced by the strain. All eigenenergies are nondegenerate, except for  $\vec{k} = (2\pi/a)(0, \pm 1, 0)$  and  $(2\pi/a)(\pm 1, 0, 0)$ . Even for these values of  $\vec{k}$ , the electronic energies are different from those at  $\vec{k} = (2\pi/a)(0, 0, \pm 1)$ . This is the intervalley splitting, vividly depicted in Fig. 1(a). Similar intervalley splitting exists for  $\vec{k}$  along the  $\Sigma$  directions. For  $\vec{k}$  at the  $\Gamma$  point, the top valence

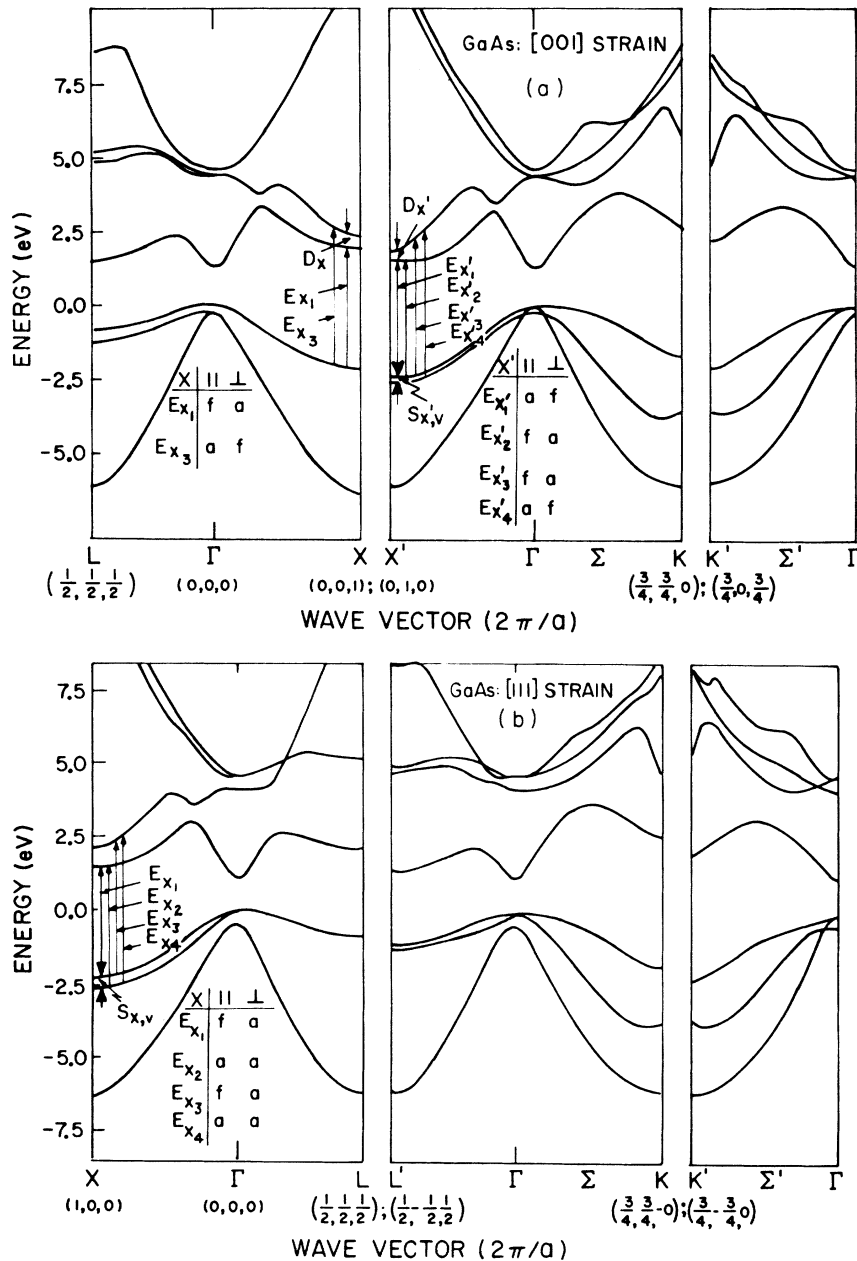


FIG. 2. Band structure of GaAs under strain. Strain-induced splittings, interband transitions, and corresponding selection rules similar to those in Ge as shown in Fig. 1 are not repeated.

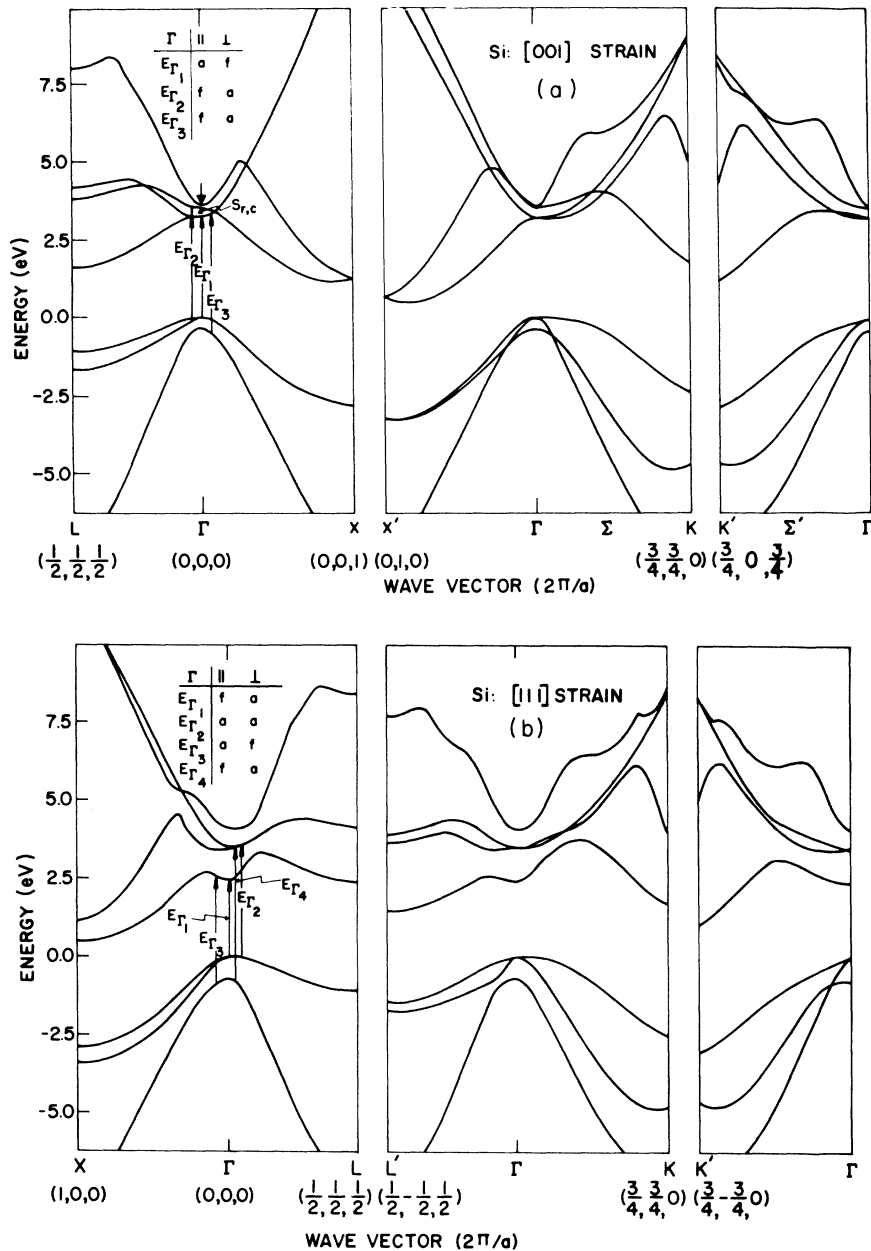


FIG. 3. Band structure of Si under strain. Strain-induced splittings, inter-band transitions, and corresponding selection rules similar to those in Ge as shown in Fig. 1 are not repeated.

states, which represent states with  $X, Y, Z$  symmetries, respectively, and hence are triply degenerate in the absence of strain, are now split into a doubly degenerate state (with  $X, Y$  symmetries) and a nondegenerate ( $Z$ -symmetry) state.

For strain applied in the  $[111]$  direction, the triply degenerate states at the  $\Gamma$  point are also split, similar to the case of  $[001]$  strain. The six  $\Delta$  directions are strained equally. No intervalley splitting results for states with  $\vec{k}$  along these directions, although the corresponding electronic energies differ from those at zero strain. On the other hand, the eight  $[\pm 1 \pm 1 \pm 1]$  directions do not

all remain equivalent, although the  $[11-1]$  and  $[1-11]$  and  $[-111]$  still remain equivalent. Thus intervalley splitting arises between states with  $\vec{k}$  along the  $[111]$  and  $[11-1]$  directions, etc. Also note that for  $\vec{k}$  along the latter directions, all the states are nondegenerate, including those lying at the boundary of the Brillouin zone.

Figure 2(a) shows the calculated band structure of GaAs under a  $[001]$  strain. A comparison of Fig. 2(a) with Fig. 1(a) indicates that they are very similar, except for splittings of energy levels at the  $X$  and  $X'$  points in GaAs. It is well known that the band structure of unstrained GaAs bears strong

resemblance to that of unstrained Ge, except again for differences regarding certain energy levels at the  $X$  point. Because the two atoms in the unit cell are dissimilar in zinc-blende-type crystals such as GaAs, the crystal potential contains a component which is antisymmetric with respect to the center of inversion. The doubly degenerate  $X_1$  level in a homopolar crystal, such as Ge, is split into nondegenerate  $X_1$  and  $X_3$  levels<sup>12</sup> in a heteropolar crystal, such as GaAs. As shown in Fig. 1(a), this particular degeneracy in Ge is not lifted by a [001] strain. In contrast, for GaAs the corresponding states at  $X$  and  $X'$  are split both when unstrained or under [001] strain. Thus the splittings in the case are not associated with strain-induced effects, but rather the polar nature of the crystals concerned.

The band structure of GaAs under a [111] strain is shown in Fig. 2(b). It is essentially identical to that of Ge under the same strain including, in particular, states at the  $X$  point. The splitting of the doubly degenerate  $X_1$  state in Ge by the [111] strain is rather interesting. It appears that so far as the energies of these states are concerned, such a strain has an effect equivalent to that of an antisymmetric potential. Of course, the similarity in band structure for Ge and GaAs under a [111] strain does not imply that all their other characteristics are similar. In fact, the optical-transition selection rules involving the  $X$ -point states are not the same, as will be indicated below.

The band structure of Si under strain is shown in Figs. 3(a) and 3(b). Remarks similar to those for Ge hold for Si as well, with the exception of the lowest conduction state at the  $\Gamma$  point. In unstrained Si, the lowest conduction state at the  $\Gamma$  point is the triply degenerate  $\Gamma_{15,c}$  state. This energy level is split by strain, similarly to the triply degenerate valence state  $\Gamma'_{25,v}$  into one doubly degenerate, and a nondegenerate state. The optical transitions involved are indicated in these figures. We note that the  $\Gamma'_{25,v} \rightarrow \Gamma_{15,c}$  transition in cubic Si has been the subject of some controversy.<sup>12</sup> Detailed calculations of the optical absorption associated with these transitions in strained Si, which may help clarify this controversy, are planned in future work.

#### B. Strain dependence of band gaps

In Figs. 4(a)–4(f), we plot the strain dependence of several critical-point band gaps, as well as the induced intervalley or intravalley splittings. It appears, with a few exceptions, that the change of energy gap with strain is essentially linear up to  $\delta \approx 0.02$ . Such a strain corresponds to a [001]

stress of about  $5 \times 10^{10}$  dyn/cm<sup>2</sup>, and to a [111] stress of about  $10^{11}$  dyn/cm<sup>2</sup>, in the three crystals concerned.<sup>18</sup> It is nearly the strain value corresponding to the elastic limit of these crystals. In conventional experiments, the static uniaxial stress applied is about one-tenth of the above values. The few exceptions that display noticeable nonlinearity are the minimum direct gaps ( $E_{\Gamma_1}$ ) in Ge and GaAs for both the [111] and [001] strain configurations. A similar nonlinearity in Ge and GaAs has been observed in piezoelectroreflectance measurements,<sup>19</sup> albeit at much lower stresses, and was interpreted in terms of stress-induced couplings between the upper stress-split valence band and the SO split band. In all three crystals, marked nonlinearity is also found in the  $L$ -point gap under a [001] strain and the  $X$ -point gap under a [111] strain. A peculiar nonlinearity concerning the  $L$ -point gap of Ge under [001] strain was also observed,<sup>19</sup> in which the center of gravity of the structure due to  $E_1$  and  $E_1 + \Delta_1$  ( $L$ -point gap split by spin-orbit interaction) was found to be linear with strain for light with parallel polarization, but pronouncedly nonlinear for light polarized perpendicular to the stress. Although we do not include spin-orbit interaction, and the maximum strain utilized is much larger than normally used in experiments, the present calculations nevertheless suggest the possibility that nonlinearities may not stem exclusively from spin-orbit effects, but may instead also have their origin in the inherently nonlinear dependences of various gaps on strain. However, since the interpretation of observed nonlinearities in terms of SO effects appears to be satisfactory at this point, extensions of the present calculations to include SO effects will be required before any meaningful conclusions can be reached.

It is conventional to define various deformation-potential constants to describe the shift of energy levels with respect to strains. For example, for electronic states with  $\vec{k}$  along certain high-symmetry directions, such as [001] and [111], the shift of an energy level with strain  $\bar{\tau}$  is given by

$$\Delta E = \sum_{\alpha\beta} (\Sigma_a \delta_{\alpha\beta} + \Sigma_a \vec{k}_\alpha \vec{k}_\beta) \tau_{\alpha\beta},$$

where  $\vec{k}_\alpha$  is the  $\alpha$ th Cartesian component of the unit vector  $\vec{k}/|\vec{k}|$ , and  $\tau_{\alpha\beta}$  is the  $\alpha\beta$  component of the strain tensor. In the present instance,  $\bar{\tau}$  takes the form

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{bmatrix} \tau \text{ for [001] strain} \quad (5)$$

and

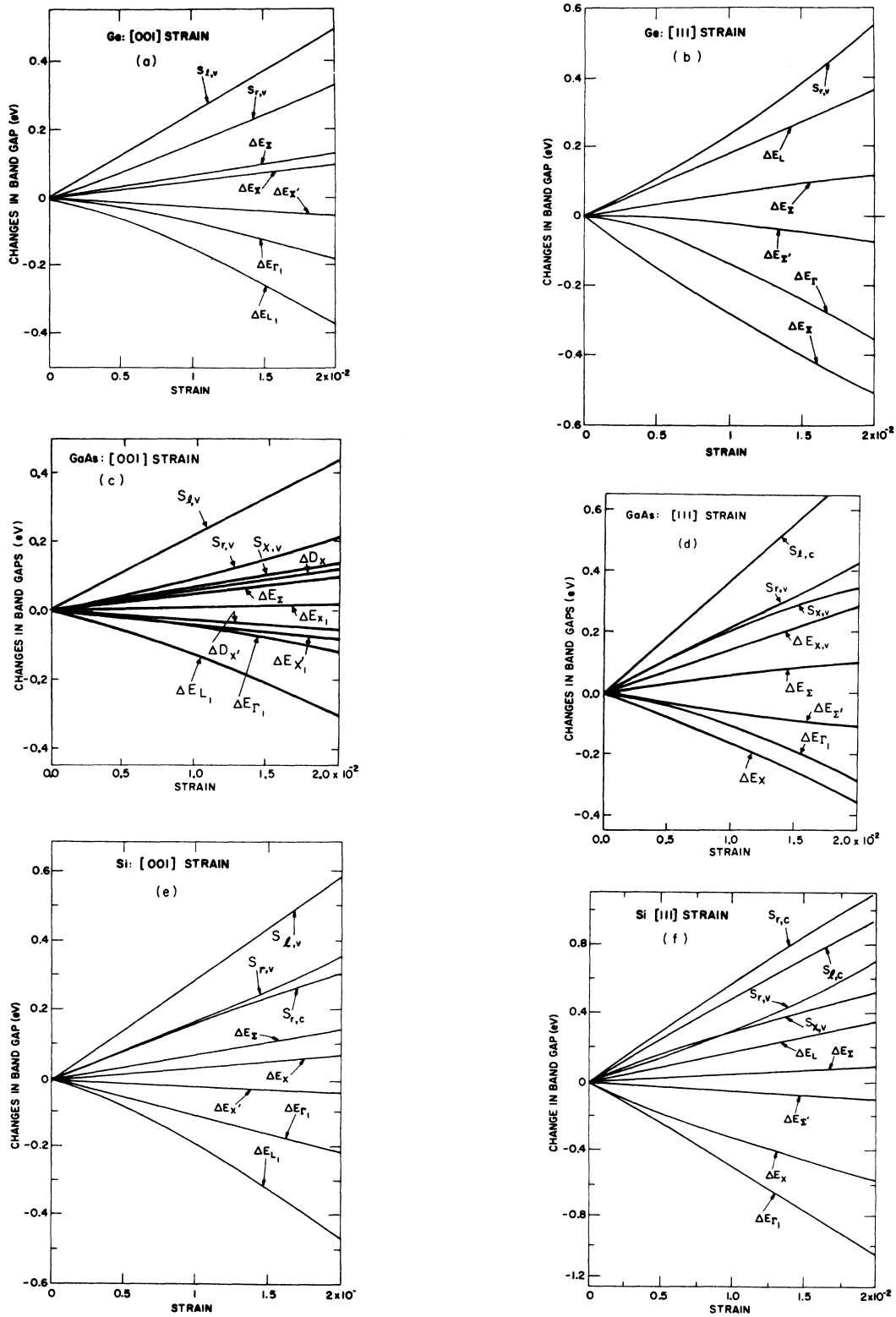


FIG. 4. Change of band gaps or strain-induced splittings as a function of strain. The meaning of the notations used are obvious by referring to the corresponding band structure. (a) Ge under [001] strain; (b) Ge under [111] strain; (c) GaAs under [001]; (d) GaAs under [111] strain; (e) Si under [001] strain; (f) Si under [111] strain.



$$\begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix} \tau \text{ for } [111] \text{ strain.} \quad (6)$$

It follows immediately, for instance, that

$$\Delta E_{[001]}^{[001]} = 2\Sigma_u \tau, \quad \Delta E_{[100]}^{[001]} = -\Sigma_u \tau, \quad (7)$$

$$\Delta E_{[111]}^{[111]} = 2\Sigma_u \tau, \quad \Delta E_{[111]}^{[111]} = -\frac{2}{3}\Sigma_u \tau, \quad (8)$$

where the superscript refers to the direction of the strain, and the subscript to the direction of the  $\vec{k}$  vector. It must be pointed out that the  $\Sigma_u$ 's in both Eqs. (7) and (8) are not the same quantity. The strain splitting  $S_{\gamma,v}$  of the top valence states at the  $\Gamma$  point, i.e.,  $\vec{k} = (0, 0, 0)$  of the Brillouin zone is related to the deformation-potential constants  $b$  and  $d$  (in the notations of Picus and Bir<sup>1,2</sup>) in the following way:

$$S_{\gamma,v}^{[001]} = 6\tau b$$

and

$$S_{\gamma,v}^{[111]} = 2\sqrt{3} \tau d. \quad (10)$$

Selected deformation constants obtained from the present calculations for Ge and Si have been given previously and compared with other theoretical results and experimental data<sup>9</sup>; we therefore do not repeat them here. Instead, in Table I we list just the results for GaAs. For completeness, the volume  $dp$ 's obtained in Ref. 20 are also included for comparison. It is seen that the present  $dp$ 's are in better agreement with experimental results than those calculated by Melz. We would like to especially comment on the results for the shear deformation constant  $\Sigma_u$  of the  $L_{3,v} \rightarrow L_{1,c}$  and  $\Lambda_{3,v} \rightarrow \Lambda_{1,c}$  transitions. We find substantially dif-

ferent values for the two transitions:  $\Sigma_u$  for the  $L_{3,v} \rightarrow L_{1,c}$  transition is found to be 7.2 eV, which is in excellent agreement with the experimental values of  $7.4 \pm 0.7$  eV obtained by Pollak and Cardona.<sup>19</sup> On the other hand, the corresponding calculated value of  $\Sigma_u$  for the  $\Lambda_{3,v} \rightarrow \Lambda_{1,c}$  transition [ $\vec{k} \approx (2\pi/a)(0.2, 0.2, 0.2)$ ] is only 4.8 eV. It should be noted, however, that the experimental value of Pollak and Cardona was deduced by interpreting the observed shift with stress of certain electro-reflectance peaks, which were ascribed by these authors as due to  $\Lambda_{3,v} \rightarrow \Lambda_{1,c}$  transitions.

### C. Strain dependence of optical-transition matrix elements

The matrix element  $M_{i,f}(\hat{\epsilon}, \vec{k})$  for a direct transition involving electronic states with wave vector  $\vec{k}$ , induced by light with polarization  $\hat{\epsilon}$  is given by

$$M_{i,f}(\hat{\epsilon}, \vec{k}) = |\langle \vec{k}, f | \hat{\epsilon} \cdot \mathbf{p} | i, \vec{k} \rangle|^2, \quad (11)$$

where  $|i, \vec{k}\rangle$  and  $|f, \vec{k}\rangle$  are the initial and final band states, and  $\vec{p}$  is the momentum operator. As in all pseudopotential band-structure calculations,  $|i, \vec{k}\rangle$  and  $|f, \vec{k}\rangle$  are obtained in the form of pseudo-wave-functions. The latter is, of course, not the real wave function, but rather represents the smooth portion thereof. Optical-spectrum calculations which utilize pseudo-wave-functions in computing the transition matrix elements have predicted spectral features in good agreement with experiments in many crystals, although in some cases the relative peak intensities of the calculated spectrum are not totally in agreement. A rigorous assessment of the accuracy of pseudo-wave-functions for matrix-element calculations is lacking at present, mainly because of the difficulty in ob-

TABLE I. Deformation-potential constants of GaAs (in eV).

Type of deformation		Theory		Experiment	
		This work <sup>a</sup>	Melz <sup>b</sup>		
$\Gamma_{15,v} \rightarrow \Gamma_{1,c}$ splitting } of $\Gamma_{15,v}$ }	b	volume	-9.9	-15.3	-9.4 <sup>c</sup> ; -7.8 <sup>d</sup> ; -9.0 <sup>e</sup>
	d	[001] strain	-1.5	-0.4	-2.0 <sup>e</sup> ; -1.7 <sup>d</sup>
		[111] strain	-6.1	-3.0	-6 <sup>e</sup> ; -4.4 <sup>d</sup> ; -5.4 <sup>f</sup>
$L_{3,v} \rightarrow L_{1,c}$ or $\Lambda_{3,v} \rightarrow \Lambda_{1,c}$ }		volume	-5.5	-8.3 <sup>g</sup>	-6.5 <sup>e</sup> ; -7.2 <sup>h</sup>
		$\Sigma_u$ , [111] strain	7.2; 4.8 <sup>g</sup>	6.7 <sup>g</sup>	7.4 <sup>e</sup> ; 5.4 <sup>h</sup>
		volume	-3.4	-4.8	...

<sup>a</sup> Volume deformation constants taken from Ref. 20.

<sup>b</sup> P. J. Melz, Phys. Chem. Solids 32, 2001 (1970).

<sup>c</sup> B. Welber, M. Cardona, C. K. Kim, and S. Rodriguez, Phys. Rev. B 12, 5729 (1975).

<sup>d</sup> I. Balslev, Solid State Commun. 5, 315 (1967).

<sup>e</sup> F. H. Pollak and M. Cardona, Phys. Rev. 172, 816 (1968).

<sup>f</sup> R. H. Bharagava and M. I. Nathan, Phys. Rev. 161, 695 (1967).

<sup>g</sup> Calculated at  $\vec{k} = (2\pi/a)(0.2, 0.2, 0.2)$ .

<sup>h</sup> D. D. Sell and S. E. Stokowski, Proceedings of the Tenth International Conference on the Physics of Semiconductors (U.S. AEC, Oak Ridge, 1970).

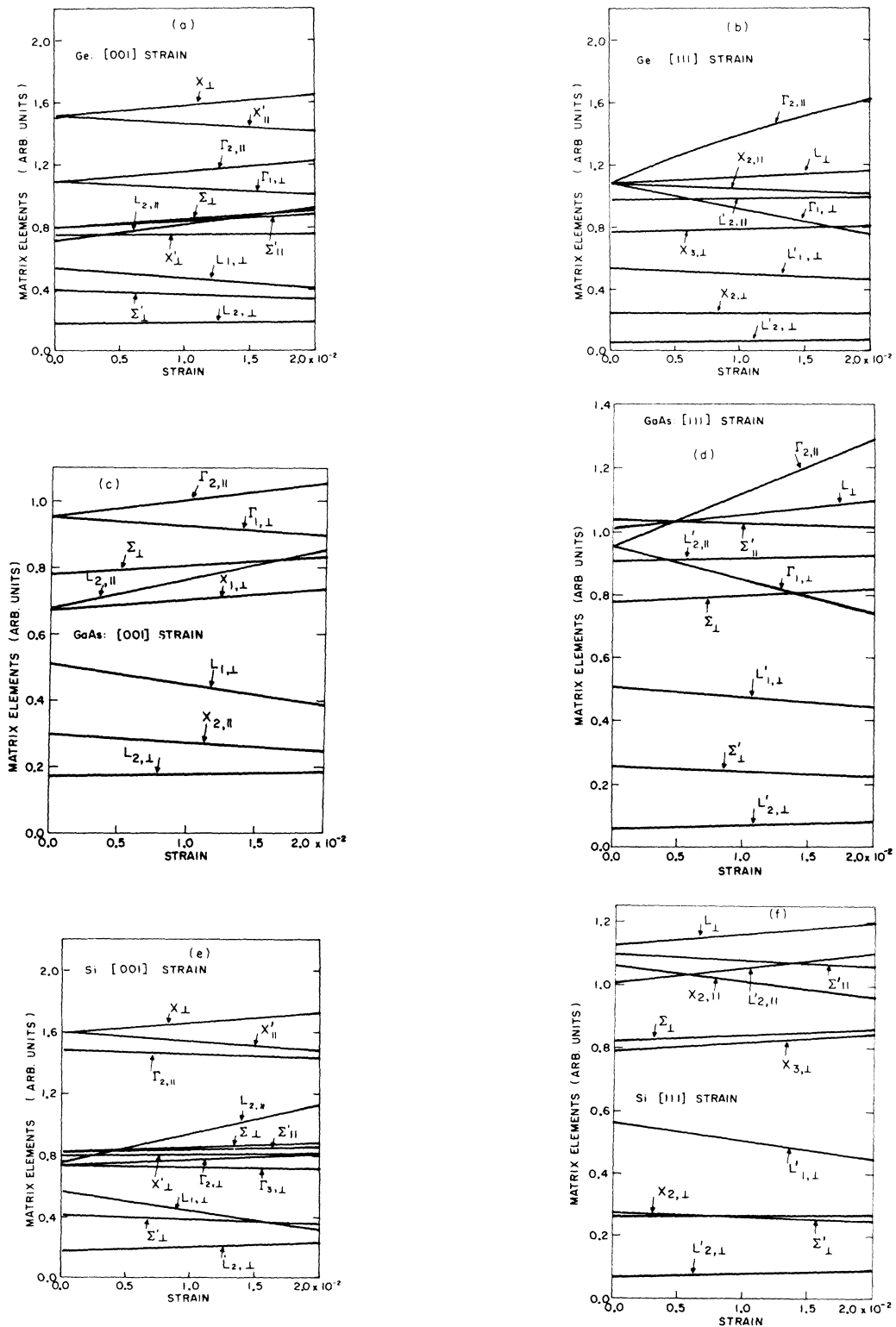


FIG. 5. Strain dependence of matrix elements of allowed interband transitions. Meaning of notation used becomes obvious by referring to the corresponding band structure. (a) Ge under [001] strain; (b) Ge under [111] strain; (c) GaAs under [001] strain; (d) GaAs under [111] strain except for certain transitions at X point; (e) Si under [001] strain; (f) Si under [111] strain, except for certain transitions at  $\Gamma$  point.

taining a sufficiently accurate real wave function for comparison. Nevertheless, calculations<sup>21</sup> of interband transition matrix elements for Ge and Si, using both pseudo-wave-functions and OPW wave functions yield results which differ by about ten percent or less in most cases. This indicates that use of pseudo-wave-functions is an adequate approximation for obtaining transition matrix elements in certain instances. Since the pseudo-wave-function has the correct symmetry of the real wave function, it can accurately provide selection rules for optical transitions. It is also useful in studying how the oscillator strength of a degenerate transition splits among its constituents when the degeneracy is lifted by strain.

Figure 5(a) shows the matrix elements of important optical transitions in Ge, under [001] strains. The figure should be read together with Fig. 1(a), in which notations for the various transitions are indicated. Also implicit in Fig. 5(a) is information as to how the oscillator strength is divided among strain-split transitions which are degenerate at zero strain. For instance, the  $\Gamma_1$  and  $\Gamma_2$  transitions combine to form the single  $\Gamma$  transition at zero strain, with equal matrix elements for both parallel polarization  $P_{\parallel}$  and perpendicular polarization  $P_{\perp}$ , as they should for cubic crystals. Also, for example, under a [001] strain, the  $X$  point and the  $X'$  points are not equivalent, but coalesce into degeneracy at zero strain. Thus we have, for zero strain,

$$2X_{\perp} + 4X'_{\perp} = 4X'_{\parallel}$$

to within computational accuracy. The factors 2 and 4 arise because there are two  $X$  points, i.e.,  $(0, 0, \pm 1)$ , but four  $X'$  points,  $(0, \pm 1, 0)$  and  $(\pm 1, 0, 0)$ . At finite strain, since the energies  $E_X$  and  $E_{X'}$  are not equal, one should in theory see in the polarized optical spectrum, a structure at  $E_X$  which is totally  $P_{\perp}$  and another structure at  $E_{X'}$  with  $P_{\parallel} \approx 2P_{\perp}$ . However, if the difference in  $E_X$  and  $E_{X'}$  is not resolved in actual experiments, one instead sees a structure at  $\sim E_X$  which becomes progressively more  $P_{\perp}$  with strain.

Similar results for Ge under [111] strain, as well as Si and GaAs under both strain configurations, are given in Figs. 5(b)–5(f). It is seen that for the majority of the transitions, the change of matrix elements with strain is linear up to strains of 0.02. There are certain exceptions, however. The first one involves the zone-center transitions from the triply degenerate (at zero strain) valence states to the lowest conduction states, which for Si (in contrast to Ge and GaAs) is also triply degenerate. The splittings of these states induced by [111] strains result in four possible transitions, as shown in Fig. 3(b). In Fig. 6, we show the

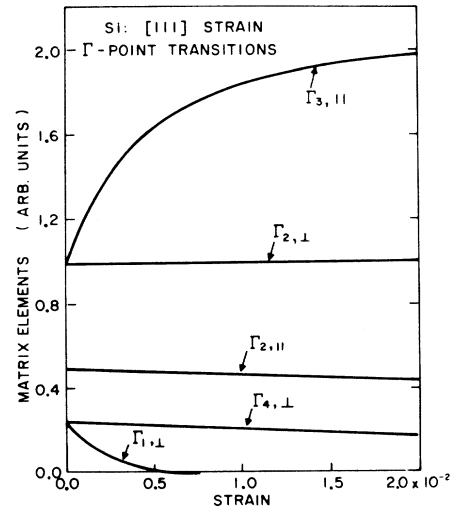


FIG. 6. Strain dependence of matrix elements of interband transitions at  $\Gamma$  point, for Si under [111] strain.

strain dependence of these transition matrix elements. The  $\Gamma_{3,\parallel}$  and  $\Gamma_{1,\perp}$  are found to display very strong nonlinearities. Since the symmetry of the initial and final states is intimately related to the transition matrix element, we expect such nonlinearities could also be found in similar transitions in Ge and GaAs, where the final state involved is the second lowest conduction state. A study of the strain dependence of the appropriate matrix elements in Ge and GaAs, however, shows no such nonlinearities. Since nonlinear dependence is not found in Si under [001] strains either, it is therefore likely that the occurrence of such nonlinearities in Si under [111] strains arises from both the unique nature of a [111] strain and the fact that the lowest conduction state at the zone center in Si is reversed from that in Ge and GaAs. The second case of nonlinearities involves transitions among levels of GaAs at the  $X$  point split by [111] strains, as shown in Fig. 2(b). The strain dependence of matrix elements for those transitions is shown in Fig. 7. We point out that essentially linear dependences are found for similar transitions in Si and Ge under the same strain configuration. The  $X$  point in GaAs becomes somewhat unique when the crystal is under a [111] strain. Reference to the band structure of unstrained Ge and GaAs and the band structure of strained Ge and GaAs, as shown in Figs. 1(b) and 2(b), leads to the following conclusion: Although the splitting of the doubly degenerate valence state in both Ge and GaAs, and the splitting of the conduction state in Ge are purely a strain effect alone, the splitting of the corresponding conduction state in GaAs could arise from the heteropolar character of the crystal as well. Thus the nonlineari-

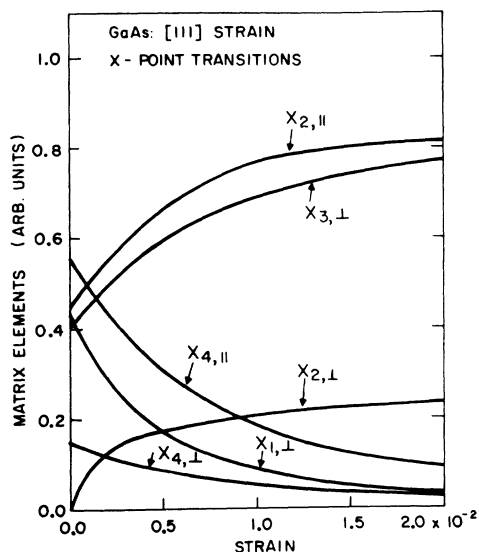


FIG. 7. Strain dependence of matrix elements of interband transitions at X point for GaAs under [111] strain.

ties found in the present calculation may result from the interplay of the heteropolar potential and the applied strain.

#### IV. CONCLUDING REMARKS

We have presented a pseudopotential method for calculating band structure under high strain, in which we regard the strained crystal as possessing a new Bravais lattice and point-group symmetry; in developing the method, the transferability of pseudopotentials is assumed. We have applied the method to model calculations of the band structure of diamond and zinc-blende-type crystals under high strains; in particular, we have presented

computed results for Ge, Si, and GaAs, in the absence of SO interactions.

The validity of the assumptions employed is partially buttressed by the good agreement between our calculated deformation constants and experimental data. We have also studied the strain dependence of band gaps and found linear dependences in most cases, up to strains of the order of the crystal elastic limit, i.e.,  $\tau \approx 10^{-2}$ . However, there are a variety of exceptions, notably, the minimum direct gap  $E_{\Gamma_1}$ , in Ge and GaAs under both [001] and [111] strain. Also, in all three crystals investigated, the gap at the L point  $E_L$  and the gap at the X point  $E_X$  are found to display strong nonlinearity when the crystal is under [001] and [111] strain, respectively.

We have also indicated the strain dependence of matrix elements for a number of interband transitions. Essentially, a linear dependence is found for most cases, except those involving certain specific transitions at the  $\Gamma$  point in Si and at the X point in GaAs, for the case of [111] strain. We have pointed out some possible origins for these nonlinearities, as relates to symmetry properties, for example.

Unfortunately, existing experiments concerning changes in optical response with strain do not provide unambiguous information on the change in band structure at particular  $\vec{k}$ 's with stress or strain, but rather reflect various combinations of effects from different  $\vec{k}$ 's, along with matrix element effects. Nevertheless, the nonlinearities we have found could possibly be instrumental in nonlinear behavior observed in optical experiments. In future work we hope to extend the present techniques to include SO effects and to obtain the strain-induced change in the dielectric response, information which may be more accessible to a variety of experiments.

\*Supported by National Research Council.

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<sup>5</sup>L. R. Saravia and D. Brust, *Phys. Rev.* **178**, 1240 (1969); a similar work based on the same method, for Si, in-

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<sup>11</sup>See, for example, J. C. Phillips, in *Bonds and Bands in Semiconductors* (Academic, New York, 1973), p. 67.

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- <sup>15</sup>D. Brust, *Solid State Commun.* 9, 481 (1971).
- <sup>16</sup>M. L. Cohen and T. K. Bergstresser, *Phys. Rev.* 141, 789 (1966).
- <sup>17</sup>Argonne National Laboratory Report Nos. ANL F202S (subroutine for calculating eigensystems of a real symmetric matrix) and ANL F150S (subroutines to perform the Householder reduction and calculate the eigen-system of a Hermitian matrix).
- <sup>18</sup>The following relations are used to relate stress  $X$  to strain  $\tau$  as defined in Eqs. (5) and (6) for [001] strain:  $X=3\tau/(S_{11}-S_{12})$ ; for [111] strain:  $X=6\tau/S_{44}$ , where  $S_{11}$ ,  $S_{12}$ ,  $S_{44}$  are elastic compliance constants.
- <sup>19</sup>F. H. Pollak and M. Cardona, *Phys. Rev.* 172, 816 (1968).
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