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ADDITIONAL P(3/2) AND P(1/2) INFRARED EXCITED STATE LINES OF GA--ETC(U)
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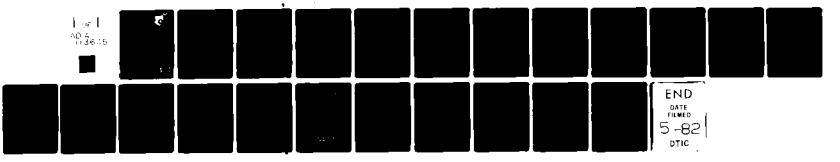

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ADDITIONAL $P_{3/2}$ AND $P_{1/2}$ INFRARED EXCITED STATE LINES OF GALLIUM AND INDIUM IN SILICON

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Infrared excitation spectra were measured for the $p_{3/2}$ lines of gallium in silicon. Two missing lines were observed, and a previous weak or doubtful one was confirmed. Spectra were also obtained of the $p_{1/2}$ lines of gallium and indium in silicon, demonstrating for the first time the $4p'$ line for both dopants. Complete correspondence now exists between all observed excited state

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lines of gallium and indium in silicon and the lines of boron and aluminum, and with those predicted by theory. From the new spectral data, the spin-orbit splitting of the valence bands is calculated to be 42.62 ± 0.04 meV.

FOR -

FOREWORD

This report describes an in-house study conducted by personnel of the Laser and Optical Materials Branch, Electromagnetic Materials Division, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio 45433 under Project No. 2306, Task No. 2306Q1, Work Unit 2306Q101. The work reported herein was performed during the period June 1979 through September 1981 by the authors John J. Rome, 1st Lt. USAF, Dr. Robert J. Spry, Thomas C. Chandler, Capt., USAF*, Mrs. Gail J. Brown, Dr. B. C. Covington, and Mr. Richard Harris. The report was released by the authors on 6 October 1981.

The authors wish to thank John Baker of Dow Corning Corporation, Dr. Harvey Winston of Hughes Research Laboratories, and Dr. Timothy Braggins of Westinghouse Research and Development Center for providing the silicon crystals used in this study. We also thank Mr. Tim Peterson of the Air Force Wright Aeronautical Laboratories and Mr. Steve Smith of the University of Dayton Research Institute for Hall effect measurements. Many helpful discussions were held with Dr. Charles DeJoseph, Jr. of the Air Force Wright Aeronautical Laboratories and Prof. J. E. Katon of Miami University, Oxford, Ohio.

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SECTION I

INTRODUCTION

The infrared excitation spectra of group III acceptors in silicon have been the subject of extensive experimental work for many years (References 1-4). Meanwhile, extended treatment of the effective mass theory has produced values of acceptor energy level positions that are more accurate than those obtained from simpler theories (References 5, 6). Technological improvements in both spectrophotometry and crystal growth have produced high resolution acceptor spectra with which to compare the latest theory (Reference 7).

A recent study (Reference 8) of the $p_{3/2}$ bands of indium in silicon revealed several lines previously not reported but believed to exist both from theory and from comparison to the spectra of the other group III acceptors. For the case of gallium in silicon, three lines of the $p_{3/2}$ series were reported by Onton et al. as missing or doubtful (Reference 3). In addition, they did not observe the 4p' line in the $p_{1/2}$ series of series of either gallium and indium, although Zwerdling et al. had observed the 4p' line for both boron- and aluminum-doped silicon (Reference 2).

We report here the observation of the missing or doubtful lines of the gallium $p_{3/2}$ series, and the 4p' line for both gallium- and indium-doped silicon. An analysis of the new data also yields a value of the spin-orbit splitting of the valence bands somewhat lower than the values previously calculated (References 2, 3).

SECTION II

EXPERIMENTAL

Gallium-doped samples were cut from two float-zone boules, one grown by Hughes Research Laboratories and the other by Westinghouse Research and Development Center. The Hughes boule had a gallium concentration of 5×10^{16} cm^{-3}, while the Westinghouse boule had a gallium concentration of 3×10^{16} cm^{-3}. The indium-doped samples were cut from a Dow Corning float-zone boule having an indium concentration of 4.2×10^{16} cm^{-3}.

The samples were cooled to 10K in either a Sulfrian liquid helium dewar or a Lake Shore Cryotronics model LTS-21-D70C closed cycle refrigeration system. Both units were equipped with cesium iodide windows, and either gallium arsenide or silicon diodes for thermometry.

All spectra were recorded at a resolution of 0.5 cm^{-1} using a Digilab model FTS-20CVX Fourier transform spectrophotometer purged with dry nitrogen. The spectrophotometric arrangement, including a potassium bromide (KBr) beamsplitter and TGS detector with KBr window, permitted investigation in the region from 4,000 to 400 cm^{-1}. The spectrometer was calibrated using known *in vacuo* positions of water vapor and carbon dioxide absorption bands (Reference 9). Our calibration deviated from these standard values by only 0.00 cm^{-1} to -0.02 cm^{-1} in the regions where data is reported. Wavenumbers were converted to *in vacuo* energy values using the factor 0.1239854 meV/cm^{-1} (Reference 10). The footnote to our previous work on indium-doped silicon spectra (Reference 8) should be disregarded because it was based upon the false assumption that our polystyrene calibration values were referenced to air when they were actually referenced to vacuum (Reference 9).

The data were measured in the single beam mode with the sample transmittance referenced to an empty sample holder. The absorption coefficient α was obtained from the transmittance by the equation:

$$\alpha = \frac{1}{d} \ell n \left[\frac{2TR^2}{\sqrt{(1-R)^4 + 4T^2R^2} - (1-R)^2} \right]$$

where d = the sample thickness
T = transmittance
R = reflectivity, taken to be 0.28

Other experimental details were the same as previously reported (Reference 8).

SECTION III

RESULTS AND DISCUSSION

The $p_{3/2}$ excitation spectrum of gallium-doped silicon is shown in Figure 1. All the $p_{3/2}$ lines, as well as the $p_{1/2}$ lines, were observed in samples cut from both the Hughes and Westinghouse boules. The lines are labeled according to the system of Onton et al. (Reference 3) and lines 1-4A are essentially the same as reported by them. We do not observe line 4B because of concentration broadening of the lines since our gallium concentration is about 10-20 times greater than that used by Onton et al. (Reference 3). While this does introduce a line broadening penalty, it enables us to observe the additional weak lines.

Figure 2 shows an expansion of the gallium spectrum in the region of the higher energy lines. Lines 9 and 10 are reported for the first time. Line 7 is also observed, which was reported by Onton et al. (Reference 3) as "weak or doubtful". A sharper line 7 was displayed by Chandrasekhar et al. (Reference 4), but they did not list its energy position.

The positions of all gallium $p_{3/2}$ lines are listed in Table 1. The position of line 2 is not given because of the optical phonon broadening phenomenon (Reference 4). Our line positions are higher in energy than those of Onton et al. (Reference 3) by a mean value of 0.08 meV, with the exception of line 5 whose energy position is 0.21 meV larger. The 0.08 meV difference may include a very slight systematic error (on the order of 0.04 meV) since the estimated experimental error of both sets of data is $\pm$0.02 meV. However, neither experimental error nor a slight systematic error can explain the discrepancy in the No. 5 line position.

The energy spacing between gallium line positions are listed in Table 2, along with those for other group III acceptors and the most recent theoretical values. Our energy spacings involving lines 7, 9, and 10 are consistent with both theory and the experimental values for the other acceptors, supporting the assignment of lines 7, 9, and 10 as the missing excited state lines. All of our gallium spacings agree well with

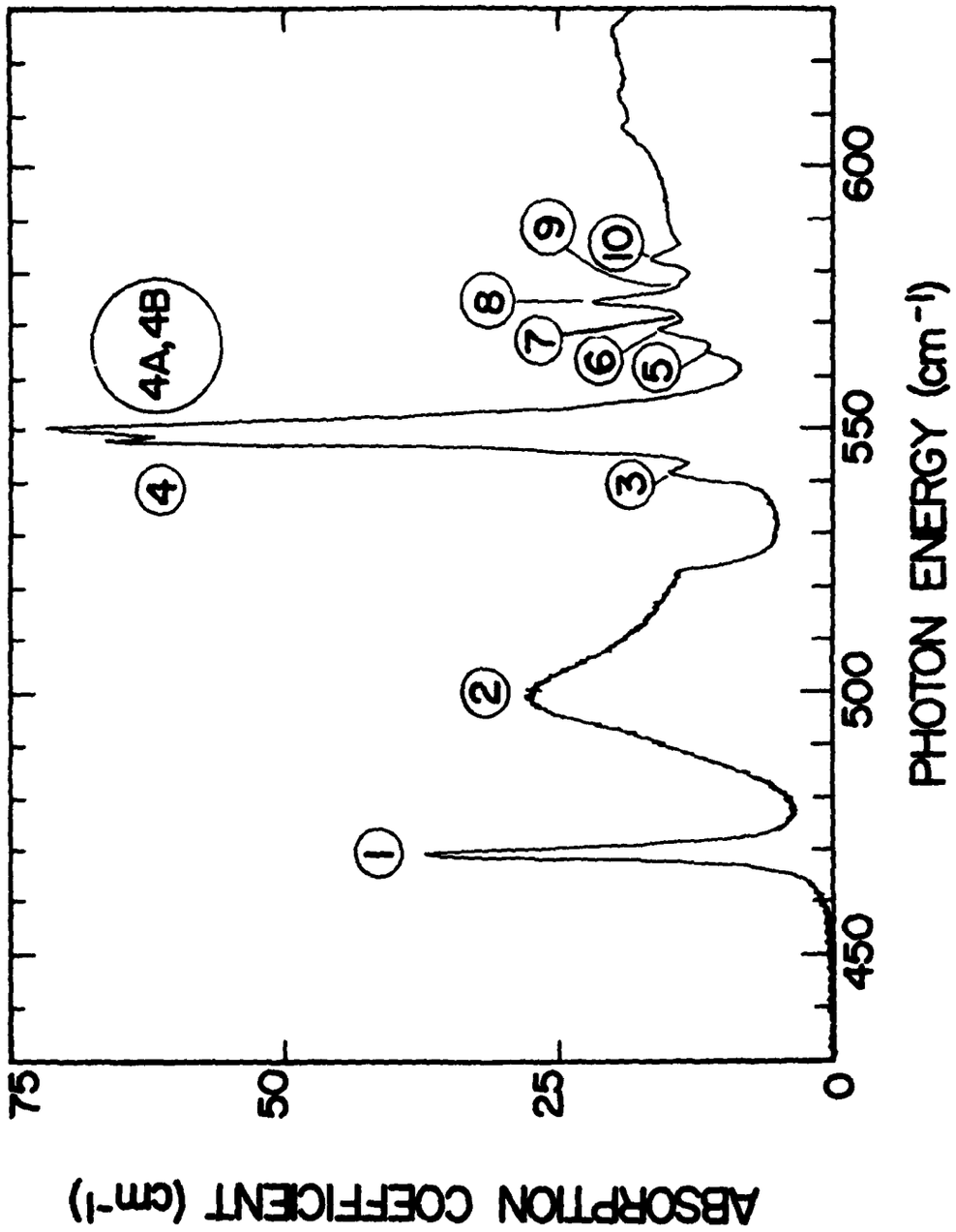

Figure 1. Absorption Spectrum ($P_{3/2}$ Series) for Gallium in Silicon. Gallium Concentration 5×10^{16} cm^{-3}. Sample Thickness 0.061 cm. Resolution = 0.5 cm^{-1}.

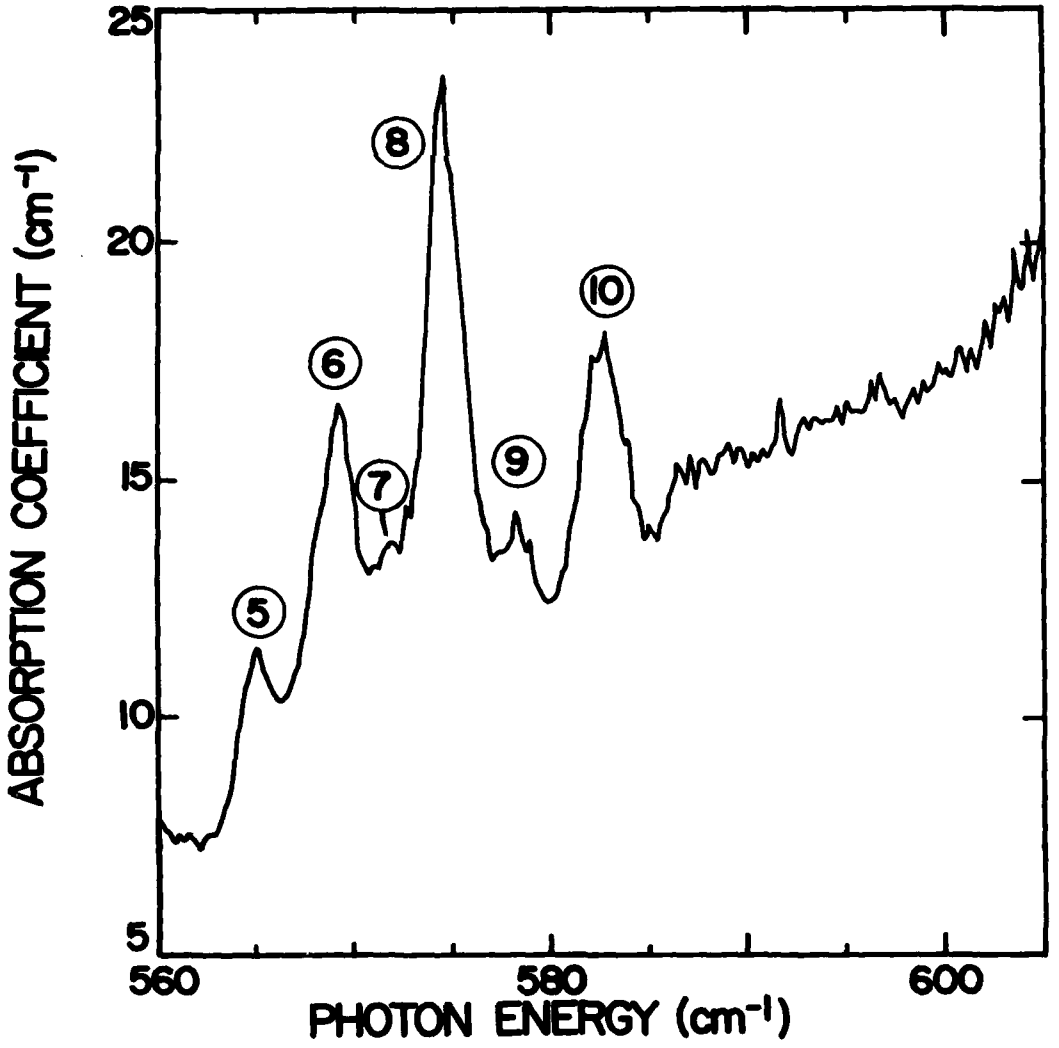

Figure 2. Expanded Absorption Spectrum for Gallium in Silicon in the Region Containing Lines 5 through 10 of the $p_{3/2}$ Series. Sample Thickness 0.175 cm. Resolution = 0.5 cm^{-1}.

TABLE 1

EXPERIMENTAL POSITIONS OF GALLIUM $p_{3/2}$ EXCITATION LINES IN SILICON.

Line	Line Position[a] Wave Number (cm^{-1})	Energy (meV)
1	470.0	58.27
2	---	---
3	541.9	67.19
4	548.8	68.04
4A	550.9	68.30
5	565.1	70.06
6	569.2	70.57
7	571.9	70.91
8	574.4	71.22
9	578.2	71.69
10	582.7	72.25

[a]Error is estimated to be ±0.15 cm^{-1} (0.02 meV) for all lines.

TABLE 2

THEORETICAL AND EXPERIMENTAL $p_{3/2}$ ENERGY-LEVEL SPACINGS FOR BORON, ALUMINUM, GALLIUM, AND INDIUM IN SILICON (UNITS OF meV)

ΔE	Theory[a]	B[b,c]	Al[b]	Ga[d]	Ga[b]	In[e]
1-3	8.24	7.97( )	---	8.92	8.89	7.75
3-4	1.22	1.29(1.23)	---	0.85	0.83	1.04
4-4A	0.33	0.27(0.08)	0.88	0.26	0.30	0.27
4A-5	1.67	1.61(1.78)	1.32	1.76	1.60	1.71
5-6	0.51	0.98(0.69)	0.47	0.51	0.64	0.53
6-7	0.16	0.29(0.59)	0.35	0.34	0.31	0.30
7-8	---	0.48(0.42)	0.29	0.31	0.31	0.36
8-9	---	0.59(0.10)	0.51	0.47	---	0.48
9-10	---	0.46(0.46)	0.50	0.56	---	0.51

[a]References 5 and 6

[b]Reference 3

[c]Reference 7

[d]This work

[e]Reference 8

the values derived from the data of Onton et al. (Reference 3) with the exception of 4A-5 and 5-6. We believe our spacings involving line 5 are more consistent with both theory and the recent indium-doped silicon spectra (Reference 8). This comparison, coupled with a pronounced sharpness in our line 5 as compared to that of Onton et al. (Reference 3) indicates that our line 5 position is the more accurate of the two.

The $p_{1/2}$ spectra for both gallium-doped silicon and indium-doped silicon are shown in Figure 3 and the energy positions of the lines are listed in Table 3. This is the first observation of the 4p' line for gallium and indium in silicon. Following Zwerdling et al. (Reference 2) we constructed a straight line approximation to an uncorrected Rydberg series describing the line positions. The results of fitting the data to both the uncorrected and corrected Rydberg formulae are shown in Figure 4 for gallium and Figure 5 for indium. We obtained an uncorrected series limit of 116.79 $\pm$ 0.02 meV for the gallium $p_{1/2}$ lines and 199.57 $\pm$ 0.02 meV for the indium $p_{1/2}$ lines. Our uncorrected gallium series limit is in agreement with the value of 116.74 $\pm$ 0.21 meV of Onton et al. (Reference 3), but our uncorrected indium series limit differs from their value of 200.16 $\pm$ 0.4 meV by more than the total allowable experimental error of both sets of data. We have utilized the corrected Rydberg formula given by Equation 2 of Zwerdling et al. (Reference 2) as a more accurate expression of the energy positions of the $p_{1/2}$ lines. Our corrected series limits ϵ_I^* are 116.86 $\pm$ 0.02 meV for gallium and 199.64 $\pm$ 0.02 meV for indium. The uncorrected and corrected series limits are not identical because a straight line is only an approximate fit to the uncorrected series energy positions.

We have calculated the value of Δ, the spin-orbit splitting, as the energy difference between the corrected $p_{1/2}$ series limit and the $p_{3/2}$ series limit. The $p_{3/2}$ series limit was obtained by adding 3.67 meV to line 6, as prescribed by Lipari et al. (Reference 6). The energy position of line 6 for indium was obtained from Table 1 of Reference 8. For gallium we obtained Δ = 42.62 $\pm$ 0.04 meV and for indium Δ = 42.62 $\pm$ 0.03 meV. The error estimate does not include the unknown error of the theoretical binding energy of the $2\Gamma_6^-$ final state of the line 6 transition. The essentially identical

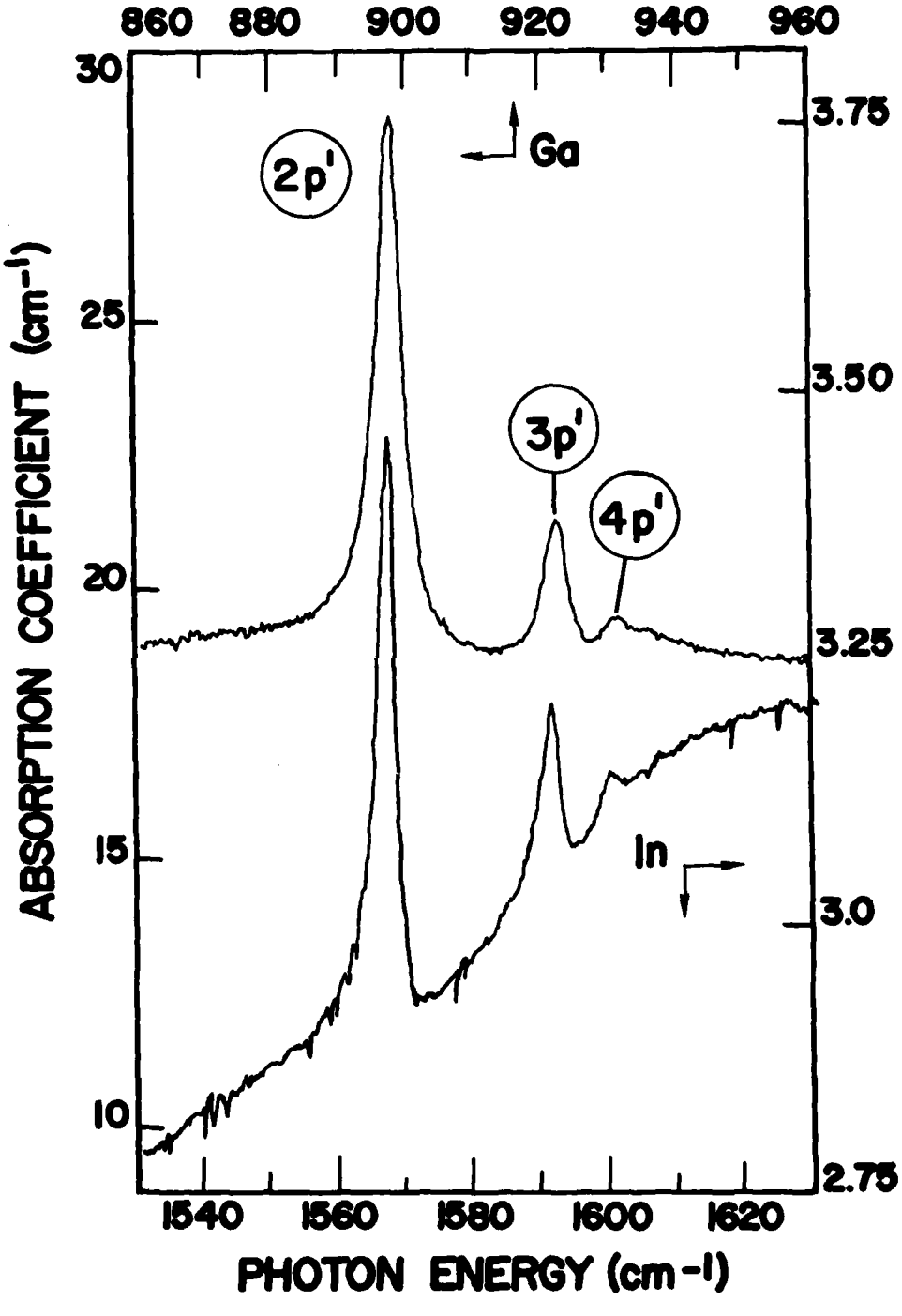

Figure 3. Absorption Spectra ($p_{1/2}$ Series) for Gallium and Indium in Silicon. Gallium Concentration and Sample Thickness Same as for Figure 1. Indium Concentration 4.2×10^{16} cm^{-3}. Indium Sample Thickness 0.397 cm. Resolution = 0.5 cm^{-1}.

values for Δ support the self-consistency of our gallium and indium spectral data. Our value of Δ is somewhat lower than the 44.1 $\pm$ 0.4 meV of Zwerdling et al. (Reference 2) and ($\leq$44.0 $\pm$ 0.2) meV of Onton et al. (Reference 3).

TABLE 3

EXPERIMENTAL POSITIONS OF GALLIUM AND INDIUM $p_{1/2}$ EXCITATION LINES IN SILICON.

	Gallium line positions[a]		Indium line positions[a]	
Line	Wave number (cm^{-1})	Energy (meV)	Wave number (cm^{-1})	Energy (meV)
2p'	897.5	111.28	1565.2	194.06
3p'	922.0	114.31	1590.0	197.14
4p'	931.0	115.43	1598.4	198.18

[a]Error is estimated to be $\pm$0.1 cm^{-1} (0.01 meV) for 2p' and 3p'; $\pm$0.2 cm^{-1} (0.025 meV) for 4p'.

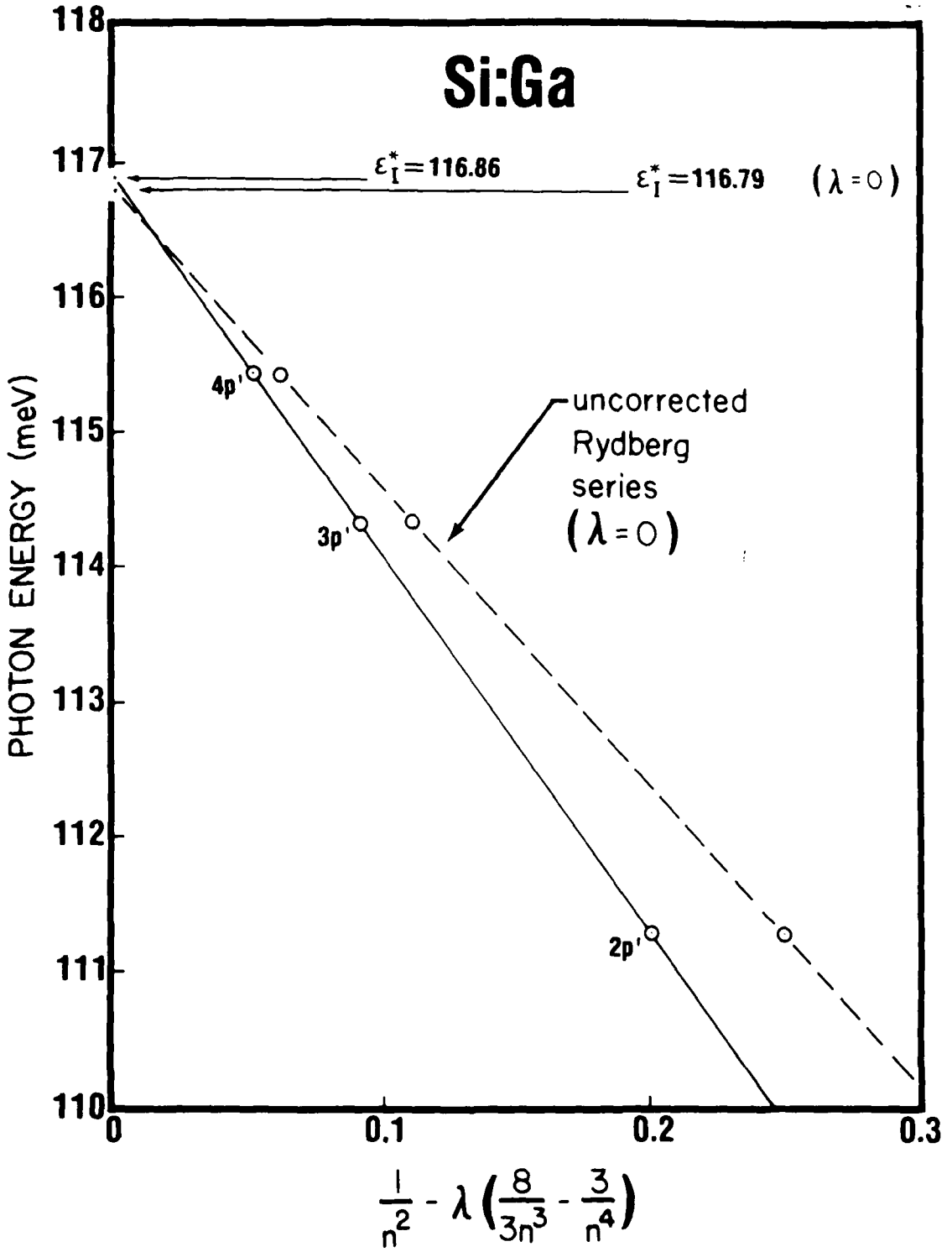

Figure 4. Plot of Uncorrected Rydberg Series (Dashed Line) and Corrected Rydberg Series (Solid Line) for $p_{1/2}$ Lines of Gallium in Silicon.

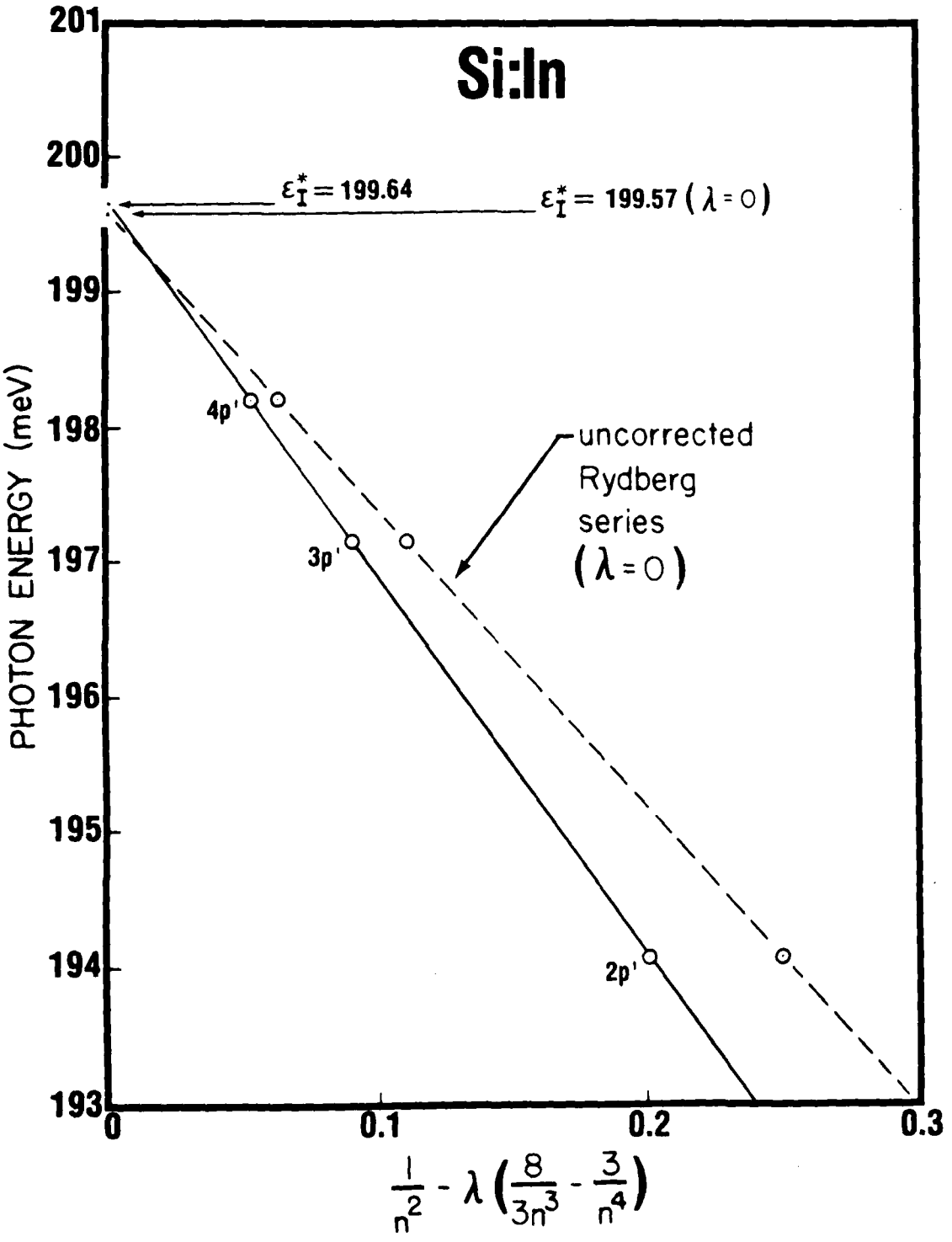

Figure 5. Plot of Uncorrected Rydberg Series (Dashed Line) and Corrected Rydberg Series (Solid Line) for $p_{1/2}$ Lines of Indium in Silicon.

CONCLUSIONS

We have obtained absorption spectra of the $p_{3/2}$ excited state lines of gallium in silicon. Two missing lines were observed and a third "weak or doubtful" one was confirmed. The energy spacings of the lines were successfully compared to theory and the other group III acceptors. We have also measured the $p_{1/2}$ spectra for gallium and indium in silicon, observing the previously unseen 4p' lines. From the spectra we calculated new values for the gallium and indium $p_{1/2}$ series limits, and for the spin-orbit splitting of the valence bands.

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