Infrared and far-infrared absorption of B- and P-doped amorphous Si

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We present measurements of the infrared and far-infrared absorption spectra of B- and P-doped a-Si(H). We have identified in these spectra local modes of the B–H and B–Si bands. The intrinsic infrared absorption of the Si-Si network is greatly enhanced by the presence of the dopants. Transverse effective charges are evaluated and discussed in terms of the bond-orbital model.

I. INTRODUCTION

The first-order ir absorption by lattice modes, forbidden by symmetry in c-Si, becomes weakly allowed in the amorphous modification of this material. Although the mechanism of this ir activity of the a-Si modification is not well understood, a model attributing it to fluctuations in the bond lengths has been published.[1,2] It has also been shown recently[3] that strongly electronegative impurities, such as fluorine, can highly enhance the infrared activity of a-Si. Strong modifications in the fundamental ir absorption spectrum of a-Si are produced by doping with H.[4] This element, believed to attach itself covalently to free Si bonds, introduces a strong quasilocal mode immediately above the top of the "transverse-acoustic" phonon band (at ~ 210 cm^{-1}).[4]

In this paper we discuss the effect of B and P, the two standard dopants for optoelectronic applications,[5] on the ir absorption of a-Si. The ir spectra of the doped samples show the characteristic vibrations of the B–H and B–Si bonds at frequencies above the fundamental vibrations of the Si-Si network. Besides these "local" modes the fundamental absorption, in the region between 50 and 550 cm^{-1}, is strongly enhanced by the doping, thus emphasizing the quasiforbidden, residual nature of this absorption in the intrinsic a-Si. From the magnitude of the absorption enhancement, effective dynamical charges for the Si–P and the Si–B bonds are derived. A charge for the Si–B bonds can also be derived from the local modes around 700 cm^{-1}. These charges are shown to agree with predictions based on Harrison's bond-charge model.[6]

II. EXPERIMENT

The samples used in these measurements were prepared on polished intrinsic Si substrates ($\rho > 400$ ohm cm) by glow-discharge decomposition of SiH_4-PH_3 and SiH_4-B_2H_6 mixtures. Their thicknesses range from 15 to 50 μm.

The partial pressures of the gases and the microwave power used during the preparation are given in Table I. The far-infrared and infrared spectra of the B- and P-doped samples were measured with a Bruker IFS 114 infrared Fourier spectrometer and a Perkin-Elmer 283 double-beam grating spectrometer, respectively. The thicknesses of the samples were measured with a Tallysurf gauge. The absorption coefficients were then calculated from the formula $T = (1-R)^2 e^{-\alpha d}/(1-R^2 e^{-2\alpha d})$, and the results are described in the next section.

In order to determine the B and P concentration in the sample we measured photoelectron spectra of the $2s$ and $2p$ levels of Si and P and the $1s$ levels of B excited by Al $K\alpha$ radiation. The observed integrated signals were corrected for photoabsorption cross section with the values

TABLE I. Preparing parameters and thickness of sample used in experiment. $P(SiH_4) = 0.4$ mbar; $[Ar]/[SiH_4] = 1$; rf input power is 0.2 W/cm^2; the microwave frequency is 1.6 MHz.

Sample	$P(B_2H_6)/P(SiH_4)$	$P(PH_3)/P(SiH_4)$	Thickness	Concentration of B or P (C_i)
a-Si (101)	1×10^{-2}		50 μm	0.01
a-Si (102)	5×10^{-2}		16 μm	0.09
a-Si (103)	2×10^{-1}		18 μm	0.29
a-Si (104)		1×10^{-2}	19 μm	0.01
a-Si (105)		1.1×10^{-1}	21 μm	0.1
a-Si (106)		2.5×10^{-1}	21 μm	0.2

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of these parameters interpolated from the tables of Leckey *et al.*[7] We found for sample a-Si (103) a ratio of B to Si atomic concentration of $40 \pm 5\%$ and for a-Si (105) a ratio of P concentration to Si of $14 \pm 5\%$. These figures agree within experimental error with the nominal ratios of gas pressures keeping in mind that the B_2H_6 molecule has two B atoms. We thus take from now on the nominal gas ratios as the measure of the impurity concentrations in the samples. In order to check the linearity of this scale, we performed electron microprobe measurements of the $K\alpha$ lines of P and Si in samples Si (104), (105), and (106) and pure a-Si. The ratio of P to Si atoms was found to follow the nominal gas values to within 10%. After correcting for penetration depth of the 15-keV electrons [~3 μm (Ref. 8)] and absorption at the K edge of Si (Ref. 9) we find for sample Si (106) a P to Si concentration ratio of $24 \pm 5\%$.

Using the proportionality constant of Ref. 10 we estimated the H concentration of the lightly doped samples (101) and (104) from the strength of the wagging band at 640 cm^{-1}.[10] We found it to be 3 at. % H for sample (101), 7 at. % for sample (104), and 20 at. % for sample (106). No reliable estimates of the H concentration could be made for the heavily B-doped samples as these wagging modes seem to overlap with other vibrations to be discussed below.

III. RESULTS

The absorption spectra of the B-doped and P-doped samples are shown in Figs. 1 and 2, respectively, in the spectral region above the fundamental absorption of the Si matrix ($\omega > 550$ cm^{-1}). The spectra of samples (101) and (104) are basically the same as those of undoped samples. With increasing B concentration, however, one notes in Fig. 1 the appearance and growth of a band at 2475. In view of the fact that the stretching mode of the bonding B–H bonds in B_2H_6 occurs at 2609 and 2520 cm^{-1} and that of BH_3 at (2560 ± 100) cm^{-1} (Refs. 11 and 12) we assign this peak to B–H bonds. No trace is seen of the stretching modes of the bridging H at ~1900 cm^{-1} (Refs. 11 and 12) in our spectra. We thus do not believe such a type of hydrogen exists in our samples in significant amounts, opinions found in the literature notwithstanding.[13] We note that as the B–H stretching mode increases in strength the Si–H counterpart decreases. Also, the wagging band of sample (101) at 640 cm^{-1} is swamped in the heavily doped cases by something broader which can be attributed to the Si–B vibrations.[14]

In Fig. 2 one sees for sample (104) the standard vibrations of the Si–H bonds.[15] In the 2000–2100 cm^{-1} bond-stretching region the spectrum is dominated by single Si–H bond vibrations at 1990 cm^{-1}. As mentioned above, an analysis of the strength of the bond-wagging bands (640 cm^{-1}) yields an H concentration of 7%. For the heavily P-doped sample (106) the strength of the wagging band increases 2.5 times with respect to that of (104). The H concentration should thus be ~20%. The spectrum of sample (106) actually looks almost identical to that of sample 53-H (prepared by sputtering) shown in Fig. 5 of Ref. 15.

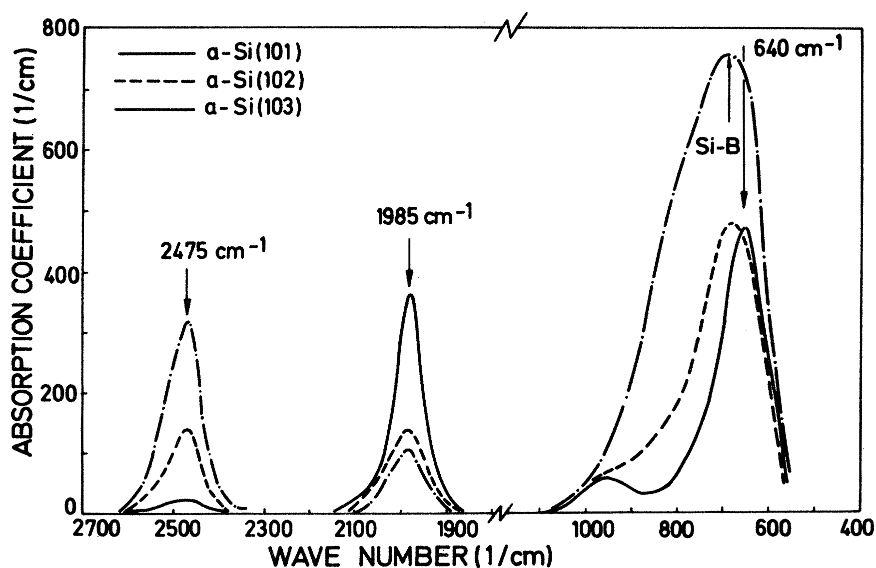

FIG. 1. Infrared-absorption spectra of three B-doped a-Si(H) samples in the region of local modes. Sample data in Table I.

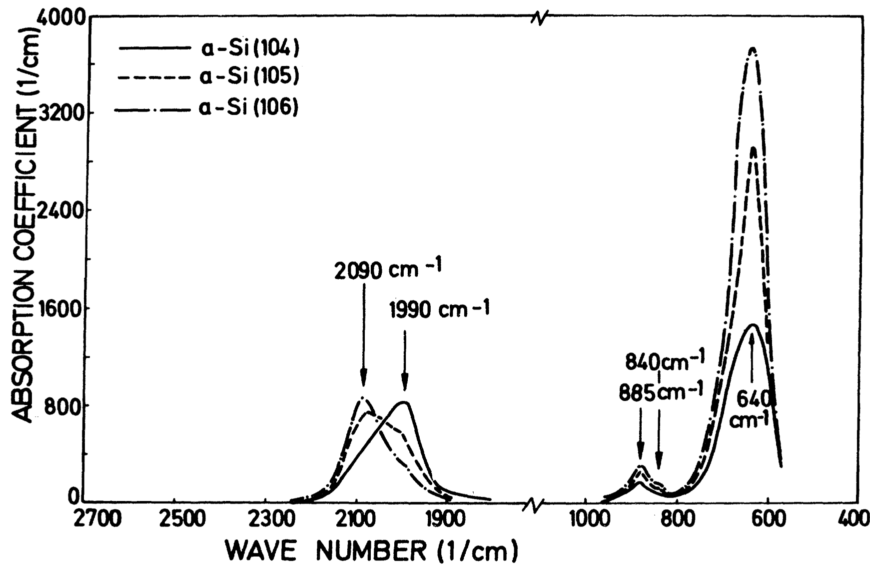

FIG. 2. Infrared-absorption spectra of three P-doped a-Si(H) samples in the region of local modes. Sample data in Table I.

Hence we do not find any evidence in Fig. 2 for the presence of P–H bonds. We point out, however, that the oscillator strength of the P–H bonds is weak[16] (see Sec. IV) and that the ir bands expected for bond stretching between 2100 and 2400 cm^{-1} may be too weak to be observed.

Figures 3 and 4 show that absorption spectra of B- and P-doped a-Si samples in the region of the intrinsic vibrations of the Si network. These spectra show similar features to those of Ref. 4. The spectra of the lightly doped samples (101) and (104) have nearly the same integrated strength (see Table II) although their shapes differ somewhat, a fact which can be attributed to the different H content [3% in (103), 7% in (104)]. Thus the LA peak at 310 cm^{-1} is suppressed for the sample with higher H content (104), a fact which was already found in Ref. 4. All samples show structure around 210 cm^{-1} corresponding to the local mode reported in Ref. 4.

The integrated strengths of all spectra of Figs. 3 and 4 are listed in Table II. Their most striking feature is their overall increase with increasing doping (irrespective of type) with relatively little deformation of the shape of the spectra.

IV. DISCUSSION

A. Stength of the B–H stretching band

As mentioned above, the band centered at 2475 cm^{-1} in Fig. 1 can be attributed to B–H stretching modes. We have tried to estimate the density N_{B-H} of B–H bonds from the integrated absorption $\int \alpha(\omega) d\omega$ of the 2475 band using the expression[15]

$$N_{B-H} = \frac{2cn}{9\pi^2} \frac{\mu}{e^{*2}_{B-H}} \int \alpha(\omega) d\omega , \qquad (1)$$

where c is the speed of light and $n = 3.4$ the refractive index of a-Si. The effective charge

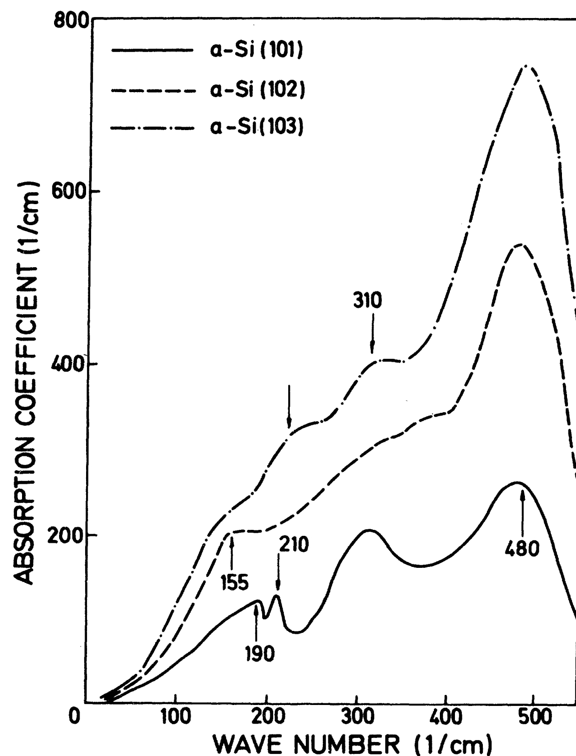

FIG. 3. Infrared-absorption spectra of three B-doped a-Si(H) samples in the region of intrinsic absorption of the Si-Si network. Sample data in Table I.

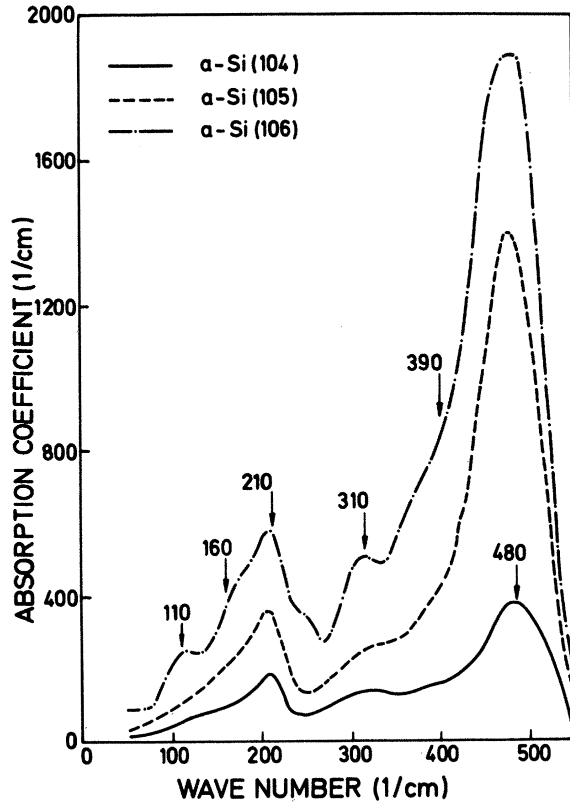

FIG. 4. Infrared-absorption spectra of three P-doped a-Si(H) samples in the region of intrinsic absorption of the Si-Si network. Sample data in Table I.

$e^*_{\text{B-H}} \simeq 0.2$ can be estimated from absorption spectra found in Ref. 11 for solid, liquid, and gaseous B_2H_6. For sample (103), with $\int \alpha \, d\omega = 2.3 \times 10^5$ cm^{-2} we find $N_{\text{B-H}} = 22\%$. If this result is taken at face value, it would mean that every other B atom is attached to one hydrogen. On the other hand, we know that Eq. (1), when applied to Si–H bond-stretching bands, overestimates the number of Si–H bonds by at least a factor of 2.

B. Strength of Si-B local mode

In order to estimate an effective charge for the Si–B bond we measure the difference between the oscillator strength of the Si–B of sample (103) and that of the Si–H bond of (101) to be $\int \Delta\alpha \, d\omega = 1.2 \times 10^5$ cm^{-2}. Equivalently we find for sample (102) $\int \Delta\alpha \, d\omega = 3 \times 10^4$ cm^{-2}. The effective charge for the Si–B bond can then be obtained with the expression[14,17]

$$e^{*2}_{\text{Si-B}} = \frac{M_B nc}{2\pi^2 N C_B (1 - C_B)[M_B \chi(0)^2]} \int \Delta\alpha \, d\omega \,, \tag{2}$$

where M_B is the mass of the B atom, C_B the density of B divided by the total density of lattice sites $N(\text{B+Si})$, and $|\chi(0)|^2$ represents the mean-square amplitude of the B vibrations. For B in c-Si, $[M_B \chi(0)^2] = 0.75$.[17] We take the same number for our evaluation of Eq. (2). The density of lattice sites N must take into account the fact that the lattice constant should decrease, according to Vegard's law, with increasing B. Taking for the B–B bond length the same as that of the C–C, we estimate $a_0 = 4.90$ Å for a-Si(103) and 5.29 Å for a-Si(102). With these numbers and the oscillator strengths given above we find $e^*_{\text{Si-B}} = 0.88$ for a-Si(103) and 0.90 for a-Si(102). These values are in excellent agreement with those found for the equivalent local mode in c-Si.[14] This charge is also to be compared with that obtained for the hypothetical tetrahedral semiconductor BSi with Harrison's bond-orbital model,[6]

$$\begin{aligned} e^*_T &= \tfrac{1}{2}(Z_B - Z_{Si}) + \tfrac{20}{3}\alpha_P - \tfrac{8}{3}\alpha_P^3 \,, \\ \alpha_P &= \frac{V_3}{(V_2^2 + V_3^2)^{1/2}} \,, \quad V_2 = 2.16 \frac{\hbar^2}{md^2} \,, \\ V_3 &= \tfrac{1}{2}(E_p^B - E_p^{Si}) \,, \end{aligned} \tag{3}$$

TABLE II. Integrated strength of lattice absorption in a-Si and various effective charges derived from it. Also, impurity concentration C_i.

Samples	(101)	B doped (102)	(103)	(104)	P doped (105)	(106)
Integrated strength (cm^{-2})	7.3×10^4	1.4×10^5	2.3×10^5	7.3×10^4	2.0×10^5	3.3×10^5
Intrinsic effective charge [Eq. (4)]	0.51	0.71	0.90	0.51	0.84	1.1
Effective charge of dopant		3.7	3.5		1.8	1.8
C_i	0.01	0.09	0.29	0.01	0.1	0.2

where $Z_B = 3$ and $Z_{Si} = 4$ represent the ion core charges, d the bond length, E_p the binding energies of the p-valence orbitals, and α_P is the polarity of the bond. Using the atomic parameters of Ref. 18 we find with Eq. (3) for the Si–B bond $e_T^* = 0.8$ in excellent agreement with the experimental results.

C. Intrinsic vibrations of "undoped" a-Si

We take the integrated absorption of samples (101) and (104) (see Table II) as representative of the undoped material. Other spectra in the literature confirm this assumption.[4] We now estimate a "formal" effective charge that would result from this integrated strength if the material were a chemically or ›red zinc-blende-like semiconductor similar to G \s, with bonds only between positive and negati ›ly charged atoms. The transverse dynamical ıarge would then be

$$e_T^{*2} = \frac{M_{Si} nc}{2\pi^2 N} \int \alpha \, d\omega , \quad (4)$$

where N is the density of Si atoms. Replacing the integrated absorption of Table II into Eq. (4) we obtain for sample (101) and (104) $e_T^* = 0.51$.

Not much is known about the mechanism responsible for this effective charge. A comparison with the results of Sec. IV B for the Si–B bond, however, shows that a value of 0.5 for the nominally nonpolar Si–Si bond is indeed very large. Recent estimates and measurements for the Si–Ge bond yield values of e_T^* between 0.1 and 0.5.[18] One model published for e_T^* is based on fluctuations in the bond charge due to fluctuating bond lengths.[2] Actually the static bond charge for Si is approximately 0.2.[19] The bond lengths in a-Si do not fluctuate by more than a few percent; hence this mechanism is not likely to yield dynamical charges larger than $\sim 10^{-2}$. Any model for the e_T^* of a-Si must involve a fairly large degree of "chemical" ordering of alternating charges within nearest-neighbor atoms similar to that which occurs in GaAs. This ordering must extend over distances of the order of the localization length of the phonons,[20] otherwise the magnitudes of the charges e_T^* required would be even larger. It is easy to speculate on the possibility of alternating positively and negatively charged Si atoms around the sixfold rings, in a way resembling the charge-density waves of the Peierls transitions. Such arrangement, while lowering the kinetic energy, would be energetically unfavorable in c-Si because of the positive Hubbard correlation energy U. In amorphous materials it is well known that U can be negative as a result of lattice rearrangements.[21] Hence alternatingly charged atoms become a possibility.

The phenomenon just proposed is actually similar to that which obtains at the surface of c-Si: Lattice rearrangement leads to the formation of reconstructed polar surfaces with ordered alternating charges. For the (111) 1×2 surface of c-Si the transfer of static charge is $\Delta e^* = 0.3$.[22] With such transfer it would be easy to explain the infrared absorption described here. Hence a possibility is also the existence of reconstructed internal surfaces with alternating + and − charged dangling bonds. In order to examine this possibility, samples with varying amounts of void areas should be investigated.

D. Impurity enhancement of the intrinsic vibrations of a-Si: P doping

As discussed in Sec. III no specific features of P are seen in Figs. 2 and 4. Hence because of the immediate proximity of P to Si in the Periodic Table we assume that the fundamental vibrational spectrum is not modified as P is added substitutionally. The P impurities, however, will add an ionic component to the bonds. The *additional* absorption $\Delta\alpha$ induced by the doping can be related to a dynamical effective charge for the Si–P bond with Eq. (2) suitably modified so as to take the presence of a concentration C_P of phosphorous into account:

$$e_{Si-P}^{*2} = \frac{M_{Si} nc}{4\pi^2 N C_P (1 - C_P)} \int \Delta\alpha \, d\omega . \quad (5)$$

For both samples (105) and (106) we obtain with Eq. (5) $e_{Si-P}^* = 1.8$ which compares favorably with the value $e_{Si-P}^* = 2$ obtained with Eq. (3).

E. Impurity enhancement of the intrinsic vibrations of a-Si: B doping

The treatment of the enhancement in the absorption spectrum of Fig. 3 produced by the presence of substitutional B is more difficult to analyze as a result of the different behavior of B and Si. Besides, the presence of B pulls out of the vibrational spectrum of the Si local modes as discussed in Sec. IV B. Nevertheless, we present below an attempt at such analysis.

The first thing we note is that the ratio of $\int \Delta\alpha \, d\omega$ for samples (103) to (102) is 1.9 and does not follow the predictions of Eq. (5). This equation would predict an inverse proportionality to $C_B(1 - C_B)$, hence a ratio of 2.8. This effect becomes even more evident if the decrease in lattice constant with incorporation of B mentioned in Sec. IV B is taken into account. We then predict for the impurity-induced absorption in samples

(103) and (102) a ratio of 3.5. The reason for this discrepancy is that $C_B(1-C_B)$ represents the number of Si–B pairs whose vibrations are *pulled out* from the region under study and move to the local mode at ~700 cm^{-1} (Sec. IV B).

It is logical to assume that only those Si atoms which have at least a B as nearest neighbor (NN) contribute to the impurity-enhanced absorption. If an Si atom has 4 B atoms as NN it contributes only to the local mode and not to the fundamental absorption. It is not possible to say with certainty at this point how much Si atoms with two or three B NN contribute to the fundamental absorption. However, if we assume that only Si atoms with one and two B neighbors contribute to the absorption it is possible to explain the observed ratio of $\int \Delta\alpha\, d\omega$ for samples (103) and (102). The concentrations of Si atoms with one ($N_{Si}^{(2)}$) and two B neighbors ($N_{Si}^{(2)}$) are

$$N_{Si}^{(1)} = 4NC_i(1-C_i)^4\,, \qquad N_{Si}^{(2)} = 6NC_i^2(1-C_i)^3\,. \tag{6}$$

We assign now to $N_{Si}^{(1)}$ an effective charge $\bar{e}_{Si-B}^{*}/4$ and a weighting factor (because of the removal of one *local* mode out of four) of $\frac{3}{4}$. To $N_{Si}^{(2)}$ we assign a weighting factor of $\frac{1}{2}$ and a charge $\bar{e}_{Si-B}^{*}/2$. We then find for the effective charge $\bar{e}_{Si-B}^{*}$

$$\bar{e}_{Si-B}^{*2} = \frac{M_{Si}nc}{2\pi^2 N\bar{C}} \int \Delta\alpha\, d\omega\,, \tag{7}$$

where

$$\bar{C} = \frac{3}{16} C_i(1-C_i)^4 + \frac{3}{4} C_i^2(1-C_i)^3\,.$$

From Eq. (7) we find for Si (103) ($\bar{C}=0.036$), after taking into account the decrease in the lattice constant due to doping, $\bar{e}_{Si-B}^{*}=3.5$. This value is in sharp contrast with that derived from the absorption of the B–Si local mode in Sec. IV B.

Although we do not know the reason for this discrepancy, one may speculate that the presence of B, or the free holes associated with it, enhances the charge ordering discussed in Sec. IV B. If we use Eq. (3) to derive a zinc-blende-ordered type of charge for the total absorption of sample Si (103) we find $e_T^{*}=0.9$, only slightly larger than found for the nearly undoped samples (101) and (104). For comparison we list also in Table II the charge e_T^{*} obtained with Eq. (3) for the P-doped samples.

The discussion above suggests an enhancement of the ordered charge fluctuations for the Si atoms with increasing B concentration. We point out that the main argument against such ordering is the Hubbard correlation energy U. In a B-doped sample we can produce an ordering of static charges up to $\Delta e^{*} = C_B$ [0.29 for Si (103)], *without spending* Hubbard U. A static charge of 0.29 could easily correspond to an $e_T^{*}=0.81$ as required by Si (103) under this model (see Table 9-4 in Ref. 6).

Note added in proof: A similar treatment was given by D. D. Klug and E. Whalley in Phys. Rev. B 15, 2095 (1977) for the effective charge of pure *a*-Ge and *a*-Si. They used, however, Sigetti local-field corrections and an additional factor of $1/\sqrt{3}$ in their effective charges. Once these changes are made, their results agree with those given here.

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