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Additional structure in infrared excitation spectra of group-III acceptors in silicon

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High-resolution infrared $p_{3/2}$ and $p_{1/2}$ excitation spectra are reported for the group-III acceptors boron, aluminum, gallium, and indium in silicon. New lines, which are believed to be due to previously unresolved excited states, are observed in the $p_{3/2}$ spectra. A $5p'$ line is observed for the first time in the gallium spectrum. Some previously reported boron $p_{3/2}$ lines are relabeled to correspond with the other group-III spectra. A feature in each of the $p_{3/2}$ spectra is defined as E_I, the ground-state binding energy. Values measured for E_I are 44.39, 69.03, 72.73, and 155.58 ($\pm$0.02) meV for B, Al, Ga, and In, respectively. The data show more complete correspondence between all the group-III excited-state lines than any previously published. The spin-orbit splitting of the valence bands is experimentally deduced to be 44.00$\pm$0.02 meV.

I. INTRODUCTION

Infrared excitation spectra of group-III acceptors in silicon have been reported previously by many different investigators. The reader is directed to a few of the more recent articles[1–5] in which most of the previous data are referenced. In addition, several theoretical models have been proposed to interpret the experimental results. One of the more successful of these models appears to be the effective-mass theory of Lipari *et al.*[6,7] Despite the rather large number of papers published in this area, there are still some unsettled issues. Two examples are the accurate determination of ground-state binding energies[7] and spin-orbit splitting of the valence bands. Furthermore, recently improved experimental techniques (primarily due to more widespread use of Fourier-transform spectrometers) and improved growth techniques for doped silicon crystals have resulted in detailed high-resolution data unobtainable by earlier workers.

We present here high-resolution infrared absorption spectra for the group-III acceptors boron, aluminum, gallium, and indium in silicon. New lines and structure, not noted by previous investigators, are observed in the spectra. It is shown that the identity of some of the previously reported boron lines must be altered to be consistent with the other group-III spectra. It is demonstrated that a feature of the high-energy side of peak 11 in each of the $p_{3/2}$ spectra can be logically defined as E_I, the ground-state binding energy. An analysis of this new data yields values for E_I and the spin-orbit splitting of the valence bands which are more consistent for all four acceptors than any of the previously reported values. A more complete correspondence of all the group-III excited-state lines is also demonstrated.

II. EXPERIMENTAL

Many different samples from a variety of sources were studied during the course of this work. The specific samples used to obtain the spectra illustrated in this paper are as follows: The boron-doped sample was cut from a float-zone boule grown by Shin-Etsu Handotai of Japan. It had a boron concentration of approximately 2×10^{15} cm^{-3}. The aluminum-doped sample came from a float-zone crystal grown by Texas Instruments. It had an aluminum concentration of approximately 5×10^{15} cm^{-3}. The gallium-doped sample was cut from a float-zone boule grown by Spectralab Inc. It had a gallium concentration of approximately 1×10^{15} cm^{-3}. The indium-doped sample was cut from a float-zone boule grown by Westinghouse. It had an indium concentration of approximately 3×10^{16} cm^{-3}.

The samples were cooled to 5.5 K in a liquid-helium Dewar during measurement. All spectra were recorded on a Digilab model FTS-20C Fourier-transform spectrophotometer at resolutions of 0.2–0.5 cm^{-1}, with signal averaging of 1000–2000 scans. The spectrometer was calibrated using an internal laser reference line (6328-Å HeNe laser at 15 800.8235 cm^{-1} *in vacuo*) and also known positions of water vapor and carbon dioxide absorption bands. A computer software program supplied with the Digilab system was used to convert transmittance to absorption coefficient. Samples

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were mounted in a stress-free manner by attaching them to the Dewar cold finger by a very small dab of conducting vacuum grease at one corner only.

III. RESULTS AND DISCUSSION

We obtained the excitation lines of both the $p_{1/2}$ and $p_{3/2}$ series by infrared absorption spectroscopy for each of the group-III acceptors boron, aluminum, gallium, and indium. In order to compare the spectra with each other on a common relative energy scale, and to make a meaningful evaluation of the results, it was necessary to find an accurate reference point on which each spectrum could be aligned. Ideally, this reference point should be a spectral feature which exhibits no chemical shift or other meaningful change in relation to the intrinsic silicon band structure when the identity of the dopant acceptor is changed. In theory, the valence-band edge should make an excellent reference point but no spectral features have been found to correspond to either the $p_{3/2}$ band edge or to the split-off $p_{1/2}$ band edge by previous workers. However, as demonstrated by Zwerdling *et al.*,[8] the $p_{1/2}$ band edge can be determined from a Rydberg series plot of the $p_{1/2}$ series absorption lines. The $p_{1/2}$ series limit obtained from such a plot is assumed to be coincident with the band edge. The $p_{1/2}$ series absorption spectra, which we have obtained for the group-III acceptors in silicon, are shown in Fig. 1.

The series limit E_I^* was determined for each spectrum by making a corrected Rydberg series plot in accordance with Zwerdling *et al.*[8] The resultant E_I^* positions are indicated in Fig. 1, and it is these positions which were used to align the spectra with each other and which serve as the zero-energy reference point. The actual values of E_I^* are listed in Table I. Zwerdling *et al.*[8] plotted only the data for boron and found that both the corrected and uncorrected Rydberg series extrapolated to the same series limit. Since then, several other investigators have made the same assumption and have used the simple uncorrected series to determine the series limit.[1] We find, however, that our data do not yield the same series limit for the corrected and uncorrected plots. In all cases the corrected series limit is higher than the uncorrected one. The difference is 0.04 meV for B and In, 0.06 meV for Al, and 0.08 meV for Ga. Energy values of the absorption lines used to make the plots are given at the bottom of Table II. Notice that a $5p'$ line is observed in the gallium spectrum. This is the first time that a $5p'$ line has been reported for any acceptor in silicon. It fits perfectly on the Rydberg series line and gives more confidence to the extrapolated series limit. Only three lines ($2p'$, $3p'$, and $4p'$) were observed in the B, Al, and In spectra.

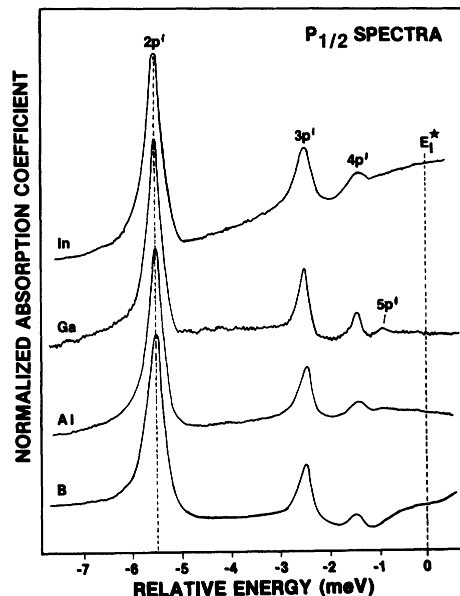

FIG. 1. $p_{1/2}$ series absorption spectra of group-III acceptors in silicon. Spectra are aligned on E_I^*, the series limit, which is placed at zero energy for comparison purposes. E_I^* was determined from a corrected Rydberg series following Zwerdling *et al.* (Ref. 8). The $2p'$ lines were normalized to same intensity for comparison.

Another feature to notice in both Fig. 1 and Table I is that the energy separation between E_I^* and $E_{2p'}$ is the same for all four acceptors. This is significant because it means that the $2p'$ line is also an accurate reference point on which to align the spectra for comparison purposes. The importance of this is that $2p'$ is an easily determined experimental position as opposed to the series limit which must be extrapolated. Onton *et al.*[1] also used the $2p'$ line as a reference point but their measured E_I^*-$E_{2p'}$ separations were not the same, particularly in the case of indium. Our data, then, show a consistency in the $p_{1/2}$ spectra which previously reported data on the group-III acceptors in silicon did not show. The $2p'$ line is also used as the reference point for comparing the $p_{3/2}$ spectra which will be discussed next.

An example of a complete $p_{3/2}$ absorption spectrum is shown for gallium in Fig. 2. Our spectrum is very similar to that shown by Chandrasekhar *et al.*[2] The main difference is that our data exhibit a little better resolution and more detail in the high-energy group of lines, i.e., lines numbered 5 and higher. Our other group-III $p_{3/2}$ spectra also agree very well with previously published spectra for lines 1–4. It is in lines 5 and above where we observe

TABLE I. $p_{1/2}$ series ionization energy[a] and some experimental energy separations in silicon. Units are meV.[b]

	B	Al	Ga	In
E_I^*	88.39	113.04	116.73	199.58
$E_I^* - E_{2p'}$	5.50	5.51	5.49	5.50
$E_I^* - E_I$	44.00	44.01	44.00	44.01
$2p' - E_I$	38.50	38.50	38.51	38.51

[a] E_I^* determined from corrected Rydberg series given by Zwerdling *et al.* (Ref. 8).
[b] Maximum error estimated to be ±0.02 meV.

some differences and to which we now direct the discussion. The high-energy portion of the $p_{3/2}$ spectra which we have obtained for B, Al, Ga, and In is shown in Fig. 3. These spectra are aligned with each other using the $2p'$ line as the reference point. Previous investigators[1,5,9] had identified a total of six lines in this region, labeled 5–10 according to the notation first used by Colbow.[10] Our spectra in Fig. 3 exhibit these six lines very clearly, more clearly, in fact, than previous results. The major feature of our spectra is that several additional distinct lines and shoulders are also observed, particularly in the boron and gallium spectra. It was considered prudent not to confuse matters by relabeling the major lines (except for boron as will be discussed shortly) and so the new additional lines were labeled by using letter suffixes (*A*, *B*, *C*, etc.). New lines and shoulders which appear to be associated with the major line 10, for instance, are labeled 10*A*, 10*B*, 10*C*, and 10*D* as seen in Fig. 3. Also notice that a very distinct line 11 is observed in each spectrum for the first time. All previous data had indicated that

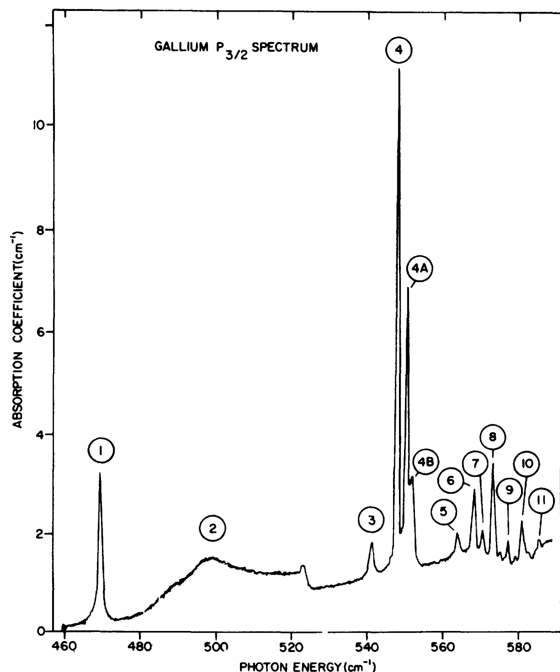

FIG. 2. $p_{3/2}$ series absorption spectrum of gallium in silicon. Sample temperature was 5.5 K. Note detail in high-energy group of lines labeled 5–11.

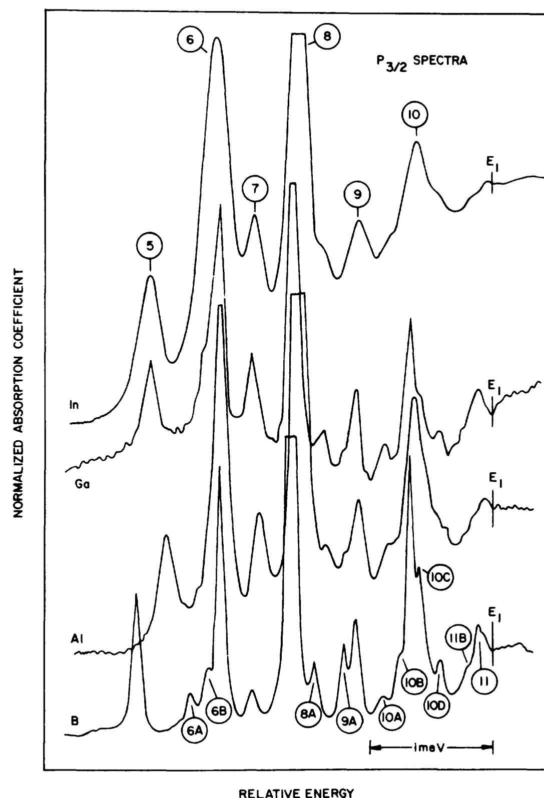

FIG. 3. High-energy region of $p_{3/2}$ absorption spectra of group-III acceptors in silicon. Spectra are aligned using $2p'$ line as reference. Rationale for labeling of peaks and band edge E_I are explained in text.

line 10 was the highest energy line. The energy positions of all the lines are listed in Table II. Some of the new lines are observed in the spectra of all four acceptors, but others occur only in some spectra and are missing in others. However, the line labels are consistent from one acceptor to another because they were chosen on the basis of corresponding line positions as will be illustrated more clearly later in Fig. 5. Our values for the previously reported main lines are in good agreement with those of Onton *et al.*[1] For completeness, the known line positions of thallium, which is also a group-III acceptor in silicon, are included in Table II. We were unable to obtain a good thallium-doped crystal and have therefore used the data of Scott and Schmit.[11]

The first acceptor for which we observed this additional structure was boron. Our initial thought was that there was something peculiar about the sample or that some experimental problem such as external stress was the cause of this structure. We first satisfied ourselves that the sample was stress free and then obtained other boron-doped silicon samples which yielded the same results. In the meantime two papers appeared[12,13] which reported boron spectra virtually identical to ours, but the additional structure was not discussed in either paper. Subsequently, we observed a similar additional structure in other group-III spectra. These extra lines are most evident in boron, and least evident in indium. It is believed that the spectra illustrated in Fig. 3 are stress free and that the additional structure is truly characteristic of the group-III impurity. High-quality samples and the use of a high-resolution Fourier-transform spectrometer are probably the main reasons why we were able to observe this structure and many previous workers were not.

One aspect of the boron spectrum that deserves special mention is line labeling. In Fig. 3, note the major boron lines labeled 8–10. In all previously reported work[1,4,10,12,13] these lines are labeled 7–9. It is evident from the comparison in Fig. 3 and Table II (and later in Fig. 5) that from the standpoint of both relative peak intensity and relative energy position the peak at 42.74 meV (previously labeled 7) should be relabeled 8 to be consistent with the labels subsequently given to the lines of the other group-III acceptors. This same argument applies to lines 9 and 10. Line 7 is actually the weak peak at 42.41 meV which is reported here for the first time. This new boron line 7 is also consistent with line 7 of the other group-III spectra in relative energy position and relative intensity. The line positions listed in Table II include the relabeled lines 7–10 of boron.

Another point to notice in Fig. 3 is the feature at the high-energy end of each spectrum which is labeled E_I. This is the point which we are tentatively defining as the $p_{3/2}$ valence-band edge. By definition, the energy position of this point also represents the binding energy of the group-III acceptor ground state E_I. The actual value of the ground-state binding energies has been the subject of much previous discussion, both experimentally and theoretically.[1,3,4,6,7] One of the problems in determining an accurate value for E_I is that in previous experimental work no spectral feature could be identified as corresponding to the band edge. In our spectra, there is a reproducible minimum on the high-energy side of line 11 beyond which there is a more or less flat featureless continuum absorption. That minimum falls at precisely the same relative energy position for each of the group-III acceptors. The rationale behind our suggestion that this spectral feature be defined as E_I is illustrated in Fig. 4.

Shown in Fig. 4 is an enlarged view of the boron spectrum from Fig. 3. One noticeable aspect of this spectrum is that the background immediately on the high-energy side of line 11 is significantly higher than the background under the main lines and that it is relatively flat and featureless. The dashed curve represents our estimate of the background position under the lines. It appears that the background gradually slopes upward as the energy increases toward the line-11 position. At the high-energy side of line 11 there is a sudden break in the slope. We are suggesting that this break represents the onset of continuum absorption into the valence band. In other words, we are observing the valence-band absorption edge which is logically the position of E_I. This same background break is also observed in the aluminum, gallium, and indium spectra. The energy value of this position is listed as E_I in Table II. The region around line 11, in fact, is very similar in appearance to some other semiconductor absorption edge spectra in which an exciton peak occurs immediately below the edge.[14,15] The minimum on the high-energy side of line 11, which corresponds to the break in the background slope, occurs at the same relative energy position for each of the impurities. This means that the energy separation between our measured E_I and E_I^* is constant for each acceptor. $E_I^* - E_I$, is, by definition, the spin-orbit splitting of the valence bands. Our measured value, as listed in Table I, is 44.00 ± 0.02 meV, which is in good agreement with the values of Onton *et al.*[1] and Zwerdling *et al.*[8] The fact that we get the same value of $E_I^* - E_I$ for each of the acceptors when the position of E_I is measured as described above is a strong point in support of our interpretation. No previously reported data show such a consistent value for the spin-orbit splitting for all four of these group-III dopants in silicon.

Our measured values of E_I, the ground-state bind-

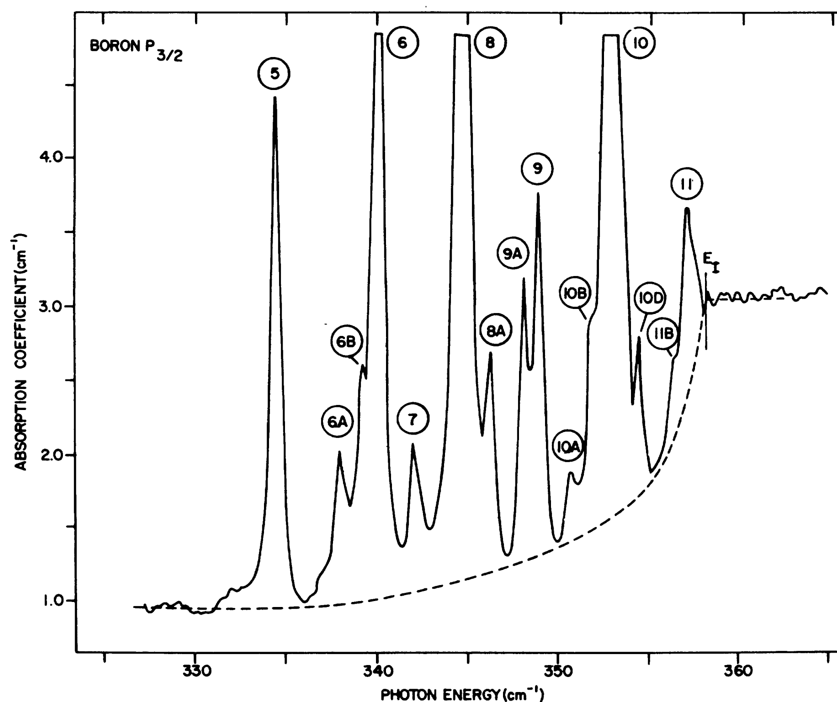

FIG. 4. High-energy region of $p_{3/2}$ absorption spectrum of boron in silicon. Dashed curve is estimated background.

ing energies, are compared with values reported by some other workers in Table III. Our values agree well with the experimental results of Jones *et al.*[3] for B and Ga, and less well for Al and In. There is not close agreement with the values of Lipari *et al.*[7] or with those of Ramdas and Rodriguez.[4] Lipari *et al.*[7] calculated the binding energies of some of the excited states for group-III acceptors in silicon. They calculated that the excited state giving rise to absorption line 6 had a binding energy of 3.67 meV and then added this energy to the experimental line-6 energy to come up with the ground-state binding energy. Ramdas and Rodriguez[4] added 6.1 meV to line 4 to obtain their ground-state binding-energy values. The problem with adding a given energy to an experimental absorption line position in this case is that the lines tend to shift around in relative energy position from one acceptor to another. This is particularly true of line 4 as illustrated in Fig. 5, and as also shown in previous work.[1]

Shown in Fig. 5 are the relative binding-energy positions of the group-III excited states in silicon as determined from our infrared absorption spectra. Our measured value of E_I is used as the zero-energy reference point for each acceptor. Positions for lines 1 and 2 are not shown because they are off scale to the top of the figure. The longer lines in Fig. 5 represent the major absorption peaks 3—11. Shorter lines represent new absorption structures 6*A*, 6*B*, 8*A*, etc., as listed in Table II. Notice that lines 3—5 exhibit significant chemical shifts. Lines 6—11, on the other hand, show good correspondence from one acceptor to another. Most of the new lines also show good correspondence. It was on the basis of such corresponding line positions, for instance, that the distinct new shoulders observed in the indium spectrum (Fig. 3) were labeled 8*A*, 10*A*, 10*D*, and 11*B* (Table II). In other words, all line labels listed in Table II were chosen on the basis of corresponding line positions as seen in Fig. 5.

Chandrasekhar *et al.*[2] have shown that the lack of a sharp line 2 in the gallium spectrum is due to a resonant interaction with optical phonons. The absence of line 3 in the aluminum spectrum is believed due to a similar interaction.[1,2] Line 4 of aluminum is also somewhat peculiar, however. As seen in Fig. 5, the relative energy positions of the line-4 components are significantly shifted with respect to the other group-III acceptors. In addition, aluminum line 4 has a strange shape and is much weaker in relation to the other spectral lines than the other three acceptors. We have observed a new line-4 component, labeled 4′, in Table II. It is pointed out that the zone-center optical phonon which causes the resonant interaction in line 2 of gallium[2] has an energy which falls between lines 4 and 4*A* in aluminum. Perhaps the strange behavior of aluminum line 4 is due to this phonon interference. At any

TABLE II. Experimental energy positions of group-III acceptor excitation lines in silicon. Units are meV.[a]

Line	B	Al	Ga	In	Tl[b]
1	30.37	54.89	58.24	142.01	232.6
2	34.49	58.51		145.78	236.4
3	38.35		67.13	149.77	240.2
4	39.59	64.04 (4) 64.12 (4′)	67.97	150.80	241.5
4*A*	39.67	64.98	68.26	151.08	
4*B*	39.91	65.16	68.44	151.19	
5	41.47	66.35	69.95	152.77	
6*A*	41.91				
6*B*	42.06		(70.40)		
6	42.16	66.79	70.51	153.31	244.0
7	42.41	67.10	70.79	153.62	
8	42.74	67.43	71.13	153.98	
8*A*	42.92	67.64	71.35	(154.15)	
9*A*	43.16	(67.81)	(71.53)		
9	43.24	67.91	71.62	154.46	
10*A*	43.49	68.16	71.85	(154.72)	
10*B*	(43.64)	(68.22)			
10	43.71	68.38	72.07	154.93	
10*C*	43.78	(68.53)	(72.13)		
10*D*	43.95	68.62	72.31	(155.08)	
11*A*		(68.80)	(72.44)		
11*B*	(44.20)	(68.87)	(72.52)	(155.40)	
11	44.27	68.96	72.62	155.51	
E_I	44.39	69.03	72.73	155.58	246.2
$2p'$	82.89	107.53	111.24	194.08	283.3
$3p'$	85.90	110.56	114.25	197.11	286.3
$4p'$	86.95	111.61	115.30	198.18	
$5p'$			115.8		
E_I^*	88.39	113.04	116.73	199.58	

[a]Error is estimated to be ±0.02 meV for all lines of B, Al, Ga, and In except those in parentheses where error is estimated to be ±0.05 meV.
[b]Reference 11. Error estimate not given.

rate, the use of line 4 to determine binding energies as done by Ramdas and Rodriguez[4] will yield doubtful results, especially for aluminum.

IV. SUMMARY

We have presented the $p_{1/2}$ and $p_{3/2}$ infrared absorption spectra of the group-III acceptors boron, aluminum, gallium, and indium in silicon. At least ten new lines were observed in the $p_{3/2}$ spectra. These new lines appear to represent additional excited states which had not been previously resolved. The previously reported identity of some of the boron $p_{3/2}$ lines was changed in favor of consistency with the other group-III spectra. A new $5p'$ line

TABLE III. $p_{3/2}$ ground-state ionization energies of group-III acceptors in silicon. Units are meV.

	B	Al	Ga	In
Lipari *et al.*[a]	45.83	70.42	74.16	156.94
Ramdas and Rodriguez[b]	45.71	70.18	74.05	156.90
Jones *et al.*[c]	44.3	68.5	72.7	156.0
This work	44.39	69.03	72.73	155.58

[a]Reference 7.
[b]Reference 4.
[c]Reference 3.

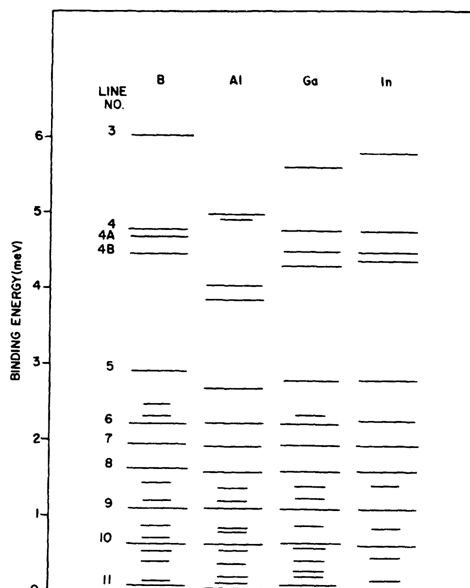

FIG. 5. Experimental binding energies of excited states of group-III acceptors in silicon. Zero energy is placed at experimentally determined band edge E_I. Longer lines represent major absorption peaks 3–11. Shorter lines represent new absorption structures 6*A*, 6*B*, 8*A*, etc., as listed in Table II.

was also observed for the first time in the $p_{1/2}$ spectrum of gallium. Corrected Rydberg series plots were made from the $P_{1/2}$ series lines and used to determine the series limit E_I^*. The value of E_I^* was of interest because it seemed to be a logical reference point on which to base a relative energy scale comparison of the various spectra. It was shown that the $2p'$ line is also an accurate reference point with the added advantage that it is easily seen experimentally. A feature on the high-energy side of peak 11 in the $p_{3/2}$ spectra was identified as E_I, the ground-state binding energy. This identification was based on the behavior of the background in the region of the valence-band edge and this position of E_I was found to be at the same relative energy position for each of the four acceptors. The specific values of E_I determined here were 44.39, 69.03, 72.73, and 155.58 meV for boron, aluminum, gallium, and indium, respectively. It was also shown that the experimentally determined spin-orbit splitting of the valence bands, $E_I^* - E_I$, was the same for each acceptor, the value being 44.00±0.02 meV. This was the first experimental data to show such a consistent $E_I^* - E_I$ value for all four group-III acceptors in silicon. Other aspects of the data such as relative line positions also show excellent consistency from one acceptor to another. In fact, our relative line positions and intensities (after relabeling some of the boron lines) are more consistent across the group-III series than any previously reported data.

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