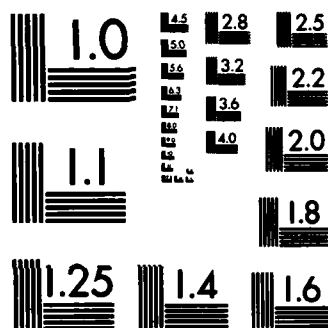END

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PHOTOELECTRIC SPECTROSCOPY OF INDIUM
IN SILICON

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October 1982

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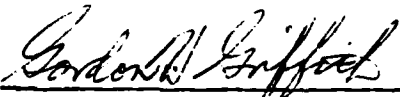DEC 20 1982

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Laser and Optical Materials Branch
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FOR THE COMMANDER

M. L. MINGES, Chief
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Photoelectric spectroscopy has been used to study $p_{3/2}$, $p_{1/2}$, and Breit-Wigner-Fano excited state transitions of indium in silicon. The photoelectric spectra were compared to absorption spectra, and measured as a function of temperature. All $p_{3/2}$ and $p_{1/2}$ absorption lines are resolved in photoelectric spectra, with the exception of no. 4B. This is the first

20. ABSTRACT - Continued

observation in photoelectric spectra of lines 3 through 10, 3p', and 4p'. The temperature dependence of the spectra demonstrates that line intensities are governed by a photothermal ionization process; in particular, the activation energy of the line 4 intensity agrees with the theoretical binding energy of the excited state. Details previously observed in the Breit-Wigner-Fano spectra associated with $p_{3/2}$ lines 2-10 have also been observed for the first time in the absorption spectra.

FOREWORD

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SECTION I

INTRODUCTION

Photoelectric spectroscopy is used to study the energy states of carriers bound to impurities in semiconductors, and to detect small concentrations of impurities (Reference 1). The spectra obtained by this mehtod are produced by a two-step process, optical excitation of the bound carrier to an excited state, followed by thermal ionization of the carrier from the excited state to a band. This photothermal ionization process has received considerable theoretical interest because of its own importance, and because of its direct relationship to the probability of carrier capture into a bound state by a charged impurity (References 2-4). Photoelectric spectroscopy has been mainly applied to III-V compound semiconductors (References 5,6) and to germanium (References 7-9).

Absorption spectroscopy has been the major method of determining the energy levels of donors and acceptors in silicon. In particular, the energy position and symmetry have been well established for most of the $p_{3/2}$ and $p_{1/2}$ acceptor states (References 10,11). Fourier transform absorption spectroscopy and improved crystal growth methods have more recently permitted the detection of the remaining missing or doubtful excited state transitions of indium and gallium (References 12,13). Meanwhile, improvements in the effective mass theory have produced more accurate acceptor energy values with which to compare the experimental spectra (References 14,15). Absorption spectroscopy was also used for the first observation of the Breit-Wigner-Fano (BWF) resonance spectra associated with the $p_{3/2}$ excited states of boron, aluminum, and gallium in silicon (Reference 16). An unanswered question

was why BWF absorption spectra showed an antiresonance dip only in connection with the first acceptor excited state, but not for the higher energy excited states.

In silicon, photoelectric spectroscopy has been used to study the energy levels of phosphorous and boron (References 1,7,8), and sulfur (Reference 17). Earlier spectral photoconductivity studies of acceptors other than boron, for example indium, (Reference 18) did not resolve discrete lines caused by transitions to excited states. More recently, Baron et al. (Reference 19) reported photoelectric spectra for aluminum, gallium, and indium in silicon. They observed most of the major $p_{3/2}$ transitions for indium, but as subtractions from the background of X-level photoconductivity. As true, positive photoelectric lines they observed only no. 2, while line 1 appeared as a plateau or shoulder, and hints of lines 3 and 4 were present as inflections in the response curve. In the case of $p_{1/2}$ transitions, their data contained the 2p´ and 3p´ lines for aluminum and gallium, and the 2p´ line for indium. Their BWF spectra for indium were highly detailed, containing features associated with all of the $p_{3/2}$ transitions. This is sharply contrasted with the BWF absorption spectra of Watkins et al. (Reference 16) containing only line no. 1.

Using a high resolution, high signal-to-noise system, we have observed photoelectric spectra for indium in silicon and compared them to our absorption spectra. We report for the first time all lines 3-10 (with the exception of 4B) of the $p_{3/2}$ transitions as positive photoelectric bands. We have made the first photoelectric observation of the indium 3p´ line of the $p_{1/2}$ series, and the first photoelectric observation of the 4p´ line for any acceptor. We have also measured the temperature dependence of the photo-electric line intensities, demonstrating that they are governed by the

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photothermal ionization process, and have obtained an experimental value of the ionization energy for the $(1\Gamma_7^-)$ state which agrees with theory. Our BWF spectra show all major features in both absorption and photoconductivity, indicating that the absorption transitions are not particularly weak because of either special selection rules or experimental sensitivity.

SECTION II
EXPERIMENTAL

Photoconductivity (photoelectric) and absorption samples were cut from dislocation-free float-zone boules containing $3 - 4 \times 10^{16}$ indium atoms/cm^3. Residual donor-impurity and acceptor-impurity concentrations were less than 2.3×10^{14} cm^{-3} as determined by Hall effect analysis. The photoconductivity samples were 1.00 cm long, 0.25 cm wide, and 0.050 cm thick. Ohmic contacts were applied by sparking of indium metal. The electric field was kept below 10 V/cm for all photoconductivity measurements. Optical absorption samples were 0.40 cm thick.

The photoconductivity samples were maintained at a constant temperature in a "Heltran" flowing gas refrigerator system (Reference 20). The photo-conductivity samples were secured on one end by GE 7031 varnish (Reference 21) to a 0.16-cm-thick beryllium oxide slab mounted on the cold finger of the "Helitran". This method provide a strain free thermal contact which kept the samples electrically isolated from the cold finger.

Photoelectric spectra were obtained with a system built around a Spex model 1704 1.0 meter spectrometer (Reference 22) employing oversize 125 mm X 100mm gratings (See Figure 1). The system included a Nernst glower, all-mirror optics, order-sorting filters, a TGS-detector for intensity calibration, lock-in detection, and a minicomputer for spectrometer control, data acquisition and data averaging. The spectral resolution was measured to be 0.88 cm^{-1} for data reported here. The wavelength calibration of the system was based upon the line positions of the emission spectra of mercury vapor in a low-pressure lamp.
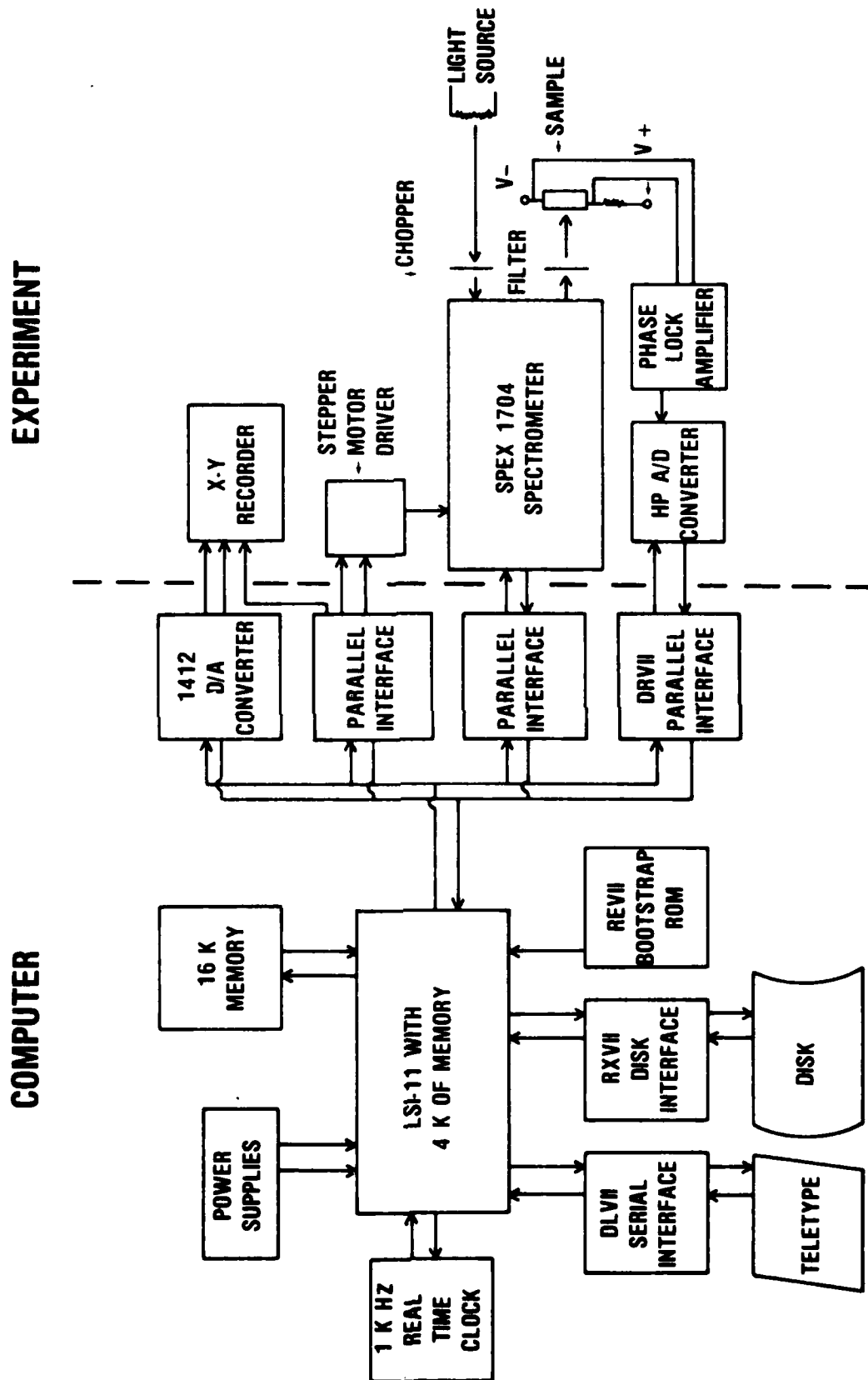
Figure 1. Photoconductivity System Block Diagram.

Absorption spectra were recorded on a Digilab model FTS-20CVX Fourier transform spectrometer at a resolution of 0.5 cm^{-1}. Further details of the absorption experiments were the same as reported earlier (References 12,13).

SECTION III

RESULTS AND DISCUSSION

Figure 2 contains photoelectric and absorption spectra in the region of lines 1, 2, and 3 of the $p_{3/2}$ series. The photoelectric line positions agree with the absorption line positions within the experimental error. The photoelectric and absorption linewidths are also essentially equal. The apparent slight shift to higher energy of line 2 of the 50K photoelectric spectrum is due to the sloping background shoulder. The absorption line positions of the $p_{3/2}$ series have been tabulated in detail elsewhere (Reference 12). Line 1 appears here only as a negative photoelectric band caused by subtraction of background signal. Line 2 is seen by background subtraction at 20K and as a positive photoelectric band at 50K. Line 3 is a positive photoelectric band at 20K but loses its distinctive features in the background. Our results are consistent with the 10K and 40K spectra of Fig. 4 of Baron et al. (Reference 19) obtained with sample electric fields of 200 V/cm and 100 V/cm, respectively. Our photoelectric spectra show line 3 as a distinct band for the first time and our photoelectric linewidths are considerably narrower than those of Baron et al. (Reference 19).

The comparison between photoelectric and absorption spectra for lines 4-10 of the $p_{3/2}$ series is shown in Figure 3. All photoelectric and absorption line energy positions agree within experimental error, as do the linewidths. At 8.8K, lines 4 and combined lines 4A, 4B appear only as a slight decrease in the background signal, while line 5 is not seen as either a positive or negative signal. However, lines 6, 7, 8, 9, 10 are all positive photoelectric bands. At 21.0K, all lines 4-10 are positive photoelectric bands. Again, the photoelectric line positions agree with
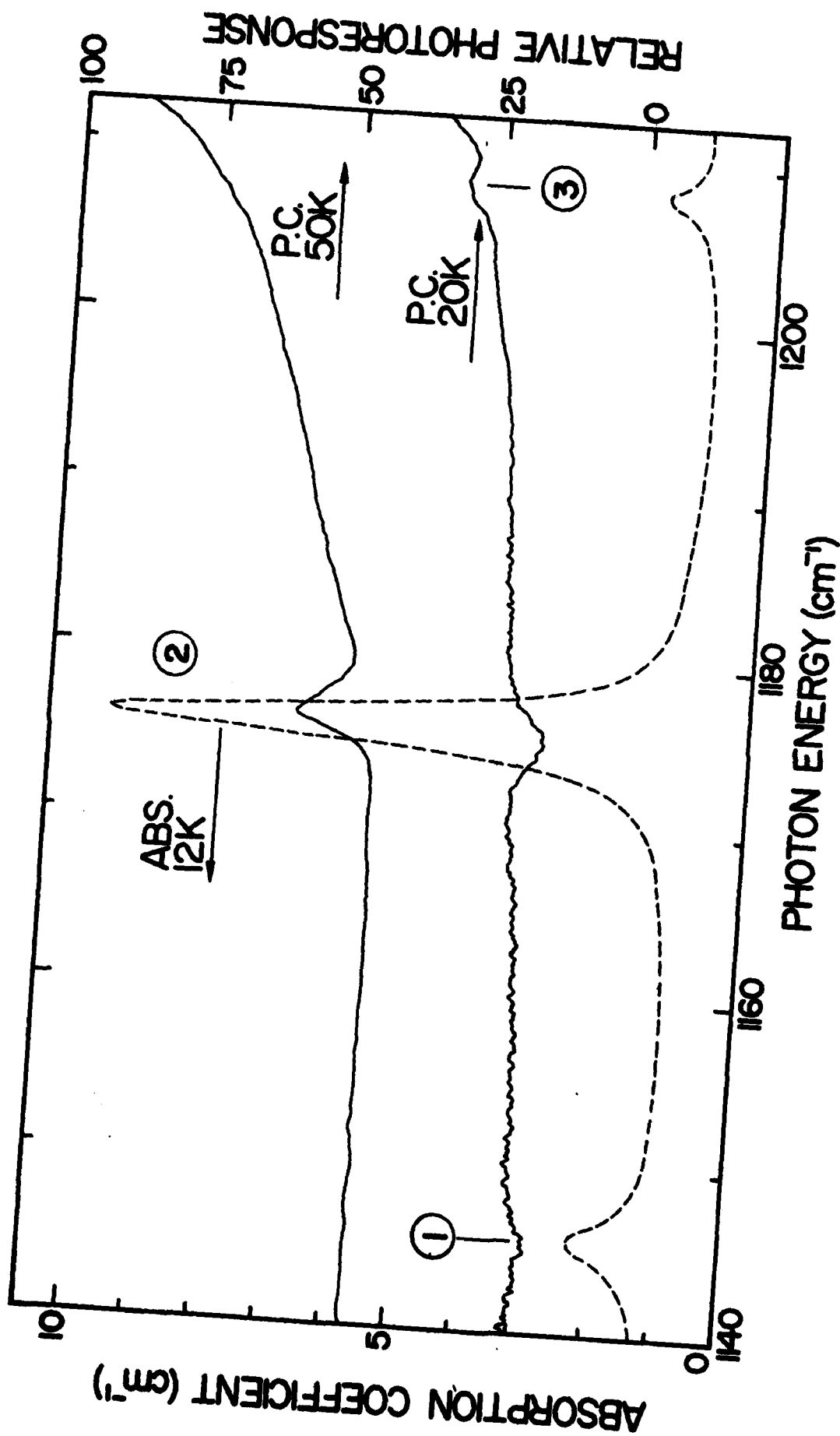
Figure 2. Photoconductivity and Absorption Spectra for Indium in Silicon in the Region of Lines 1-3 of the $P_{3/2}$ Series.
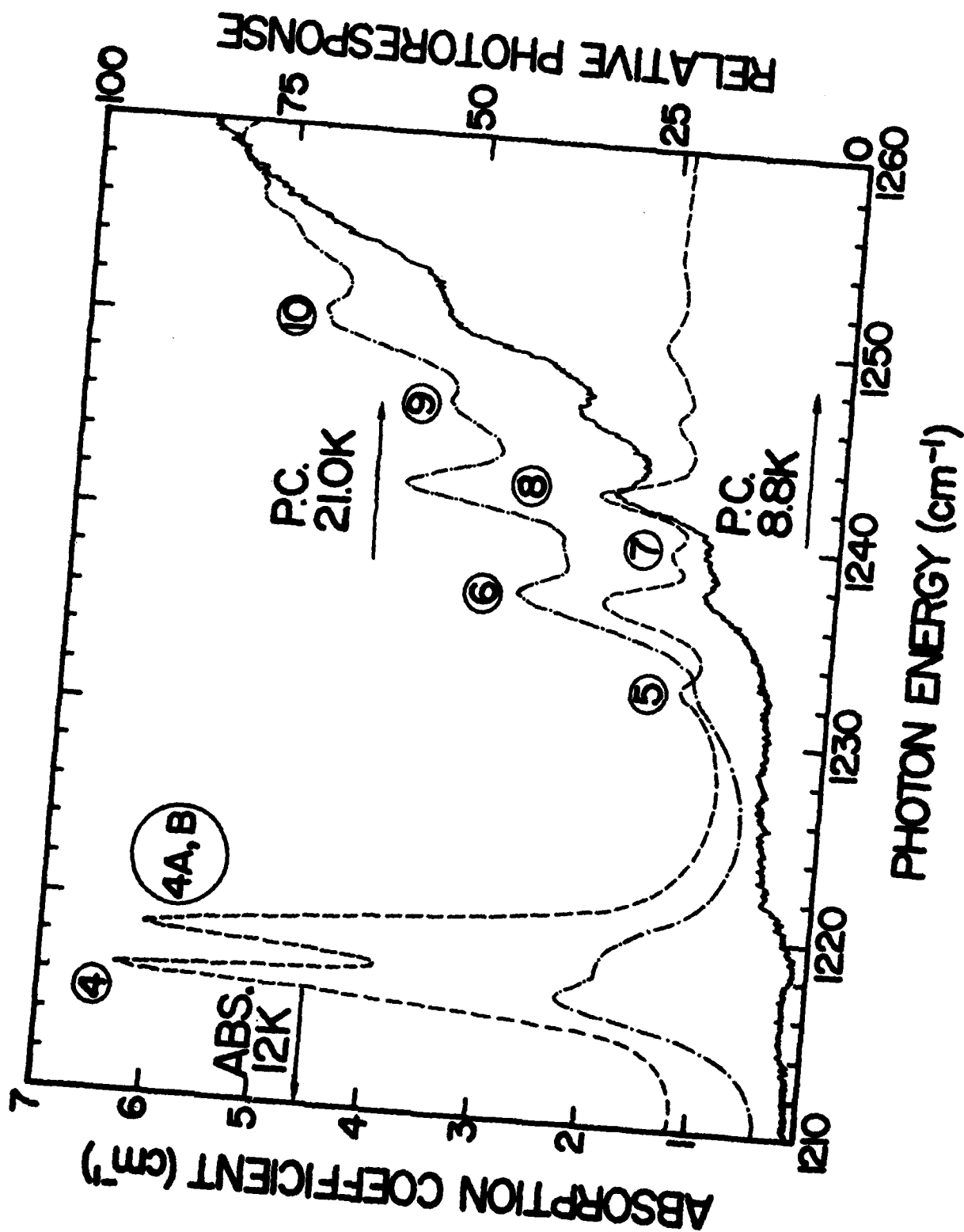
Figure 3. Photoconductivity and Absorption Spectra for Indium in Silicon in the Region of Lines 4-10 of the $P_{3/2}$ Series.

the absorption line position within experimental error, and the photo-
electric and absorption linewidths are nearly equal. This is the first
observation of lines 3-10 as distinct photoelectric bands for indium in
silicon. The temperature dependent intensity of the photoelectric lines
in Figures 1 and 2 qualitatively agrees with the behavior expected from
photothermal ionization.

The temperature dependence of lines 4, 4A, and 4B is shown in
Figure 4. The zero location of the ordinate is different for each spectrum
but is labeled according to sample temperature. Positive photoelectric
signals are not seen for data recorded with a sample temperature below
11.1 K. The signal continues to increase less rapidly above 13.9 K but the
spectra are not shown because the linewidths increase rapidly because of
phonon broadening (Reference 23).

The intensity of line 4 vs. temperature has been analyzed following
the methodology of Kogan and Lifshitz (Reference 1) and Stillman et al.
(Reference 5). Eq. 27 of Stillman et al. (Reference 5) gives the photothermal
ionization probability as

$$I_{n,\ell} = \frac{R_{n,\ell}}{R_c} \frac{\sigma}{\sigma_{n,\ell}} \tag{1}$$

where n and ℓ refer to the principal and angular momentum quantum numbers of
the (n,ℓ) excited state, $R_{n,\ell}$ is the photoelectric response due to photo-
thermal ionization of the (n,ℓ) excited state, R_c is the photoconductive
response from the ground state to the continuum (1280 cm^{-1} used here), $\sigma_{n,\ell}$
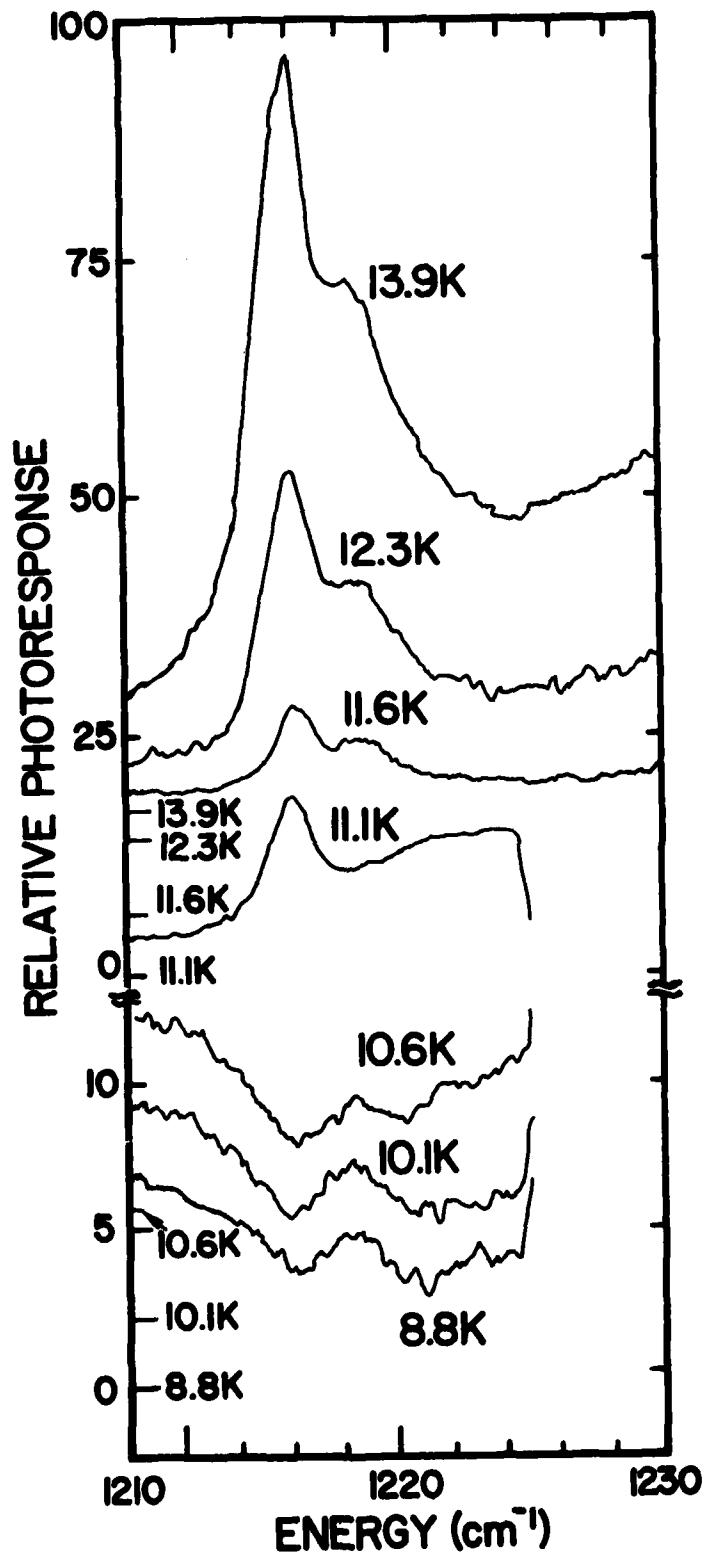
Figure 4. Temperature Dependence of the Photoelectric Spectra for Lines 4, 4a and 4b of the $P_{3/2}$ Series.

is the optical absorption cross section for transitions from the ground state to the (n,ℓ) excited state, and σ is the optical absorption cross section section for transitions from the ground state to the continuum.

We have analyzed the photothermal ionization process using peak heights only and the approximation:

$$I_{n,\ell} \propto \frac{R_{n,\ell}}{R_c} \qquad (2)$$

with the following justification:

1) σ and $\sigma_{n,\ell}$ are constant over the 11K-14K temperature interval.

2) We have carefully measured the absorption linewidths and found them to change by only 11% over this temperature interval. The size of this broadening is probably no more severe than the overlap of lines 4 and 4A, and its effect on the integrated intensity is in a direction opposite to the effect of the overlapping lines.

The data from each separate experiment were fit to a simple exponential function, as typified by the example of Figure 5. The mean activation energy for several experiments was 6.4 $\pm$ 0.4 meV, where the error is a standard deviation.[*] This activation energy is interpreted to be the separation of the line 4 excited state $(1\Gamma_7^-)$ from the valence band. This experimental value compares favorably with the 6.1 meV value of the most recent theoretical calculations (Reference 15). The agreement is much better than that observed for other systems, such as donors in GaAs, (Reference 5) and is further evidence that the photothermal ionization process is the mechanism producing the discrete photoelectric lines.

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[*]See Reference 24 for calculation of the standard deviation of the slope of a linear least squares fit.
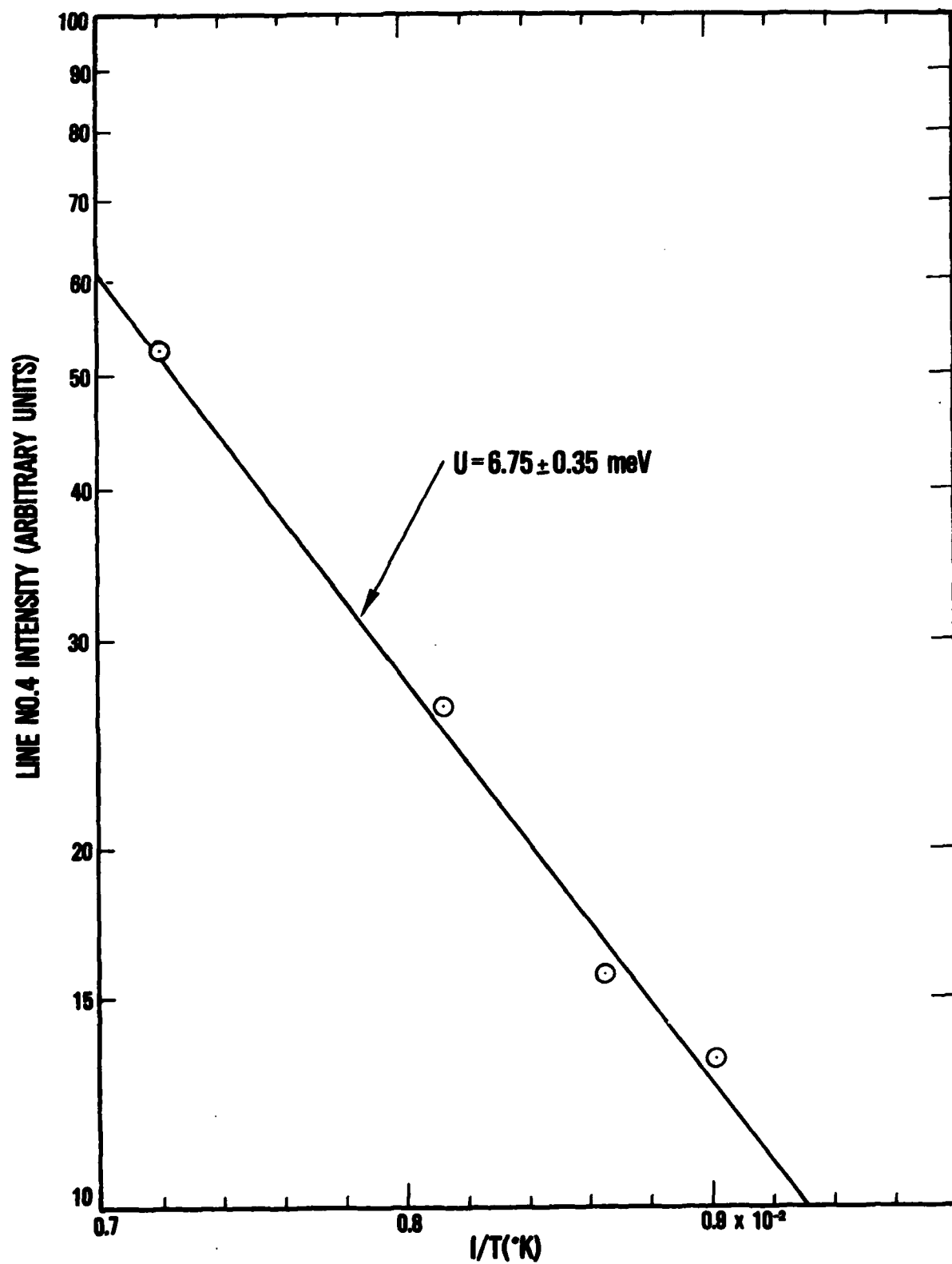
Figure 5. Line No. 4 Intensity vs. Reciprocal Temperature
for a Typical Experiment.

More recent theories of photothermal ionization probability do not follow simple exponential behavior (References 2-4). We have compared Eq. 31 of Abakumov and Yassievich, (Reference 2), and Eq. 5 of Jongbloets et al. (Reference 5) with a simple exponential function (See Figure 6), and have reached the following conclusions:

1) It would be nearly impossible to distinguish between the two more complete theories given the accuracy of most experiments.

2) The two more complete theories approach simple exponential behavior at lower temperatures, which include the 11K - 14K interval.

3) Our experimental accuracy, as well as the broadening and overlap problems, do not justify attempting to fit the data to any function more complex than a simple exponential over the 11K - 14K temperature inverval.

We are thus confident that fitting the data to a simple exponential function is a reasonable procedure. This is the first known report of an analysis of the temperature dependence of the intensity of the photoelectric lines for any impurity atom in silicon.

Photoelectric and absorption spectra in the region of the $p_{1/2}$ excitation series (Reference 10) and the BWF resonances (Reference 16) are shown in Figure 7. The 3p´ photoelectric line is clearly resolved for the first time for indium in silicon, and the 4p´ photoelectric line is seen for the first time for any acceptor in silicon. The energy position of the photoelectric lines agree well with the absorption values, which were reported earlier (Reference 12). The linewidths also are essentially equal.

In order to demonstrate the origin of BWF resonances, a $p_{3/2}$ absorption spectrum is also shown in Figure 7, but is shifted to higher energies by 519 cm^{-1}, the energy value of a zone center optical phonon. The BWF
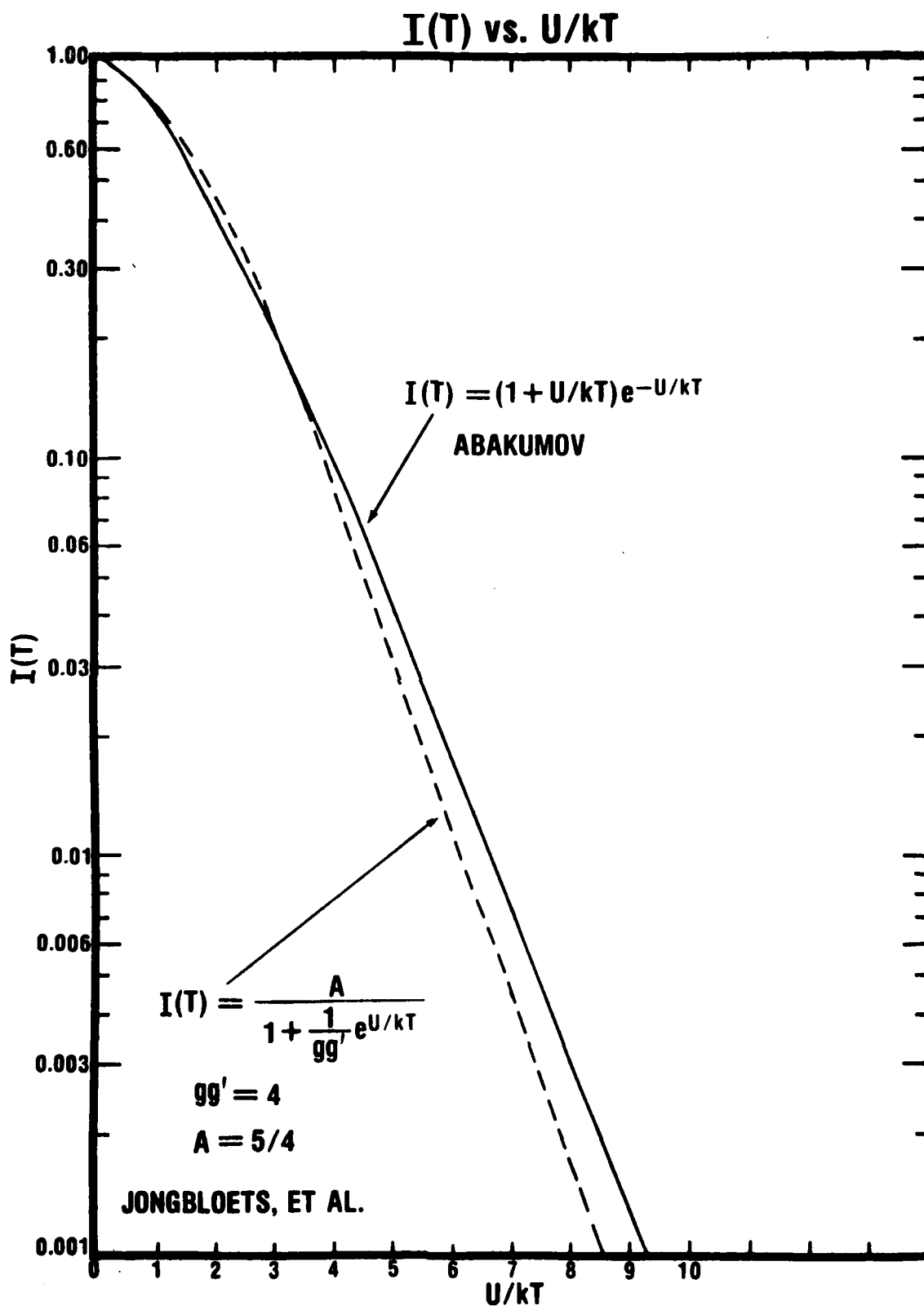
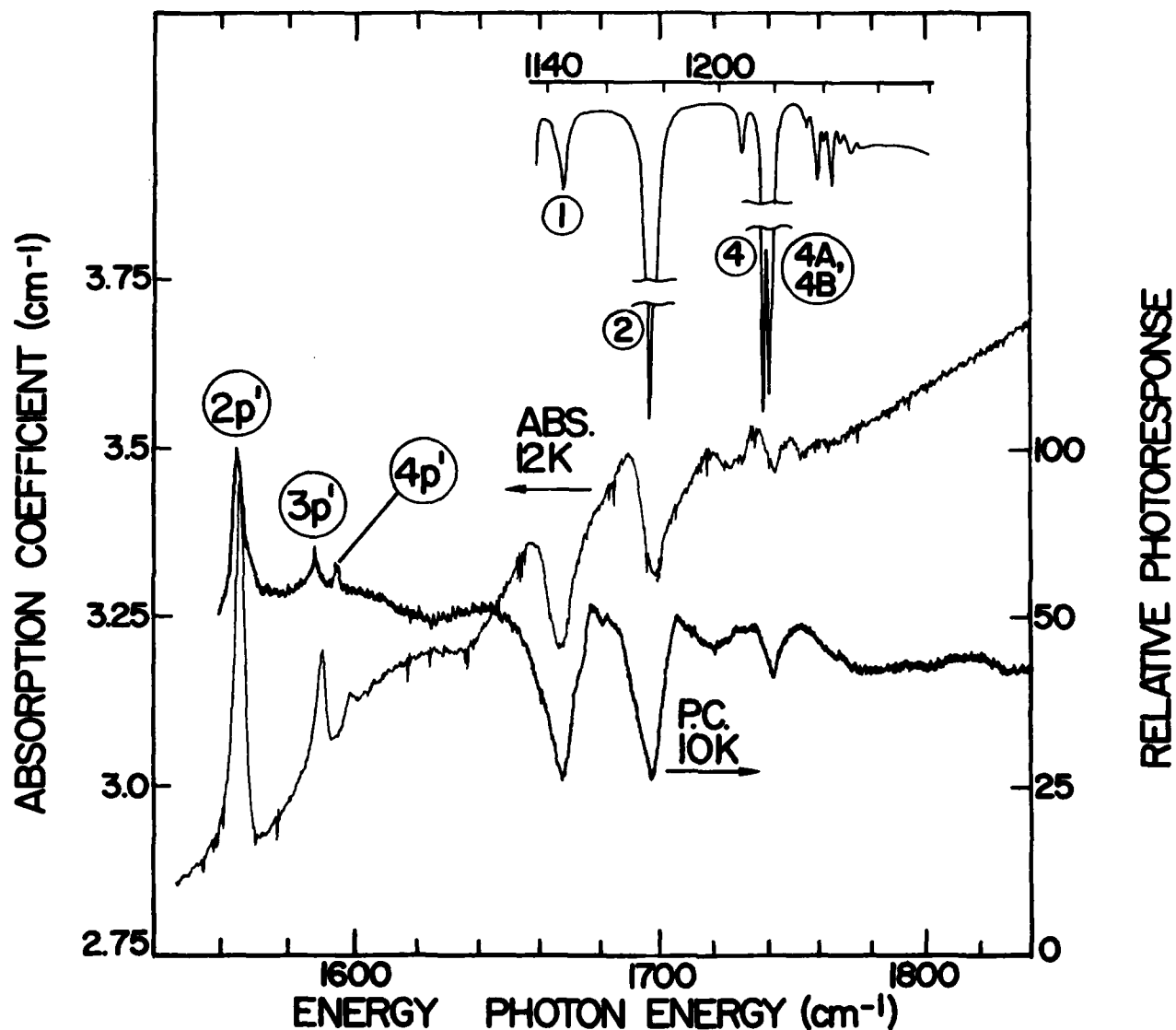Figure 6. Theoretical Photothermal Ionization Probability vs. Reciprocal Temperature.

Figure 7. Photoconductivity and Absorption Spectra for Indium in Silicon in the Region of the $p_{1/2}$ Series Lines and the Breit-Wigner-Fano Resonances. The $p_{3/2}$ Absorption Spectrum Is also shown Displaced by the Energy (519 cm^{-1}) of the Zone-Center Optical Phonon.

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phenomenon is the resonant interaction of two separate processes; 1) excitation from the indium ground state to the $p_{3/2}$ excited states, followed by absorption of the 0^{Γ} phonon to the $p_{1/2}$ continuum; 2) direct excitation from the ground state to the $p_{1/2}$ continuum. In absorption, a series of resonance and anti-resonances are produced, the dip in the antiresonance corresponding almost exactly to the sum of the 0^{Γ} phonon energy and the $p_{3/2}$ excitation energy (Reference 16). In photoelectric spectra, the resonance (positive) features are surpressed (Reference 25).

Watkins and Fowler (Reference 16) studied the BWF absorption phenomenon in silicon doped with boron, aluminum, and gallium, but not indium. They saw only BWF features associated with line 1 of the $p_{3/2}$ series, and explained the absence of the features produced by the other $p_{3/2}$ lines as a mismatch in k-space between $p_{3/2}$ excited states and the $p_{1/2}$ continuum. Baron et al. (Reference 19) reported BWF features in photoconductivity corresponding to the major $p_{3/2}$ lines for aluminum, gallium, and indium in silicon. Our photoconductivity spectrum contains the same features reported by Baron et al. (Reference 19), but we also see the same major features in the absorption spectrum. Thus, there is no theoretical impediment to the appearence in absorption spectra of BWF resonances associated with lines 2-10 of the $p_{3/2}$ series as proposed by Watkins et al. (Reference 16), or experimental impedi-ment as implied by Baron et al. (Reference 19). The dips (antiresonances) in the photoelectric and absorption spectra shown in Figure 7 occur at very nearly the same photon energy. The displaced $p_{3/2}$ lines do not lie exactly at the minima of the antiresonances but are shifted slightly to lower energies. The data of Baron et al. (Reference 19), show the same shift for indium in silicon, but not for aluminum or gallium. We do not yet have an expla-nation for this shift.

CONCLUSIONS

We have obtained photoelectric spectra for indium silicon in the region of the $p_{3/2}$, $p_{1/2}$, and Breit-Wigner-Fano transitions. The energy positions and linewidths of the $p_{3/2}$ and $p_{1/2}$ photoelectric transitions agree with those in absorption. We report the first photoelectric observation of lines 3-10 of the $p_{3/2}$ series and line 3p´ of the $p_{1/2}$ series for indium in silicon, and the first observation of line 4p´ for any acceptor in silicon. The temperature dependence of the photoelectric line intensities demonstrates that they are governed by a photothermal ionization process. From the temperature dependence of line 4 of the $p_{3/2}$ series, we measured a binding energy of 6.4 ± 0.4 meV for the excited state. We have seen the major features of the $p_{3/2}$-associated Breit-Wigner-Fano resonances in both absorption and photoelectric spectra, demonstrating that there is no fundamental reason to preclude the observation of lines above no. 1 in absorption.

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