Uniaxial stress study of photoluminescence defects created by noble-gas implantation into silicon

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We report uniaxial stress measurements on the I_1 photoluminescence spectrum in silicon at 1.0182 eV associated with a multivacancy or self-interstitial complex, and on similar spectra arising from modifications of the I_1 defect by implantation of the noble gases He, Ne, Ar, Kr, and Xe. The splittings are in all cases due to orientational degeneracy effects and all defects belong to the C_{3v} symmetry group except the Xe defect which has tetragonal symmetry. In the former cases, the splitting rates are unusually small and highly nonlinear even at stresses as low as 100—200 MPa. We give evidence for excited states and suggest that they are mixed by the stress with the optical ground states causing the nonlinearities. It is concluded that the lack of electronic degeneracy—obvious from the present stress measurements and recent Zeeman data—is due to large internal local strains around the defects. Thermal dissociation energies of ≈ 50 meV are found for all of the defects. The line shifts under temperature variation do not follow the band-gap shift as is characteristic of deep defects.

I. INTRODUCTION

Implantation of arbitrary ions into silicon or irradiation of silicon with neutrons creates a defect which emits a photoluminescence spectrum at 1.0182 eV usually labeled I_1 or W.[1] This very common, intrinsic defect has been associated with multivacancies, and in particular, tentative correlations were made with the EPR $P1$ center (a pentavacancy with C_{1h} symmetry),[2] the EPR A3 center (a tetravacancy with C_{3v} symmetry),[3] or an interstitial-related center like the theoretically predicted trigonal di-interstitialcy.[4] A recent photoluminescence study has shown that the I_1 defect belongs to the C_{3v} trigonal symmetry group[5] and hence, correlations with EPR centers of different symmetry were excluded.

Photoluminescence spectra of very similar general appearance to I_1 arise when the noble-gas ions He, Ne, Ar, or Kr are implanted into silicon with high energy (≈ 1—2 MeV) followed by heating at moderate temperatures (200—550 °C). The no-phonon (NP) transitions appear at 1.0118 eV (He), 1.0144 eV (Ne), 1.0093 eV (Ar), 1.0045 eV (Kr), and 1.0008 eV (Xe).[6,7] These line positions exhibit systematic shifts as a function of the noble-gas mass, and similar systematic trends were found for the energies of various local modes, the vibronic coupling of the defects, and the formation temperatures of the defects. Based on these and other observations it was obvious that they form a "family" of related centers in which a noble-gas atom slightly modifies the basic I_1 defect, e.g., by substituting for a vacancy and introducing mass- or volume-dependent local strains. The new defects were also observed after low-energy noble-gas ion bombardment—as in ion-beam etching processes—without the need of annealing.[8] In addition, the present authors observe these defects in low concentrations after implantation with arbitrary ions (e.g., with ^{28}Si) when the subsequent annealing is performed in a noble-gas ambient. These findings also suggest that the basic I_1 defect produced in a primary damage event traps a noble-gas atom to form a new modified defect.

Only the I_1 and the He defect spectra have been studied in some detail under uniaxial stress.[5,6] For the other defects, merely preliminary stress data are available in the low-stress regime.[6,7] It is the main purpose of the present paper to study all of the noble-gas-induced centers including the Xe case up to high stress. Data on the temperature dependence of the transition energies, linewidths, and intensities are also presented and thermal dissociation energies of the excited defect are obtained.

II. EXPERIMENTAL

The samples for the stress experiments were cut from different p- and n-type Czochralski and float-zone silicon crystals (resistivity 0.3—1000 Ω cm). Typical dimensions were $2\times2\times7$ mm^3 and stress was applied along the long axis parallel to ⟨001⟩, ⟨111⟩, and ⟨110⟩ crystal directions. The ion implantation was carried out at room temperature at energies of 350 keV and doses of 10^{16} cm^{-2}. For each defect the intensity of the spectrum was optimized by appropriate annealing treatments[7] carried out in argon atmosphere. The luminescence was excited by argon (514.5 nm) or krypton (647.1 nm) ion lasers; for the temperature-controlled measurements the excitation power was kept below 30 mW. The samples were immersed in liquid helium or cooled by a helium-gas stream. The spectra were recorded using a grating monochromator (Spex 1702), a cooled germanium-diode detector (North Coast E0 817L), and conventional lock-in amplification.

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III. UNIAXIAL STRESS MEASUREMENTS

A. Low-temperature data

Figure 1 shows the response to uniaxial stress **X** along ⟨001⟩, ⟨111⟩, and ⟨110⟩ of the I_1, He, Ne, Ar, and Kr defect NP lines. The results are in all cases strikingly similar.

(a) For **X**||[001], the lines do not split and are unpolarized. The shift rates are nonlinear even for X as low as ≈ 0.2 GPa. Initially, the lines shift to higher energies

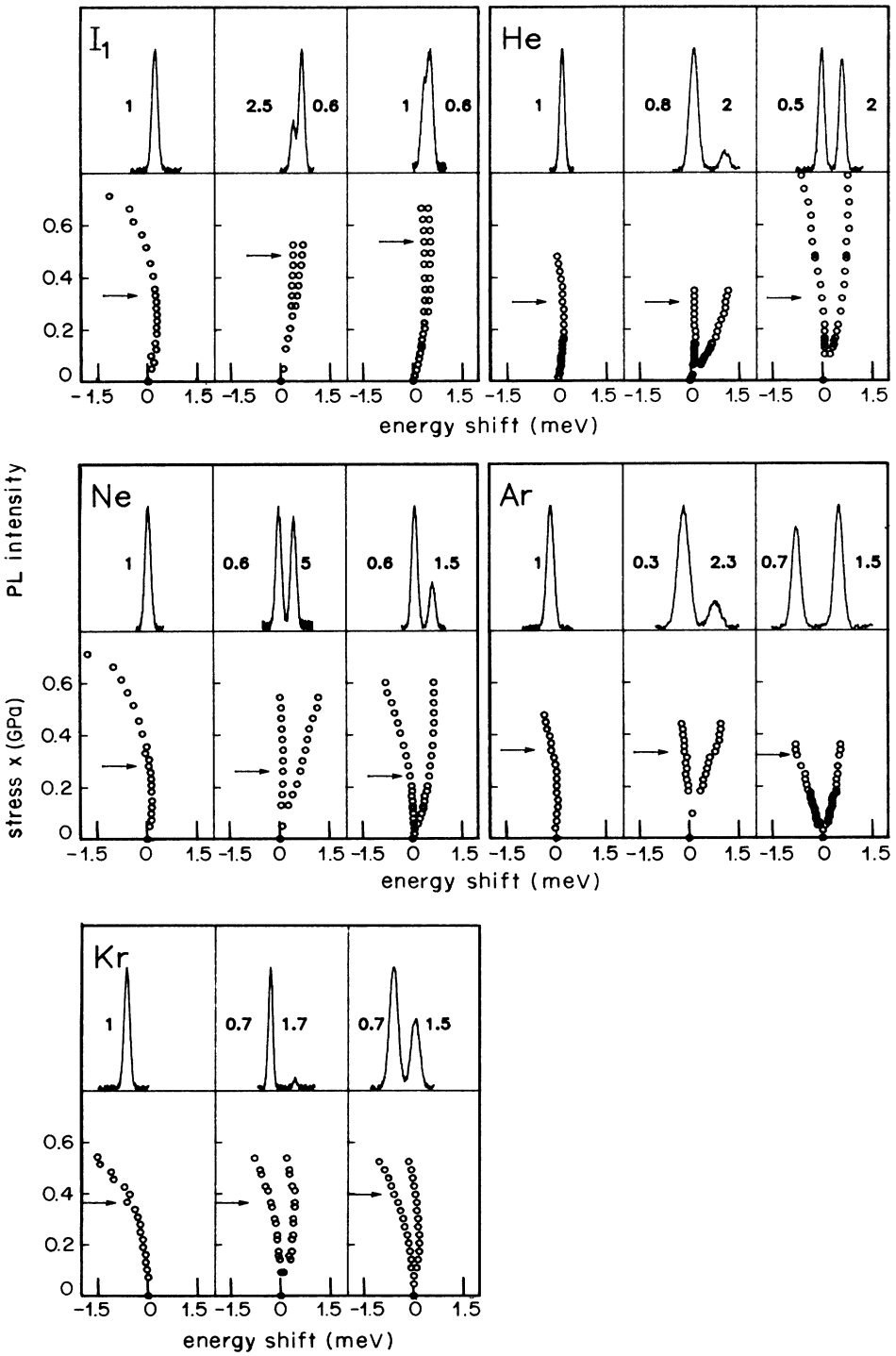

FIG. 1. Stress dependence of I_1 and the He-, Ne-, Ar-, and Kr-related NP lines for stress **X**||[100], **X**||[111], **X**||[110] from left to right. The spectra displayed were recorded at the stress values indicated by an arrow in the diagrams below. Numbers give the experimental degree of polarization π/σ. Fit parameters for the low-stress region are listed in Tables I and II.

with smaller rates for larger noble-gas mass, this shift vanishing in the Kr case. For larger stress, the shifts become negative.

(b) For $\mathbf{X}||[111]$, the lines spilt into two components with unequal intensities showing no thermalization among each other. The weaker component is always predominantly π polarized (i.e., the electric field vector is parallel to the stress, $\mathbf{E}||\mathbf{X}$) while the stronger component is mainly σ polarized, $\mathbf{E}\perp\mathbf{X}$. The stronger component is higher in energy for I_1 but the opposite ordering applies to all other defects. The nonlinearities of the shift rates are smaller than for $\mathbf{X}||[001]$.

(c) For $\mathbf{X}||[110]$, the lines split into two components with comparable intensities. The lower-energy component is mainly σ polarized, the higher-energy component is π polarized except for I_1 which again shows the inverted order. Also for this stress direction, the shift rates are nonlinear even at low stress.

Our data on the He and I_1 defect lines are very similar to those in Refs. 5 and 6. Using standard perturbation theory,[9] the number of components, the relative intensities, and the polarizations are only consistent with the assumption of a (π oscillator) transition between nondegenerate states at defects of trigonal (C_{3v}) symmetry; i.e., all splittings are due to the partial lifting of the orientational degeneracy of randomly oriented defects. This interpretation also explains that the line components split apart by the stress do not thermalize (cf. also Sec. III B).

In view of the strong nonlinearities we have confined ourselves to the low-stress regime in the evaluation of piezo-optic parameters A_1 and A_2 applying to trigonal centers in linear perturbation theory. Values of A_1 and A_2 obtained from the data are given in Tables I and II. Within a factor of 2, the mean values are the same as those reported by Tkachev *et al.* for He...Kr.[6] For I_1, our data are inconsistent with those of Ref. 5, obviously due to a mistaken interpretation of the spectra in that work.[10] Table I shows the systematic trend of the center-of-gravity shifts mentioned above as reflected in the parameter A_1. No corresponding trend can be stated for A_2 which describes the splitting of the lines. Table II is a compilation of the center-of-gravity shifts in the nonlinear region ($X=0.3$ GPa). For all defects, the shifts have a clear ordering being largest for $\mathbf{X}||[001]$, smaller for $\mathbf{X}||[110]$, and least for $\mathbf{X}||[111]$.

TABLE I. Center-of-gravity shifts for $X=0.3$ GPa and splitting parameters A_2 as averaged from Table II.

	Shift of center of gravity (meV) for $X=0.3$ GPa			Splitting parameter A_2 (meV/GPa)
	$\vec{X}\|\|\langle 100\rangle$	$\vec{X}\|\|\langle 110\rangle$	$\vec{X}\|\|\langle 111\rangle$	
I_1	0.25	0.41	0.42	−0.19
He	0.18	0.28	0.36	1.1
Ne	0.05	0.19	0.25	1.0
Ar	-0.09	-0.05	0.0	1.2
Kr	-0.29	-0.11	-0.11	0.75

TABLE II. Piezo-optic parameters A_1 and A_2 as experimentally determined for stress along the three principle crystal directions (in meV/GPa).

	I_1	He	Ne	Ar	Kr
		⟨100⟩ direction			
A_1	2.2	1.9	1.7	0.1	−0.4
		⟨111⟩ direction			
A_1	1.64	2.7	1.2	0.06	−0.32
A_2	−0.23	1.25	0.9	1.0	0.72
		⟨110⟩ direction			
A_1	2.16	1.3	1.6	0.43	−0.1
A_2	−0.2	0.9	1.45	1.46	0.8
		Mean values			
A_1	2.0	1.97	1.5	0.2	−0.27
A_2	−0.22	1.08	1.18	1.2	0.76

This ordering is reminiscent of the lowest valley-orbit state (of symmetry Γ_1) of substitutional donors in silicon, however scaled down in our present case by a factor of ≥ 10. The "hardness" of the defects under stress expressed by the small values of A_2 is remarkable; the splitting rate is essentially smaller than for other optical defects in silicon[11] and also smaller by a factor of ≈ 100 than the splitting of the conduction- or valence-band edges.[12] Therefore, the electron and the hole involved in the excitonic recombination process cannot even approximately be described as simple bandlike particles. Zeeman measurements[7] show that none of the NP lines under discussion splits in a magnetic field up to 5.3 T. This confirms that there are no electronic degeneracies in the upper and lower transition ground states. In particular, the orbital momentum of the excitonic hole must be quenched consistent with a deep hole binding in the strain field of the ⟨111⟩ axially symmetry defect.[13] Exciton states produced by large internal perturbations can be rather insensitive to externally applied stress smaller than the built-in stress. This would explain the "hardness" of the defect under stress. An increasing size of the noble-gas atom that is incorporated in the defect will increase the internal strain and, hence, could reduce the shift rate A_1 under external stress in accordance with the experimental observations.

The observed nonlinearities in the stress response require at least one interacting excited state to lie close (i.e., within a few millielectron volts) to the upper state of the luminescence transition. In no case have measurements at increased temperatures (up to ≈ 40 K) led to the direct observation of emission from such excited states. However, the existence of at least one excited state for each defect can be concluded from the temperature dependence of the NP lines (see Sec. IV) where energies in excess of the luminescing ground state of order 10 meV are obtained.

The defect properties discussed so far could be related

to a dangling bond left over after reconstruction in a (multi-) vacancy complex. In the EPR A_3 defect, e.g.—tentatively associated with the I_1 defect in previous works[5]— the magnetic resonance is interpreted as resulting from an unpaired electron in a dangling bond.[3] Such a highly localized state is expected to be rather insensitive to changes in its neighborhood such as the introduction of a noble-gas atom. Also, the dangling bond would have the correct ⟨111⟩ axial symmetry required by the experiments.

The unpaired electron in the dangling bond (i.e., a deep hole state) could then capture an additional electron to form the emissive state. The recombination of these particles could account for the luminescence signal.

B. Reorientation effects

Tkachev and Mudryi[14] did not resolve the line splitting under [110] directed stress but they reported the observation of frozen-in dichroism in the I_1 line, and interpreted it as a consequence of atomic reorientation. We tried to verify this phenomenon by directly measuring the intensity ratio of the two stress-induced components for **X**||[110] of each defect NP line. This experiment was performed in emission since all lines absorbed only weakly. (The absorption coefficient in our best neutron irradiated sample is $\alpha \leq 0.3$ cm^{-1} for I_1.) When the temperature was varied from 4.2 K to ~40 K at constant stress the intensity ratios did not essentially change up to 30 K (Fig. 2). Variations of a factor of 2 between 30 and 40 K are considered to be artifacts as the absolute intensities decrease rapidly (see Sec. IV) essentially reducing the experimental accuracy;[15] also, an increasing intensity ratio at one selected stress value should not be inverted to a decreasing ratio at a slightly lower stress as for the Ar⟨111⟩ case in Fig. 2. When the stress is varied at constant sample temperature, only modest variations of the intensity ratios are observed (Fig. 3). They are much smaller than expected for a Boltzmann population of the luminescing states with an energy spacing equal to the spectroscopic line splitting (compare the solid lines in Fig. 3). Stress-induced mixing of excited states and hence, stress-dependent transition probabilities could rather explain these slight variations. From these results, reorientation of the noble-gas defects at low temperature seems very unlikely.[16] Therefore, we conclude that the defects do not incorporate a highly mobile atom like an interstitialcy.

C. The xenon case

The xenon NP line exhibits a phonon side-band structure totally different from the other noble-gas defect lines.[7] Under stress it shows also different behavior (see

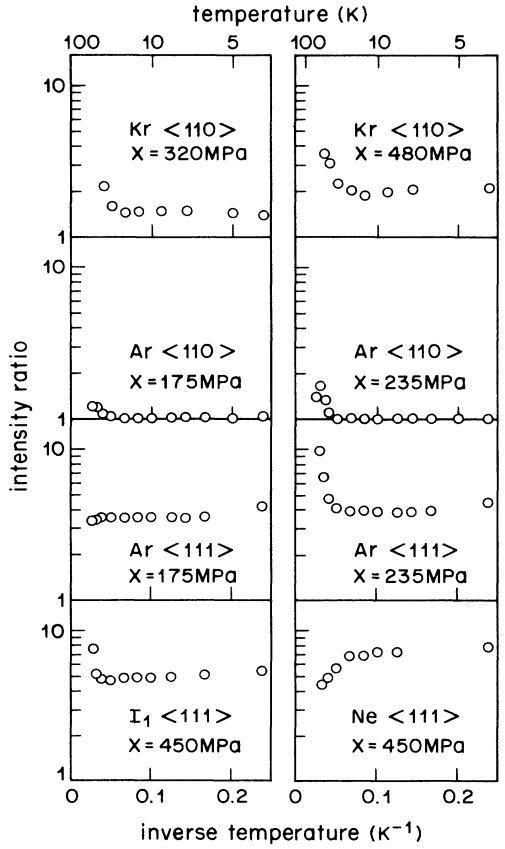

FIG. 2. Intensity ratios of stress split components versus temperature for several NP lines. For temperatures > 30 K the absolute line intensities drop off and the results become unreliable.

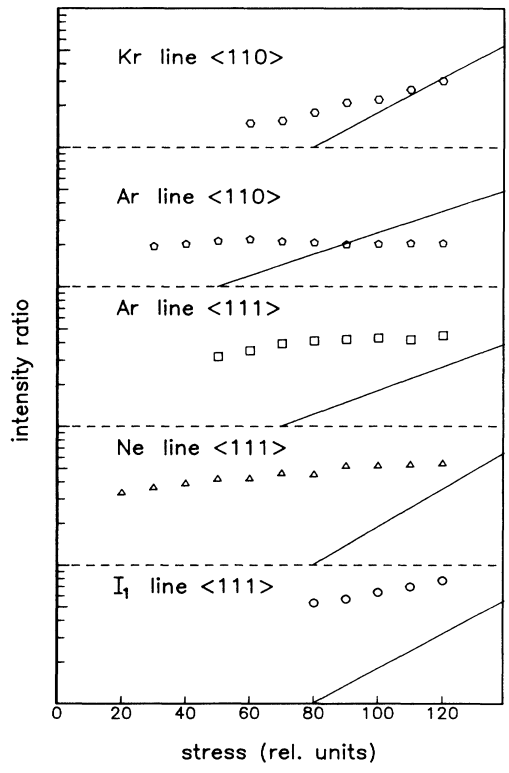

FIG. 3. Intensity ratios of stress split components versus stress for several NP lines (temperature kept constant). Solid lines represent Boltzmann laws $\exp(-E/kT)$ with E set equal to the line splittings.

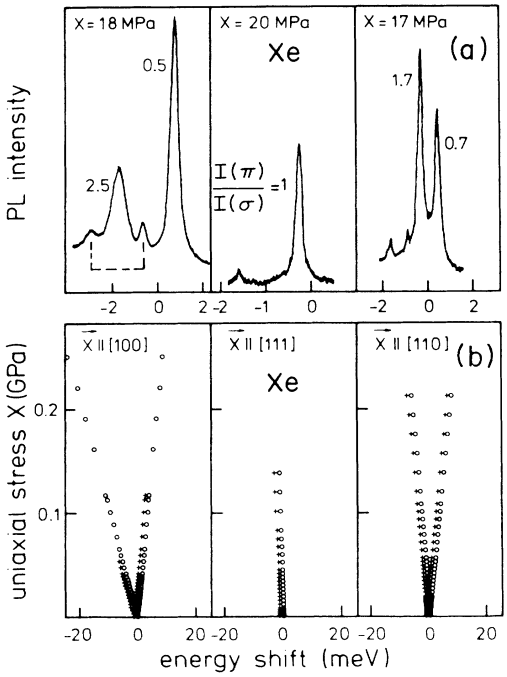

FIG. 4. (a) Splitting of the Xe-related NP line under uniaxial stress $\mathbf{X}\|[100]$, [111], and [110]. (b) Spectra at selected stress values. Numbers give the degree of polarization π/σ. The small peak at ~ 1.5 meV lower energy shows exactly the same splitting as the NP line (dashed lines).

Fig. 4). The line splits into 2, 1, and 2 nonthermalizing components for stress $\mathbf{X}$ parallel to [100], [111], and [110], respectively. All splittings are linear and exactly identical for the main line and a weak additional peak ≈ 1.5 meV lower in energy. All experimental findings including line shifts, polarizations, and intensities of the two lines follow closely the theoretical predictions for a π oscillator transition between nondegenerate states at a center of tetragonal symmetry.[9] The splitting parameters which we evaluate are $A_1 = -93$ meV/GPa and $A_2 = 33$ meV/GPa. These values are comparable to the parameters describing the splitting of the conduction band under stress.[12] The simplest theoretical explanation for the stress behavior of the xenon PL can be given in a pseudodonor model, i.e., this defect is assumed to bind a hole deeply and an electron in a shallow state. The sixfold multiplicity of valley-orbit states split in the T_d crystal environment into irreducible states of group-theoretical character A_1, E, and T_1,[17] is further lifted by a defect-produced, internal $\langle 100 \rangle$ distortion (like in the case of the C-line defect[18]). The states must be ordered so that the lowest-lying level is of character T_z because T_z is the only nondegenerate state splitting linearly with the rate of the conduction band[18] as required by our stress data.

IV. TEMPERATURE-CONTROLLED EXPERIMENTS

At elevated temperatures up to ≈ 40 K, no emission from excited upper defect states emerges in any of the noble-gas centers. Dipole transitions from such states whose existence is evident from the stress data seem to be forbidden. However, the temperature-controlled data corroborate their existence and yield excitation energies from the upper ground state between 10 and 20 meV.

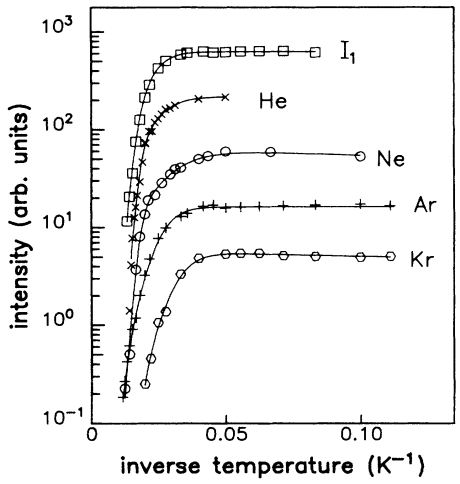

FIG. 5. Temperature dependence of the PL intensity of the various NP lines. Solid lines are least-squares fits using the expression in the text and the parameters of Table III. For Ne and Kr, the sample dependent initial increase in intensity for 4 K $< T <$ 20 K was formally taken into account introducing into the expression an additional energy term with $E = -1$ meV.

In Fig. 5, we plot absolute PL intensities as a function of temperature for I_1 and the He, Ne, Ar, and Kr modified defects. We neglect effects due to vibronic coupling since this is weak, and fit the experimental points with the conventional expression

$$I(T)/I(0) = [1 + C_1 \exp(-E_1/kT) + C_B T^{3/2} \exp(-E_B/kT)]^{-1} .$$

This expression describes the thermal partition of localized carriers between the radiative ground state, an excited state at an excess energy E_1, and the closest band edge at an activation energy E_B. The intensity of all lines drops sharply beyond 40 K with a dissociation energy (equal to the activation energy E_B) of ~ 50 meV (see Table III). The total exciton binding energies, on the other hand, as given by the displacement of the NP lines from the excitonic gap, $E_{gx} = 1.1548$ eV, range from 135.9 meV (I_1) to 150.3 meV (Kr). Hence, E_B is related to the release of *one* particle from the localized exciton whereas the remaining

TABLE III. Parameters describing the temperature dependence of the NP lines (see the text).

	I_1	He	Ne	Ar	Kr
E_B (meV)	50	50	55	45	55
$C_B(T^{-3/2})$	20	300	103	30	8×10^3
E_1 (meV)	20	10	10	15–20	20
C_1	150	30	20	400	10^3

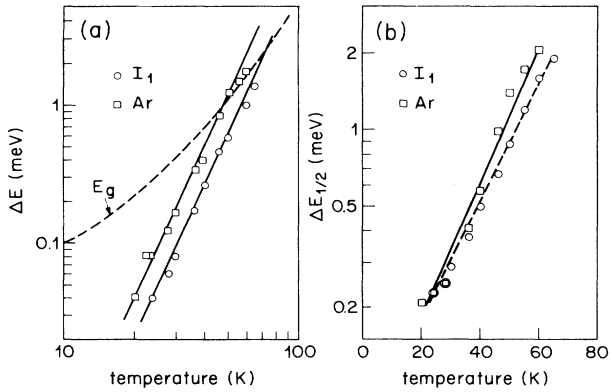

FIG. 6. (a) Shift of the Ar and I_1 NP lines with temperature. The temperature dependence of the band gap (Ref. 26) is shown by a dashed line for comparison. (b) Dependence of the halfwidth of the lines on temperature. Solid and dashed lines are least squares fits to the data points of I_1 and Ar.

energy difference, between 100 and 115 meV, is related to the binding of the primarily bound particle. The binding energy E_B of the more weakly localized particle is close to the ionization energies of common shallow donors or acceptors in silicon. Good fits to the data points in Fig. 5 are not possible for any of the defects unless an intermediate excited defect state is assumed at $E_1 = 10$–20 meV (see Table III). These excited states may be the levels which cause the nonlinear behavior of the NP transitions under stress.

The NP linewidths and NP line positions which we observe as a function of temperature for the I_1 and Ar defects are typical of deep defects. The position of both lines does not follow the temperature shift of the gap [Fig. 6(a)] but can be described by $\Delta E = h\nu(2K) - h\nu(T) \sim T^x$ with $x = 3.7 \pm 0.5$ between 25 and 60 K. The width of both lines [Fig. 6(b)] is approximately constant from 2 to 20 K. It is probably determined by inhomogeneous microscopic strain since it is slightly sample dependent. Above 20 K, the widths are proportional to $\exp(T/T_0)$ with $T_0 = 18$ K (I_1) or $T_0 = 16$ K (Ar).

V. SUMMARY

We have studied under uniaxial stress the photoluminescence of the I_1 defect and similar spectra modified by the incorporation of the noble gases He, Ne, Ar, and Kr into the I_1 defect. Our stress measurements show that all defects possess trigonal (C_{3v}) symmetry. The luminescent transition occurs between nondegenerate states and is polarized along the defect axis (π oscillator). The splittings are unusually small, by a factor of ~ 100 less than the band splittings. In all cases stress-induced mixing with excited states a few meV in excess of the luminescing ground states are observed. The existence of such excited states is corroborated by temperature-controlled experiments. The thermal dissociation energies of the defect lines are close to 50 meV in all cases. For sample temperatures between 4 and 30 K no reorientation of the centers was found. The dependence of the linewidths and the line positions on temperature are typical for deep centers.

The xenon-related defect is fundamentally different from the He, Ne, Ar, and Kr cases consistent with the different side-band structure of the spectrum. Its symmetry is tetragonal ⟨100⟩, the no-phonon emission being polarized along the defect axis.

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[14]V. D. Tkachev and A. V. Mudryi, in *Radiation Damage Defects in Semiconductors—1976 (Dubrovnik)*, Proceedings of the International Conference on Radiation Effects in Semiconductors, Inst. Phys. Conf. Ser. No. **31**, edited by N. B. Urli and J. W. Corbett (IOP, Bristol, 1977), p. 231.

[15]The main source of errors are temperature drifts during the spectral scans, especially in the region where the PL intensity varies strongly with T. For Ar, e.g., temperature fluctuations from 40 to 41 K results in intensity fluctuations of 10%.

[16]In disadvantageous cases reorientation can escape observation in luminescence experiments. If, e.g., reorientation can occur only in an excited state of the defect, but due to the center density, transition lifetime and pumping conditions the defects remain most of the time in the ground state, no change in orientation statistics will be observed.

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