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Breathing-mode lattice relaxation accompanying emission and capture by deep electronic levels in silicon

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The breathing-mode (volume) lattice relaxations associated with carrier emission and capture by a variety of deep electronic levels in silicon are evaluated from high-pressure measurements of the emission rates and capture cross sections. Included are (1) the vacancylike acceptor levels associated with the oxygen-vacancy pair (or A center) and the gold, platinum, and palladium impurities, (2) the chalcogenide donors in their singly and doubly charged states, (3) a number of $3d$ transition-metal donors, and (4) the phosphorus-vacancy pair (or E center) acceptor. The signs and magnitudes (which range from ~ 0 to 5 Å^3/emitted-carrier) of these relaxations are discussed in terms of models for the impurities and defects responsible for the associated levels. The results on the chalcogenides are compared with recent theoretical results. The experimental method used appears to be the only viable experimental method for determining these relaxations which are a direct manifestation of the effective electron-phonon coupling at deep levels and which are important to the understanding of many of the properties of deep levels.

I. INTRODUCTION

In recent work[1,2] we proposed and demonstrated a method for the quantitative determination of the lattice-volume (or breathing-mode) relaxation accompanying the emission or capture of electrons or holes by deep electronic levels in semiconductors. The existence of these relaxations is a much discussed and debated subject,[3-5] but apparently before our recent results[1,2] there had been no experimental measurements of them, and theoretical methods have only recently begun to evaluate them.[4,5]

Our method is based on measurements of the isothermal hydrostatic-pressure dependences of the carrier's thermal-emission rate and capture cross section. We have performed such measurements on several deep levels in silicon (Si), and there are in the literature some similar results on other deep levels in Si, but these latter results were not interpreted in terms of lattice relaxation. In this paper we evaluate, compare, and discuss the lattice relaxations for (1) several vacancylike acceptors, (2) the chalcogenide donors, (3) several $3d$ transition-metal donors, and (4) the phosphorus-vacancy pair (or E center) acceptor in Si.[6] Of special interest in this evaluation and comparison are the sign and magnitude of the breathing-mode relaxation accompanying carrier emission or capture for the different centers and the possible existence of trends in the results which could lead to new insights and understanding of the nature of the different defect centers responsible for the deep levels. Of much interest also is the availability of some pressure data on different charge states of certain centers, thereby allowing evaluation of the relaxations associated with the successive emission or capture of carriers from a given center.

In Sec. II we provide a brief background on lattice relaxations and the experimental method. In Sec. III we present a summary of the results and their interpretation, and in Sec. IV we provide some brief concluding remarks.

II. BACKGROUND

The presence of defect centers caused by impurities, vacancies or interstitials in covalent semiconductors can be expected to produce significant lattice relaxation (or distortion) whereby the host atoms surrounding the defect center assume new equilibrium positions. Additional lattice relaxation results from the change in local charge density brought about by the emission or capture of electronic charge carriers by deep electronic levels produced by such defect centers. It is these latter relaxations which are the topic of the present paper.

Lattice relaxations, of course, determine the local atomic geometry around the defect, and knowledge of their magnitude and symmetry is crucial to the understanding of many of the properties of defects and deep levels.[3-5] These properties include the defect's formation and migration energies, the positions and order in the gap of the electronic energy levels associated with the different charge states of the defect, and such deep-level phenomena as the Jahn-Teller effect, the persistent photoconductivity (PPC) effect, the negative-U phenomenon, and recombination-enhanced defect reactions.

Two types of lattice relaxation can be distinguished: symmetry-conserving (or breathing-mode) and symmetry-breaking relaxations. In the first type, the defect's nearest-neighbor host atoms move either inward or outward in a "breathing-mode" fashion, and it is necessary to know both the sign and magnitude of the relaxation. This type of relaxation is expected to accompany both defect-formation and -capture (or -emission) processes, but knowledge about both its sign and magnitude (i.e., changes in bond lengths) is essentially nonexistent. Superimposed on this breathing-mode relaxation there can be a symmetry-breaking relaxation such as the well-known Jahn-Teller effect in which a partially filled, orbitally degenerate system lowers its energy and lifts its degeneracy by distorting to lower symmetry. Information on the symmetry of this latter relaxation can be obtained from optical and resonance (especially EPR) techniques, but knowledge about its magnitude is also nonexistent. Consequently, a very important aspect of the defect and deep-level relaxation problem remains unknown.

Fortunately, however, recent advances in both theoretical and experimental methods have begun to address the problem. With regards to breathing-mode relaxations accompanying carrier-emission and -capture processes, there are a few relevant theoretical calculations.[4,5] These calculations are based on self-consistent Green's-function total-energy and force methods. They are difficult and there is no calibration on their accuracy. On the experimental side, we have recently proposed and demonstrated techniques based on deep-level transient-capacitance or current and deep-level transient spectroscopy (DLTS) measurements under hydrostatic pressure for quantitatively determining these relaxations.[1,2] These spectroscopies have extremely high sensitivity, being able to detect deep-level defect concentrations as low as $\sim 10^{12}$ cm^{-3}, and hydrostatic pressure couples directly to the totally symmetric breathing-mode distortion of the lattice.

Extended x-ray-absorption fine-structure (EXAFS) measurements are beginning to be used to determine relaxations associated with the presence of impurities in semiconductors. For example, in recent studies the local relaxations around the arsenic impurity in Si (Ref. 7) and sulfur impurities in GaAs (Ref. 8) were determined. Such measurements require very high impurity concentrations (generally $> 10^{19}$ cm^{-3}). These concentrations are much higher than those of practical interest in semiconductors, and the method is thus not likely to be useful for determining relaxations associated with most carrier emission and capture processes in semiconductors.

Our method for determining breathing-mode relaxations (discussed in detail in Refs. 1 and 2) consists of measuring the isothermal hydrostatic pressure (P) dependences of the carrier's thermal-emission rate (e) and capture cross section (σ), from which the isothermal pressure dependence of the change in Gibbs free energy ($\Delta G_{n,p}$) accompanying emission can be determined. $\Delta G_{n,p}$ represents the total-energy difference between the two different charge states (i.e., before and after emission) of the defect in their relaxed condition with the electron (hole) in the conduction (valence) band. It can be shown that to a good approximation for many deep levels[1,2]

$$\left[\frac{\partial \Delta G}{\partial P}\right]_T = kT\left[\left[\frac{\partial \ln \sigma_{n,p}}{\partial P}\right]_T - \left[\frac{\partial \ln e_{n,p}}{\partial P}\right]_T\right] , \qquad (1)$$

where the subscripts n and p refer to electrons and holes, respectively. Note that evaluation of $(\partial \Delta G/\partial P)_T$ generally requires knowledge of the isothermal pressure dependence of both e and σ. However, for many of the levels to be discussed in Sec. III, direct experimental results show that σ is independent of pressure (as well as of temperature), and thus Eq. (1) reduces to the simple result

$$\left[\frac{\partial \Delta G}{\partial P}\right]_T = -kT\left[\frac{\partial \ln e_{n,p}}{\partial P}\right]_T . \qquad (2)$$

For the other levels to be discussed, the authors have assumed, by analogy, that σ is independent of pressure as well. This is most likely a good approximation for the levels in question, but it is an assumption. In a summary table of the results in Sec. III we shall identify those levels for which this assumption is made.

Now from the well-known thermodynamic relation $dG = V\,dP - S\,dT$, where V is the volume and S is the entropy, it is readily seen that

$$\left[\frac{\partial \Delta G_{n,p}}{\partial P}\right]_T = \Delta V_{n,p} , \qquad (3)$$

i.e., the isothermal pressure dependence of $\Delta G_{n,p}$ measures a volume change (or activation volume) which we represent by $\Delta V_{n,p}$. We have conjectured[1,2] that, in the absence of an energy barrier to the capture process, this ΔV is the volume change, or the breathing-mode relaxation, of the defect center which accompanies carrier emission.

In interpreting experimental results there is one complicating factor which must be taken into consideration. Carrier emission is measured from the deep level to either the conduction-band edge (E_c) or the valence-band edge (E_v), so that E_c and E_v are the reference-energy states relative to which the change in ΔG between the two different charge states of the level is measured. However, since the energy gap of Si changes with pressure, these reference-energy states are not fixed, and their changes contribute to the measured pressure dependence of $e_{n,p}$ and thereby to $(\partial \Delta G/\partial P)_T$. It is necessary to consider these contributions in the analysis of the data in order to determine the intrinsic pressure effect, $(\partial \Delta G_{n,p}/\partial P)_T$, associated with the emission process. By the intrinsic pressure effect we mean the effect which would be present in the absence of any contribution from the shift of the gap, as it is this effect which is relevant to the determination of the breathing-mode relaxation accompanying emission and capture. This point has been discussed elsewhere.[1,2]

In order to evaluate the intrinsic effect $(\partial \Delta G_{n,p}/\partial P)_T$ it is necessary to know how much do the individual band edges E_c and E_v contribute to the known pressure shift of the gap[1,2] [$(\partial \Delta G_{\text{gap}}/\partial P) = -1.5$ meV kbar^{-1}], i.e., we need to known the absolute hydrostatic deformation potential of one or both of the band edges, E_v and E_c, relative to the vacuum level. These deformation potentials ($\bar{a}_{v,c}$), defined as the change in E_v or E_c per unit volume (V) strain, i.e., $\bar{a}_{v,c} = dE_{v,c}/d\ln V$, have been the subject of considerable theoretical and empirical interest, but unfortunately there is considerable uncertainty in their signs and magnitudes.[9-11] For Si, there are four recently reported values for $\bar{a}$ of the highest valence-band edge at zone center, which we take to represent $\bar{a}_v$; these are -1.6, -1.0, $+0.8$, and $+0.9$ eV.[9,10] Although Nolte *et al.* recently proposed to use the $+0.9$-eV value and/or the corresponding $\bar{a}_c = 2.4$ eV,[10] there are serious uncertainties,[11(a)] and it is not clear to us how to choose among the different values of $\bar{a}_v$ at this time. In view of this situation, we have adopted for our analysis a procedure[1,2] which we believe to be fairly accurate and which, as we shall see later, yields ΔV's which are in qualitative agreement with expectations based on established models for the defect centers of interest. Any uncertainties introduced by this procedure can be easily corrected later when sufficiently accurate values of $\bar{a}_v$ or $\bar{a}_c$ become available.

In this procedure we consider two cases.[11(b)] In *case 1*, the total pressure-induced shift of the gap is taken up by a shift in E_v, with E_c remaining fixed. In this case emission from a deep level to E_c is not affected by the shift of the gap and $\partial \Delta G / \partial P$ corresponds to the intrinsic effect. For emission from a deep level to E_v, however, the full shift of the gap must be subtracted from the total effect $\partial \Delta G / \partial P$ in order to obtain the intrinsic effect. *Case 2* represents an opposite case where the total pressure shift of the gap is taken up by a shift in E_c with E_v remaining fixed. Here emission to E_v is not affected by the shift of the gap, but emission to E_c requires a full correction.

These two cases define two bounds on the intrinsic effect $(\partial \Delta G_{n,p} / \partial P)_T$ and thereby the breathing-mode relaxation, $\Delta V_{n,p}$. The difference between these two bounds is 2.4 Å^3 per emitted carrier.[1,2] In a simplistic tight-binding picture, $\Delta V_{n,p}$ lies in the middle of these two bounds, and, for specificity in the discussion in Sec. III, we shall make this assumption. On the basis of our adopted procedure, this assumption leads to a maximum uncertainty in $\Delta V_{n,p}$ of ± 1.2 Å^3 per emitted carrier. Because all of the levels to be discussed in Sec. III are in Si, the uncertainty is the same for all of them, and the relative changes in ΔV upon comparing different levels or different charge states of a given level should be accurately established.

Finally, we note that the above considerations, although based on well-founded detailed-balance and thermodynamic arguments, yield ΔV indirectly. Thus, a question can be raised as to how realistic the ΔV's are. A few remarks can be made to shed some light on this issue. Similar arguments to the above have been used to determine the activation volumes associated with the formation and motion of Schottky and Frenkel defects in ionic crystals from measurements of the isothermal pressure dependences of the Gibbs free energies for these processes.[12] The results are in generally good agreement with modern theoretical calculations of these volume changes. As for semiconductors, with the exception of the following two recent observations,[13] there appears to be no other information to compare to.

In one observation it was noted that the ΔV associated with the formation of the neutral phosphorus-vacancy pair (E-center) defect in Si deduced experimentally from high-pressure annealing data[14] is comparable to theoretical values[4] for the volume relaxation associated with the formation of the neutral vacancy in Si. Arguments can be made that, to a first approximation, the two relaxations may be about the same.[13] In the second observation[13] it was noted that measurements of the pressure dependence of the annealing kinetics of the phosphorus-vacancy pair in its neutral and negatively charged states yield an upper bound for the volume relaxation associated with electron *capture* by this defect. This estimate (-4.8 Å^3) is in agreement with the upper bound of the relaxation associated with electron *emission* ($+5.0$ Å^3) deduced from the present method. Although the close agreement may be fortuitous in view of the assumptions involved in interpreting the annealing data, it is good that the two methods yield comparable results.

III. RESULTS AND DISCUSSION

A. Summary of results

The available results are summarized in Table I, which gives for each level the type of Si in which the level is observed, the transition involved in the emission process, the level (or trap) energy E_T measured relative to the band edge (E_c or E_v) to which the emission takes place, and the reported quantity $(\partial \Delta G / \partial P)_T$ which is deduced (before correction for the shift of the band gap) from the experimentally determined derivative $(\partial \ln e / \partial P)_T$ according to Eq. (2). The experimental uncertainty in $(\partial \Delta G / \partial P)_T$ is believed to be no more than ~10%. $(\partial \Delta G / \partial P)_T$ is expected to exhibit a weak temperature dependence[1,2] and, consequently, the temperature at which it was evaluated is also listed in Table I when this temperature is given, or it could be inferred from figures in the cited references. The temperature is not listed for several of the levels in the table, but this is not a very serious omission as the temperature dependence is relatively weak, and it is not of much consequence for the present purposes.

As already noted in Sec. II, $(\partial \Delta G / \partial P)_T$ contains a contribution from the pressure-induced shift of the Si band gap. By taking this latter shift into consideration, we can determine the two bounds on ΔV discussed in Sec. II. We illustrate the procedure for one of the levels in Table I, namely the oxygen-vacancy ($\mathrm{O}\cdot V$) pair acceptor. For this level the electron emission is from E_T to E_c, and the total experimentally deduced effect is $(\partial \Delta G / \partial P)_T = -3.6$ meV kbar^{-1}. This effect yields an upper bound of $\Delta V = -5.8$ Å^3 per emitted electron (i.e., case 1 of Sec. II). For case 2, on the other hand, the full shift of the gap (-1.5 meV kbar^{-1}) contributes to $(\partial \Delta G / \partial P)_T$. This shift has to be subtracted from the total effect (-3.6 meV kbar^{-1}) to obtain the intrinsic effect (-2.1 meV kbar^{-1}), which then yields a lower bound of $\Delta V = -3.4$ Å^3 per emitted electron. Table I lists for each level the average ΔV between the two bounds. As noted in Sec. II, this average ΔV should (within the adopted procedure) reflect the true ΔV to a maximum uncertainty due to the pressure dependence of the gap of (probably much less than) ± 1.2 Å^3 per emitted carrier. For the $\mathrm{O}\cdot V$ pair acceptor this average ΔV is -4.6 Å^3 per emitted electron.

Examination of Table I reveals some general observa-

TABLE I. Summary of parameters for several deep levels in silicon. Given are the type of transition involved (A, acceptor; D, donor), the trap energy measured relative to either the conduction-band edge (E_c) or the valence-band edge (E_v), the total pressure dependence of the change in Gibbs free energy on carrier emission, and the lattice volume relaxation (ΔV) accompanying emission. This ΔV is the average between the upper and lower bounds discussed in the text. The asterisk signifies that the pressure dependence of the capture cross section, σ, was not measured directly for these levels. σ was assumed to be independent of pressure in analogy with the other levels in the table.

Level	Si type	Transition	Trap energy (meV)	$\partial \Delta G/\partial P)$ (meV/kbar)	T (K)	ΔV[a] (Å^3 per emitted carrier)
$(O\cdot V)$	n	$A^- \rightarrow A^0$	$E_c - E_T = 164$	-3.6[b]	100	-4.6
Au	n	$A^- \rightarrow A^0$	$E_c - E_T = 553$	-1.9[c]	250	-2.0
Pt	n	$A^- \rightarrow A^0$	$E_c - E_T = 235$	-2.4[d]	~ 130	-2.6*
Pd	n	$A^- \rightarrow A^0$	$E_c - E_T = 230$	-2.4[e]	~ 110	-2.6*
S	n	$D^0 \rightarrow D^+$	$E_c - E_T = 320$	-1.7[f]		-1.5
		$D^+ \rightarrow D^{2+}$	$E_c - E_T = 590$	-2.05[f]		-2.1*
Se	n	$D^0 \rightarrow D^{2+}$	$E_c - E_T = 300$	-1.8[f]		-1.7*
		$D^+ \rightarrow D^{2+}$	$E_c - E_T = 520$	-2.1[f]		-2.2*
Te	n	$D^0 \rightarrow D^+$	$E_c - E_T = 190$	-0.9[f]	~ 70	-0.2
		$D^+ \rightarrow D^{2+}$	$E_c - E_T = 370$	-1.2[f]	~ 130	-0.7*
Fe	p	$D^+ \rightarrow D^0$	$E_T - E_v = 390$	-3.3[g]	~ 270	-4.1
V	p	$D^{2+} \rightarrow D^+$	$E_T - E_v = 289$	-2.5[g]		-2.8
Ti	p	$D^{2+} \rightarrow D^+$	$E_T - E_v = 245$	-2.0[g]		-2.0
Mn	p	$D^{2+} \rightarrow D^+$	$E_T - E_v = 234$	-0.5[g]		$+0.4$*
$P\cdot V$	n	$A^- \rightarrow A^0$	$E_c - E_T = 445$	$+1.6$[h]		$+3.8$

[a]The ΔV in this table is the ΔV accompanying *electron emission* from all the deep levels listed except those of Fe, V, T, and Mn. For these latter levels the ΔV is associated with *hole emission* (or electron capture).

[b]References 1 and 3.

[c]References 1 and 2.

[d]Reference 19.

[c]Reference 20.

[f]Reference 27.

[g]Reference 28.

[h]Reference 32.

tions. First, for all levels, except the phosphorus-vacancy pair ($P\cdot V$) deep level, which will be discussed later, $(\partial \Delta G/\partial P)_T$ is negative, a fact which is a manifestation of the experimental finding that the emission rate increases with pressure. The negative sign implies that the energy separation between the trap and the nearest band edge, i.e., $E_c - E_T$ or $E_T - E_v$, decreases with pressure.[15] Some of this decrease may be due to the decrease in the band gap with pressure, as already discussed in Sec. II. Secondly, the ΔV's are mostly negative. A negative (positive) sign for ΔV implies that the lattice relaxes *inward (outward)* [i.e., contract (expands)] upon carrier emission from these levels. An *outward (inward)* relaxation of the same magnitude should occur on capture.

The quantity we deduce is ΔV. In dealing with the lattice relaxations of interest here, an important issue is how much do the nearest-neighbor Si atoms around the defect move upon emission or capture, i.e., the change in bond length Δr. How the deduced ΔV relates to Δr is an involved issue, even for the case of totally symmetric relaxations. To determine the relationship properly requires an accurate description of the interatomic forces involved, as well as the use of elasticity theory.[16] The necessary calculations are difficult and uncertain for the relatively small relaxations of present interest. Consequently, we have resorted to approximations (discussed below), motivated by experimental and theoretical results, which we believe do lead to a reasonably accurate description. In doing so, it should be emphasized that it is the ΔV's which are the quantities deduced from the experiments, and the approximations are merely used to provide an estimate of the Δr's.

The magnitude of the ΔV's in Table I can best be appreciated by putting it in the proper perspective. The nearest-neighbor (NN) Si—Si bond length, r_0, in Si is 2.35 Å, which, for the purposes of this discussion we take to be the average distance between the defect and its four nearest neighbors for the defects in Table I. A sphere of radius 2.35 Å around the defect has a volume $V_0 = 54.33$ Å^3. If, to a first approximation, we assume that the four NN Si atoms relax equally, and that all of the relaxation ΔV is taken up by the first shell of atoms around the defect, then a relevant measure of the relaxations in Table I is the ratio $\Delta V/V_0$, or alternatively the change in bond length, $\Delta r/r_0 = \Delta V/3V_0$. Taking the $O\cdot V$ pair acceptor level as an example, the ΔV in Table I yields

$\Delta V/V_0 = -8.1\%$ and $\Delta r/r_0 = -2.7\%$, which implies an *inward* relaxation of the four nearest Si neighbors of $\Delta r = -0.06$ Å.

The approximation that all of the experimentally deduced volume relaxation ΔV is taken up by relaxation of the first shell of Si atoms around the defect cannot, of course, be strictly correct, but it does not seem to be too bad. Theoretical results[5(b)] show that the amplitudes of the atomic displacements decrease rapidly with distance from the impurity, and this is supported by experimental EXAFS results.[7,8] The EXAFS results[7] on the relaxation of the Si lattice around substitutional arsenic atoms show that the relaxation of the first shell is 6–10 times larger than that of the second shell. Similarly, EXAFS results[8] on the relaxation of the GaAs lattice around substitutional sulfur atoms show that the relaxation is largely taken up by the first-neighbor shell with "relatively unperturbed second and third neighbor shells." On the basis of the experimental[7] and theoretical[5(b)] results on Si, we estimate that our above approximation could overestimate the magnitude of Δr by as much as 30–40 %. It should also be noted that some of the centers in Table I have a symmetry-breaking Jahn-Teller distortion superimposed on the breathing-mode relaxation, so that the assumption that the NN Si atoms relax equally, is a strong approximation which has to be viewed with caution.

A third important feature of the results in Table I is the finding that in those cases where there are data on more than one charge state of a given defect (specifically the chalcogenide donors) the ΔV associated with the higher charge state (double-donor transition) is larger than that associated with the lower charge state. The trap energy for the higher charge state is also larger. We shall come back to this point later.

In an effort to obtain a meaningful comparison of the results in Table I, the levels have been divided into four groups, as indicated by the dashed lines. The first group consists of the vacancylike acceptor levels associated with the O·V pair (or A center) and the gold (Au) platinum (Pt), and palladium (Pd) impurities. The second group consists of the chalcogenide donors in their singly and doubly charged states. The third group consists of a number of 3d transition-metal donor levels, and the fourth group is simply the phosphorus-vacancy (P·V) pair acceptor.

B. Vacancylike acceptors

The results on the Au and O·V pair (or A center) acceptors were recently discussed elsewhere,[1,2] where it was concluded that they are consistent with the vacancylike character of these levels according to a model proposed by Watkins[17] and supported by cluster-model energy-level calculations.[18] Similarly, the results of Stoffer and Weber[19,20] on the Pt$^-$ acceptor (at $E_c - 0.235$ eV) and the Pd$^-$ acceptor (at $E_c - 0.230$ eV) can be interpreted in terms of this model. Specifically, all four acceptor levels are determined by vacancylike Si dangling-bond states. Their energy levels move up higher in the gap with pressure, reflecting their antibonding character.[1,2,19,20] The sign of ΔV is consistent with expectation, and the larger ΔV for the A center compared with that for the Au (and Pt$^-$ and Pd$^-$) acceptor can be qualitatively rationalized.[1,2]

To shed more light on the physical picture involved in the case of the A center and Au, Pt$^-$, and Pd$^-$ acceptors, it is helpful to recall briefly a few of the ideas behind Watkins's model. Watkins[17] considered deep levels associated with the 3d transition-metal–ion impurities in Si. His conclusions are not only relevant to the third group of levels in Table I (as discussed below), but have implications for other impurities. His analysis points to a strong contrast between interstitial and substitutional 3d impurities and leads to the following important conclusions.[17] For interstitials, the interaction between the impurities and the Si host confines the d levels to the forbidden gap, providing many deep levels. On substitutional sites, on the other hand, the impurity can be visualized as occupying a vacant Si site, and the interaction between the d levels and the four Si dangling-bond wave functions tends to repel the deep a_1 symmetry and $t(d)$ symmetry levels from the gap. Consequently, a t_2 level can be expected to appear in the gap only when there is no impurity t_2 level nearby in energy (see Fig. 1). The resulting t_2 level will be that of the vacancy (which level is known to exist in the gap), but perturbed by the impurity. This result was partly motivated by energy-level–structure calculations for the 3d ions in Si by Hemstreet,[21] which showed that

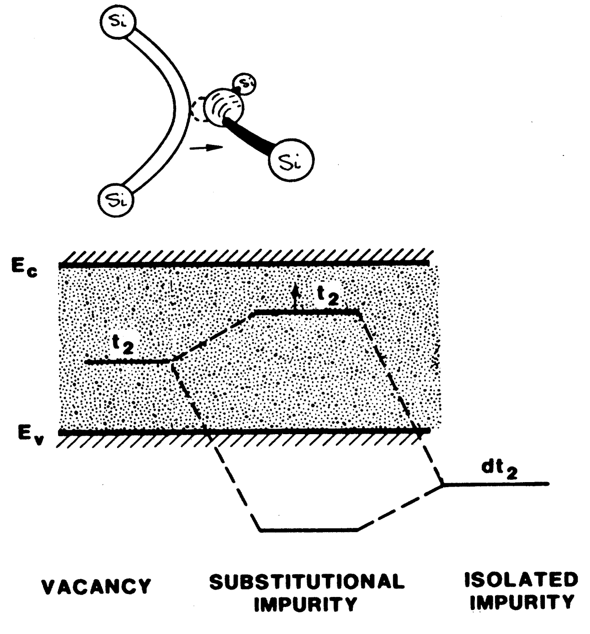

FIG. 1. (a) Configuration of substitutional closed-d^{10}-shell impurity atoms (e.g., Pt$^-$ and Pd$^-$) in Si. EPR results indicate a dihedral distortion characteristic of the negatively charged vacancy (Refs. 23 and 17). (b) The vacancylike, antibonding deep acceptor in the gap results from the interaction of a substitutional impurity dt_2 state with a Si vacancy t_2 state. The arrow indicates the expected shift of this level with pressure.

the t_2 levels in the gap are not d-like at all, but rather are mostly dangling-bond-like on the four Si neighbors, i.e., these t_2 orbitals are mostly vacancy orbitals, like those of the Si vacancy.

Watkins[17] proposed that the above vacancylike character should be generally applicable to filled d-shell substitutional transition-metal impurities near the end of each series in the Periodic Table and suggested that this should be the case for Au^0, Pt^-, and Pd^-. Pt and Pd are believed to occupy substitutional sites in Si, but Au is still controversial. The situation can be qualitatively visualized as follows. Considering Au first, we note that Au^0 has the electronic configuration $5d^{10}6s^1$. As a substitutional the Au atom occupies a vacant Si site, and the center behaves basically as a perturbed vacancy whose electronic structure is that of a closed $5d^{10}$ shell inside a vacancy. The filled Au $5d$ level is localized well below the valence-band edge, and the in-gap acceptor level (of t_2 symmetry) is vacancylike with its orbitals consisting mostly of dangling-bond states on the four Si neighbors. The Au $6s^1$ electron goes into the antibonding t_2 state and makes the center essentially isoelectronic with the negatively charged Si vacancy (V^-). The center's electronic structure can thus be designated[17] as $5d^{10}+V^-$.

This view is consistent with EPR hyperfine-interaction results,[22] which show that the $6s^1$ is largely delocalized from the Au atom. As the Au^0 center is negatively charged and antibonding in character, the capture of an electron by it can be expected to lead to a repulsive Coulombic interaction and an *outward* relaxation of the lattice, as concluded from the data in Table I. Upon subsequent emission of this electron, the lattice should then relax *inward* as we found.

Platinum has the electronic configuration $5d^9 6s^1$, so that Pt^- has the same configuration as Au^0, i.e., $5d^{10}6s^1$, and the formation of the Pt^- center can be visualized in the same way as the Au^0 center, both having the configuration $5d^{10}+V^-$. Similarly, Pd has the electronic configuration $4d^9 5s^1$, so that Pd^- has the configuration $4d^{10}5s^1$, and the Pd^- center has the configuration $4d^{10}+V^-$. In support of this picture, Watkins[17] notes that the EPR spectra[23] of Pt^- and Pd^- in Si display the unusual dihedral ($D_{2d} \rightarrow C_{2v}$) distortion characteristic of V^-.

Support for the above picture comes from cluster-model calculations of the electronic structure of Au^0 and Pt^- in Si by Alves and Leite.[18] These calculations show that the $5d$ levels of Au in Si are atomiclike, the electrons interacting very weakly with the lattice. These levels of symmetry e and t_2 lie deep below the valence band. The t_2 levels in the gap are not d-like at all, but rather mostly dangling-bond-like on the four Si neighbors. This is analogous to earlier results on $3d$ impurities.[21] Alves and Leite[18] also find nearly identical energy-level spectra and charge distribution for Au^0 and the vacancy. Thus, these results qualitatively support the vacancylike model proposed by Watkins.

The calculations[18] for Pt^- in Si show a somewhat more complicated picture than that for Au, but nevertheless the main conclusion is that the Pt^- level can be viewed primarily as vacancylike. One aspect of the results is that the $t_2(d)$ level of Pt^- is not as deep in the valence band as that of Au^0, and the interaction of this level with the t_2 vacancy orbitals forces the t_2 gap level of the vacancy higher in the gap. This finding is consistent with Watkins's model and explains why the Pt (and presumably Pd) acceptor, measured relative to E_c, is shallower than the Au acceptor (see Table I).

While the above qualitative picture probably contains much of the essential physics, some important questions remain. Unlike the EPR spectra of Pt^- and Pd^-, which are consistent with off-center substitutional sites with dihedral (C_{2v}) symmetry, the spectrum of Au^0 exhibits a distinct trigonal (C_{3v}) symmetry and is more consistent with Au occupying an interstitial position.[22] The large size of the Au atom makes it unlikely that the Au would be present as a simple interstitial, however, and the center is then most likely an interstitial Au/Si vacancy pair as was suggested some time ago by Van Vechten and Thurmond.[24] Again, in view of the large size of the Au atom, the distinction between this pair and Watkins's model of a distorted substitutional Au in a Si vacancy would appear to us to be largely a matter of semantics. The trigonal distortion can be explained by an off-center site for the Au (which is different from the distortion for Pt and Pd). The origin of such a distortion remains unknown.

The EPR results reveal the presence of an anisotropic hyperfine interaction for the Au nucleus.[22] A possible explanation for this observation is some configurational mixing interaction between $5d^{10}6s^1$ and $5d^9 6s^2$. Such an interaction is allowed in C_{3v} symmetry.[22]

The vacancylike character of the $O\cdot V$ center has long been known. The structure of this center in its negatively charged state, as seen by EPR,[17] is almost identical to that for V^-.

On the basis of the above discussion, a strong case can be made for the vacancylike character of the $O\cdot V$ acceptor and Au, Pt^-, and Pd^- acceptors. Relatively large lattice relaxation is expected to accompany electron capture or emission from vacancylike centers,[17] and the results in Table I show that the breathing-mode relaxations are fairly large. Thus, the results for these four levels are consistent with the model and provide support for it. They also suggest that the volume relaxation for the Si vacancy itself upon capture or emission should be comparable to the values for the above three acceptors, i.e., in the range of $\sim 3-6$ Å^3 per emitted electron.

C. The chalcogenide donors

The chalcogens sulfur (S), selenium (Se), and tellurium (Te) are scientifically and technologically important impurities which introduce deep donor levels in n-type Si.[25] It is well known that these impurities occupy tetrahedral sites (T_d symmetry), but there has been controversy as to whether they are interstitial or substitutional.[5,25] EPR and electron-nuclear double-resonance (ENDOR) studies have not been able to definitively resolve the controversy. Recent self-consistent total-energy calculations,[5] however, strongly favor the substitutional positions. As substitutional donors, these impurities can be visualized as occupying an undistorted Si vacancy position, and their energy levels result from the interaction between chalcogen *s* and *p* orbitals and the a_1 and t_2 states of the vacancy.[5,26] This is illustrated schematically in Fig. 2. As shown, the resulting deep level in the gap is antibonding and of a_1 symmetry. Thus, only breathing-mode relaxations are expected to accompany emission and capture processes at this level.

Jantsch *et al.*[27] reported the pressure dependences of both the single- and double-donor states of these impurities. Their $(\partial \Delta G/\partial P)_T$ results are summarized in Table I. Note that in each case the double-donor level is deeper in the gap and exhibits the larger total shift $(\partial \Delta G/\partial P)_T$ or ΔV. Both of these latter quantities have about the same values for S and Se, with the corresponding values for Te being considerably smaller. The pressure results show that the S and Se levels move higher in the gap (i.e., closer to E_c) with compression. This is what we would expect for antibonding levels. Bringing the impurity and four nearest-neighbor Si atoms closer by compression increases the level splitting depicted in Fig. 2, forcing the a_1 level higher in the gap. The situation for Te is somewhat less clear. In this case the total shifts $(\partial \Delta G/\partial P)_T$ for both donors are about half as large as those for S and Se. If the shift of the gap were taken up totally by E_c (an unlikely circumstance), then the results in Table I would imply that both Te donor levels move deeper in the gap.

Jantsch *et al.*[27] interpreted the pressure dependences of the chalcogen levels in terms of a deep-level model developed by Hjalmarson *et al.*[26] In this tight-binding model an impurity produces a deep trap if its central-cell potential alone, without any long-range Coulomb potential, is sufficiently strong to bind a state within the gap of the host. The shift of the level energy with pressure arises from the change in the interatomic transfer-matrix elements with bond length. Using this model, Jantsch *et al.* calculated energy shifts which are comparable to the observed values. The lower shifts for the Te donors are attributed to the conclusion that Te is intermediate between a deep and a shallow impurity, it being a fact that energy shifts with pressure are much smaller for shallow levels.[2,27]

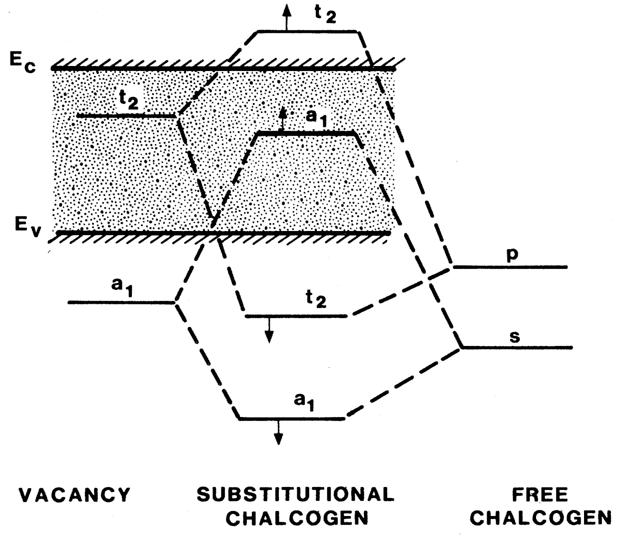

FIG. 2. Schematic energy-level scheme for the chalcogen donors in Si showing that the in-gap donor level is an antibonding level of a_1 symmetry resulting from the interaction of the vacancy a_1 orbital with the chalcogen *s* orbital (see, e.g., Refs. 5 and 26). The arrows indicate the expected shift of the levels with pressure.

For both donor levels in S and Se the breathing-mode relaxations accompanying emission (Table I) are definitely *inward.* This is what we would expect for antibonding levels. Capturing electrons at these levels can be expected to weaken the bonding between the S and Se and their four NN Si atoms; consequently, the Si atoms move away from the S and Se and strengthen their bonds with the next shell of Si atoms, i.e., *outward* relaxation. Emission of electrons, on the other hand, would strengthen the bonding and pull the four NN Si atoms closer to the S and Se, i.e., *inward* relaxation, as the results in Table I show.

The results in Table I show that the *inward* relaxation for the $D^+ \rightarrow D^{2+}$ transition is larger than that for the $D^0 \rightarrow D^+$ transition. This finding can also be rationalized in terms of the antibonding nature of the levels and the theoretical result[5] that the presence of the neutral chalcogen impurity (which has two electrons in the deep level) causes an *outward* relaxation of the NN Si atoms. This latter relaxation is a consequence of the anisotropic, antibonding charge density around the impurity. Reducing this charge density by electron emission ($D^0 \rightarrow D^+$) causes some reversal of this effect, i.e., *inward* relaxation relative to the already relaxed Si atoms around the impurity. Emission of the second electron ($D^+ \rightarrow D^{2+}$) empties the antibonding deep level and greatly strengthens the bonds of the impurity to the NN Si neighbors. Evidently, this yields a larger relaxation than that for the $D^0 \rightarrow D^+$ transition.

These considerations also explain why the level associated with the $D^0 \rightarrow D^+$ transition sits higher in the band gap than that associated with the $D^+ \rightarrow D^{2+}$ transition (see Table I). The reason is simply the following: the stronger the antibonding character of the level is, the higher its energy.

These results can be compared with self-consistent Green's-function calculations by Scheffler *et al.*[5] These authors calculated the breathing-mode relaxations associated with the presence of S, Se, and Te impurities in Si in their neutral, singly positive and doubly-positive charge states. They reported quantitative results for S and state that the relaxations for Se and Te are qualitatively similar but larger in magnitude. They find *outward* relaxations of the four NN Si atoms in the amounts of ~0.055, 0.035, and 0.02 Å for S^0, S^+, and S^{2+}, respectively. These results imply *inward* relaxations upon electron emission of ~0.02 Å for $S^0 \rightarrow S^+$ and 0.015 Å for $S^+ \rightarrow S^{2+}$. Assuming, to a first approximation, that all of the relaxation is taken up by the first shell of Si atoms around the S impurity, the experimental results in Table I yield *inward* relaxations of 0.022 Å for $S^0 \rightarrow S^+$ and 0.030 Å for $S^+ \rightarrow S^{2+}$. As can be seen, there is remarkably good (perhaps fortuitous) agreement between the experimental results and the calculations for the $S^0 \rightarrow S^+$ relaxation, but the calculations disagree with the experimental results in yielding a smaller relaxation for $S^+ \rightarrow S^{2+}$ than for $S^0 \rightarrow S^+$. Despite this fact, and given the difficulty of the theoretical results, the agreement between experimental and theoretical results could be viewed as satisfactory. The agreement may be better for Se, as the theoretical relaxations are said to be larger,[5(b)] and the experimental relaxations are about the same (Table I) as for S.

For Te the relaxation upon emission is also most likely inward, but is much smaller than S and Se. Here, also, the relaxation associated with $Te^+ \rightarrow Te^{2+}$ is larger than that for $Te^0 \rightarrow Te^+$. These features are not reproduced by the theoretical results which suggest a larger relaxation for Te than for S, but they are qualitatively consistent with the above discussion for S and Se and the view that Te is intermediate between a deep and a shallow impurity in Si.

D. 3*d* transition-metal impurities

The third group of levels in Table I consists of donor levels associated with 3*d* transition-metal impurities in *p*-type Si. These impurities are believed to be interstitials, but Mn in its different charge states can be substitutional also.[17,28] They introduce levels in the lower half of the gap, and the emission is to the valence band. Wünstel *et al.*[28] studied the effects of pressure on the emission and capture processes from the lowest levels of several of these impurities and reported the values of the trap energies and $(\partial \Delta G/\partial P)_T$ in Table I. The levels are associated with the single donor (D^0/D^+) in the case of Fe and with the double donor (D^+/D^{2+}) for V, Ti, and Mn. As we are dealing with *p*-type Si, in the present case the transient-capacitance experiment yields the thermal emission rate of holes from the singly ionized Fe center and the doubly ionized V, Ti, and Mn centers. Hole emission is equivalent to electron capture. To emphasize this point, in Table I we designate the transitions involved in the hole-emission process as $D^+ \rightarrow D^0$ for Fe and $D^{2+} \rightarrow D^+$ for V, Ti, and Mn.

Taking into consideration the shift of the band gap of Si with pressure (−1.5 meV/kbar), the data of Wünstel *et al.* show that with increasing pressure the Fe, V, and Ti levels move deeper into the gap, i.e., closer to E_v, whereas the Mn level moves higher, i.e., closer to E_c. For the Fe, V, and Ti levels there appears to be a qualitative correlation between the magnitude of $(\partial \Delta G/\partial P)_T$ and the trap energy, namely $(\partial \Delta G/\partial P)_T$ is smaller the closer the level is to E_v. The ΔV's, which, of course, follow the same trend as the $(\partial \Delta G/\partial P)_T$'s, are relatively large and negative (i.e., *inward* relaxation on hole emission or electron capture) for these levels. The Mn level is clearly different in these regards. Its ΔV is much smaller and positive, the sign being subject to the uncertainty due to the shift of the gap (see Sec. II).

Because they are interstitials (with the possible exception of Mn) and their deep levels involve the *d* electrons, these 3*d* transition-metal impurities are more complicated than the vacancylike acceptors and chalcogen donors discussed above. Wünstel *et al.*[28] examined their results in terms of a model involving hybridization between the Si and the 3*d* impurity. It is argued that pressure (or decrease in interatomic spacing) would most likely increase the hybridization, and this increase should force the levels higher in the gap, contrary to the experimental results for Fe, V, and Ti.[28] In view of this finding, the authors suggested that the observed effects may be due to the interatomic Coulomb repulsion involving the *d* electrons. Such an effect can be expected to depend systematically on the number of *d* electrons, and the authors find a linear dependence of the magnitude of $(\partial \Delta G/\partial P)_T$ on the number of *d* electrons for Fe^+, V^{2+}, and Ti^{2+}. Mn^{2+} does not follow the trend, and the authors suggest that the Mn^{2+} level may not be due to an isolated Mn interstitial.

As mentioned earlier in the paper, Watkins[17] proposed a model for interstitial 3*d* impurities in Si. The model was partly motivated by cluster-model calculations,[29] which revealed trends in the degree of hybridization between the impurity and the Si host in going across the 3*d* series. Early EPR work showed that the 3*d* impurities have well-defined localized *d* levels which are split by the T_d crystal field of the host's interstitial site with the t_2 levels below *e*.[30] Their deep levels in the gap result from a level-repulsion interaction of the impurity $e(d)$ and $t_d(d)$ orbitals with the near-valence-band edge $4t_2$ and *e* orbitals of the Si host that forces the latter orbitals into the gap and tends to confine them there.[17] The situation is depicted schematically in Fig. 3. The 3*d* orbitals of the interstitial transition-metal ion interact primarily with the $4t_2/2e$ and $7t_2/3e$ orbitals of the surrounding Si atoms. As the de/t_2 orbitals rise with decreasing number of 3*d* electrons (or atomic number *Z*), they undergo a level-repulsion (anticrossing) interaction with the near-valence-band edge $4t_2/2e$ orbitals forcing the latter into the gap. These antibonding gap states are the deep levels of the system. Ultimately, as these gap states enter the conduction band another level-repulsion interaction occurs with the Si $7t_2/3e$ orbitals as shown.

Since according to this model the deep levels in the gap are determined by antibonding states, one might expect these levels to move higher in the gap with pressure and that the relaxation would be *outward* on electron capture (or hole emission). These effects are contrary to the experimental results for the Fe, V, and Ti levels summarized in Table I. The disagreement could be due either to shortcomings in the model or to the inadequacy of simple qualitative arguments (which seem applicable to the first two groups of levels in Table I) when dealing with the complicated charge-localization effects associated with the 3*d* impurities.

As already noted, the behavior of the Mn deep level is different from those of Fe, V, and Ti. The results in Table I, despite some uncertainty due to the shift of the Si band gap, indicate that ΔV for Mn is positive upon hole emission. This would be the expected result if the Mn were a substitutional instead of an interstitial impuri-

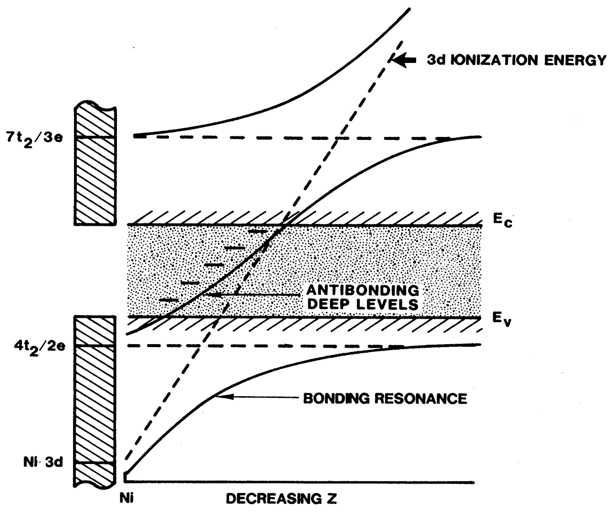

FIG. 3. Model for the interaction between the interstitial transition-metal–atom 3*d* levels and the near-band-edge Si cluster states (after Watkins, Ref. 17).

ty in Si. It is thus tempting to suggest that this is indeed the case. As a substitutional impurity, the Mn would occupy a Si vacancy site, and its deep level in the gap would, according to Watkin's model,[17] be a t_2 antibonding, vacancylike state. As discussed in Sec. III B, electron capture into this level would be expected to yield an outward relaxation of the NN Si atoms, or a positive ΔV, as observed.

E. The phosphorus-vacancy ($P \cdot V$ pair or *E* center)

The $P \cdot V$ pair defect is a dominant radiation-induced defect in phosphorus (P) -doped Si. Early EPR results,[31] observed only in the neutral state, showed that the defect is formed by the trapping of a mobile lattice vacancy next to a substitutional P impurity. It produces an acceptor level at $E_c - 0.44$ eV.

We have recently measured the pressure dependence of the electron-emission rate and capture cross section of this level and find that the level moves deeper into the gap (i.e., away from E_c) with compression.[32] The resulting $(\partial \Delta G / \partial P)_T$ and ΔV are given in Table I. These results clearly show that this level is different from the $O \cdot V$ pair and the other acceptors and most of the donors in Table I: ΔV in this case is relatively large and *positive*, i.e., *outward* (inward) relaxation upon electron emission (capture).

The sign of this relaxation can be understood in terms of the accepted model for the $P \cdot V$ pair defect.[31] The neutral charge state of the defect has five valence electrons: two are paired in the P orbital pointing towards the vacancy, two are involved in a pair bond between two of the three Si atoms around the vacancy, and the remaining unpaired electron (which is responsible for the EPR signal) is largely localized in a dangling-bond orbital on the remaining Si atom. Because of the deficiency in the number of valence electrons, this Si atom can be expected to pull away from the vacancy and strengthen its bonds to the next shell of Si atoms, i.e., it relaxes outward. Upon electron capture, the captured electron pairs with the existing unpaired electron increasing the covalent character of the bond and the Si atom relaxes toward its normal position (i.e., inward relaxation). Upon emission we expect the opposite effect, i.e., outward relaxation, and this is what is observed (Table I). Additionally, one would expect pressure to further stabilize the paired bonding configuration, and the energy level should fall deeper in the gap, as is also observed.

IV. CONCLUDING REMARKS

In this paper we have quantitatively evaluated the breathing-mode lattice relaxation accompanying carrier emission from four groups of much studied deep levels in Si: vacancylike acceptors, chalcogen donors, 3*d* transition-metal donors, and the phosphorus-vacancy pair (or *E*-center) acceptor. The evaluation method, which is based on results of high-pressure experiments, appears to be the only viable experimental method for determining these relaxations, which are important to the understanding of many of the electronic and structural properties of the defect centers involved. For the vacancylike acceptors and the chalcogen donors (which occupy substitutional sites), the relaxation is found to be *inward* (contraction) on electron emission and *outward* (expansion) on electron capture. This result is consistent with relatively simple models which reveal the antibonding character of the deep levels for these two groups. For the 3*d* transition-metal (Fe, Ti, and V) donors the relaxation is inward upon hole emission (or electron capture) and outward upon hole capture (or electron emission). This group of deep levels is more complicated than the first two groups because of the nature of the interaction between the 3*d* electrons and the Si host for these interstitial impurities. The sign of the relaxation is difficult to rationalize in terms of simple models. The behavior of the Mn deep donor is different from those of the Fe, V, and Ti deep donors in that the magnitude of the relaxation is smaller and of the opposite sign. This result suggests that the Mn may be a substitutional impurity in Si, and its deep level would then be expected to be vacancylike. Finally, the *E*-center relaxation is *outward* upon emission and *inward* upon capture, and this behavior can be explained in terms of the accepted model for this center.

Throughout the paper the comparison between the experimentally deduced relaxations and the models was largely qualitative. Unfortunately, with the exception of the chalcogen donors (and more specifically S), there are no theoretical results to compare with. However, significant advances in theoretical calculations are being made on several fronts,[3] and some of these are being applied to the lattice-relaxation problem.[33] The present results, in addition to their relevance to the better understanding of the electronic structure of the defect centers involved, provide a valuable data base for testing the calculational results and improving them.

Finally, we wish to reemphasize an important point discussed in Sec. II. The biggest uncertainty in the calculated volume relaxations in Table I derives from a lack of sufficiently reliable values for the hydrostatic deformation potentials of the band edges of Si. In addition to their importance to the present work and to the understanding of other pressure effects, these deformation potentials enter into the treatment of many properties of Si, such as the scattering of carriers by acoustic phonons and the elastic properties. Thus, there is a strong need for their accurate determination.

Note added in proof. After submitting the present work, we received a copy of a work prior to publication [D. Weider, M. Scheffler, and U. Scherz, in Proceedings of the International Conference on Defects in Semiconductors (ICDS), Budapest, 1988 (unpublished)], which presents, for sulfur in Si, self-consistent, Green's-function calculations of the local distortion at the defect and of the total crystal volume change due to electron emission. The results show that our assumption of nearly equal local and total volume changes is indeed close to reality. We thank Professor Scheffler for the copy of the unpublished work.

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[1] G. A. Samara, Phys. Rev. B **36**, 4841 (1987).

[2] G. A. Samara and C. E. Barnes, Phys. Rev. D **35**, 7575 (1987).

[3] See, e.g., *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986).

[4] M. Scheffler, J. P. Vigneron, and G B Bachelet, Phys. Rev. B **31**, 6541 (1985). This paper deals with the relaxations associated with different charge states of the Si vacancy. Other results on the vacancy can be found in G. A. Baraff, E. O Kane, and M. Schlüter, Phys. Rev. B **21**, 5662 (1980), and P. J. Kelly, R. Car, and S. T. Pantelides, in *Defects in Semiconductors,* Vols. 10–12 of *Materials Science Forum,* edited by H. J. von Bardeleben (Trans Tech, Aedermannsdorf, 1986), p. 115.

[5] (a) M. Scheffler, F. Beeler, O. Jepsen, O. Gunnarsson, O. K. Andersen, and G. B. Bachelet, in *Proceedings of the 13th International Conference on Defects in Semiconductors,* edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of AIME, New York, 1985), p. 45; (b) see also M. Scheffler, Physica B+C **146B**, 176 (1987).

[6] A brief account of some of this work was presented in *Proceedings of the 1987 Boston Meeting of the Materials Research Society,* edited by M. Stavola, S. J. Pearton, and G. Davies (MRS, Pittsburgh, 1988), Vol. 104, p. 111. The data on the $3d$ impurities in this reference were incorrectly taken to represent electron emission rather than hole emission. This has been corrected in the present paper.

[7] A Erbil, W. Weber, G. S. Cargill III, and R. F. Boehme, Phys. Rev. B **34**, 1392 (1986).

[8] F. Sette, S. J. Pearton, J M. Poate, J. E. Rowe, and J. Stöhr, Phys. Rev. Lett. **56**, 2637 (1986).

[9] M. Cardona and N E. Christensen, Phys. Rev. B **35**, 6182 (1987), and references therein. The first three values of a_v given in the text were taken from Table III of this reference and present three independent evaluations of this deformation potential attributed, respectively, to the authors, to J. Tersoff, and to C. G. Van de Walle, C. Herring, and R. M. Martin.

[10] D. D. Nolte, W. Walukiewicz, and E. E. Haller, Phys. Rev. B **38**, 6316 (1988); **36**, 9392 (1987).

[11] (a) G. A. Samara and C. E. Barnes, Phys. Rev. B **38**, 6318 (1988). (b) We presume that the $P\Delta V$ work associated with the compression of the lattice raises the energies of all the levels, especially the valence levels, relative to the vacuum level; but, for our present purposes it is the relative changes in the energies of the levels which are relevant.

[12] G. A. Samara, in *Solid State Physics,* edited by H Ehrenreich and D. Turnbull (Academic, New York, 1984), Vol. 38, p. 1.

[13] G. A. Samara, Phys. Rev. B **37**, 8523 (1988).

[14] C. E. Barnes and G. A. Samara, in Vol. 46 of *Materials Research Society Symposium Proceedings,* edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (MRS, Pittsburgh, 1985), p. 471.

[15] We recall here that $\Delta G = \Delta H - T\Delta S$, where ΔH and ΔS are the total enthalpy and entropy changes accompanying carrier emission. ΔH is a measure of the trap energy $E_c - E_T$ or $E_T - E_v$. In the absence of a large entropy contribution, a negative $\partial \Delta G/\partial P$ implies a negative $\partial \Delta H/\partial P$.

[16] M. Stoneham, B. Pajot, and H. Schober, J. Phys. C **21**, 4687 (1988).

[17] G. D. Watkins, Physica B+C **117&118B**, 9 (1983).

[18] J. L. A. Alves and J. R. Leite, Phys. Rev. B **30**, 7284 (1984). See also J. Phys. C **17**, L771 (1984).

[19] W. Stöffler and J. Weber, Phys. Rev. B **33**, 8892 (1986).

[20] W. Stöffler and J. Weber, in *Defects in Semiconductors,* Vols. 10–12 of *Materials Science Forum* edited by H. J. von Bardeleben (Trans Tech, Aedermannsdorff, 1986), p. 705.

[21] L. A. Hemstreet, Phys. Rev. B **15**, 834 (1977).

[22] M. Höhne, Phys. Status Solidi B **99**, 651 (1980); **109**, 525 (1982).

[23] H. H. Woodbury and G. W. Ludwig, Phys. Rev. **126**, 466 (1962).

[24] J. A. Van Vechten and C. D. Thurmond, Phys. Rev. B **14**, 3539 (1976).

[25] H. G. Grimmeiss, in *Annual Reviews of Materials Science,* edited by R. A. Huggins (Annual Reviews, Inc., Palo Alto, CA, 1977), Vol. 7, p. 341

[26] H. P. Hjalmarson, P. Vogel, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

[27] W. Jantsch, K Wünstel, O Kumagai, and P. Vogel, Phys. Rev. B **25**, 5515 (1982); Physica B+C **117&118B**, 188 (1983).

[28] K. Wünstel, O Kumagai, P. Wagner, and W. Jantsch, Appl. Phys. A **27**, 251 (1982).

[29] G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. B **23**, 1851 (1981); **25**, 4962 (1982).

[30] G. W. Ludwig and H. H. Woodbury, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1962), Vol. 13, p. 223.

[31] G. D. Watkins and J. W. Corbett, Phys. Rev. **134**, A1359 (1964).

[32] G. A. Samara (unpublished).

[33] See, e.g., Refs. 3–5 and 16, and references therein.