AN OPTICAL STUDY OF LITHIUM AND LITHIUM-OXYGEN COMPLEXES

AS DONOR IMPURITIES IN SINGLE CRYSTAL SILICON

by

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I. INTRODUCTION

Certain impurities may drastically affect the electrical and
optical properties of host semiconductor crystals due to the small
amount of energy required to release an electron from the impurity
atom into the crystal conduction band. In the effective mass theory
(14), a shallow donor impurity ion and its loosely bound electron are
considered as a hydrogen-like system embedded in a dielectric medium.
The effects of the crystal upon the system are concealed in the
dielectric constant of the crystal and in the effective mass of the
donor electron within the crystal.

For sufficiently low temperatures the donor electrons are found
in significant numbers only in the ground state of the system, from
which transitions to excited states may be induced, say by infrared
radiation. The resonances observed in optical absorption spectra may
then be used to determine the excited state energy levels relative to
the ground state level, the level widths, and the relative transition
probabilities, which are proportional to the products of the absorption
line intensities and the corresponding transition energies.

Several optical studies of the electronic energy levels for
shallow donors in silicon have been performed (1, 2, 22, 26). The
results of these studies are in good agreement with the effective mass
theory for the excited states, but agree poorly with the predicted
ground state energy. This disparity in the predicted and the observed

donor ground state energies has been attributed to the neglect of effects in the vicinity of the donor nucleus.

Of all the known shallow donors in silicon, lithium (14) possesses those properties most closely matching the assumptions of the effective mass theory. Bell (1) conducted an optical study of lithium-doped silicon; however, in view of the lithium-oxygen interaction in silicon (20) and the large oxygen concentrations of his samples, it seems highly unlikely that any free lithium existed in the samples studied.

This thesis reports research which includes an optical study of the donor structure of both monatomic lithium and lithium-oxygen complexes in single crystal silicon.

II. REVIEW OF LITERATURE

Shallow Donor Theory

The theory presented here follows the work of Kohn (14), although in a more phenomenological form. For a more detailed treatment, the reader is referred to the original publication.

In our attempt to arrive at a simple understanding of the behavior of donor impurities in semiconductors, we consider the impurity as a positive singly charged ion and an extra electron in an otherwise perfect semiconductor crystal. We are interested in the energy levels assumed by the electron under the influence of the periodic potential of the lattice and the electrostatic potential of the ion. If it were not for the ionic potential, we would expect that at low temperatures the electron would occupy a state near the bottom of the conduction band. Due to its interaction with the periodic potential of the lattice, such an electron would move under the influence of an applied field as though it had a mass m*, called the effective mass, which is generally different from the free electron mass m. Although the effective mass of the electron is dependent upon the electronic state wave vector $\bar{k}$, we consider it a constant for small wave vector displacements about the bottom of the conduction band.

Next, we consider the potential within the semiconductor due to an impurity ion of atomic number Z and charge + e. The semiconductor will be polarized so that at large distances the electrostatic potential $V(r)$ will be

$$V(r) = e/\kappa r,$$

(1.1)

where κ is the static dielectric constant of the semiconductor and r is the distance from the impurity ion. For small r however, the electrostatic potential becomes that of the ionic nucleus screened by the $Z - 1$ remaining atomic electrons and approaches Ze/r as r approaches zero.

For the interaction between the impurity ion and the extra electron, we consider two possibilities. First, the electron may be tightly bound to the ion so that the electron spends much of its time in a region where (1.1) does not apply. A description of such a "deep" donor state becomes quite complicated and we will pursue the matter no further. On the other hand, the electron may be so loosely bound even in the ground state that the electron spends most of its time in the region where (1.1) applies. It is in such "shallow" donor states that we are interested, and we shall assume that the potential energy $U(r)$ of the electron in the field of the donor ion is

$$U(r) = -e^2/\kappa r. \tag{1.2}$$

With the assumption that the effective mass of an electron at the bottom of the conduction band and the potential energy (1.2) are appropriate to shallow donor systems, we write the Schroedinger equation describing a shallow donor as

$$\left[\frac{-\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{\kappa r} \right] F(r) = E\ F(r). \tag{1.3}$$

This differs from the equation for the hydrogen atom only by the

inclusion of the dielectric constant κ and the use of the effective

mass m^* in place of the free electron mass. The static dielectric

constant is used since the frequency of oscillation of the impurity

electron is much lower than that of the other electrons in the

crystal whose polarization gives rise to κ in a homopolar material

(12). The allowed energies are

$$E(n) = -\frac{m^*(e^2/\kappa)^2}{2\hbar^2 n^2}, \quad n = 0, 1, 2 \ldots \tag{1.4}$$

The eigenfunctions are of course identical in form to those of the

hydrogen atom and the normalized ground state wave function is

$$F(r) = (\pi a^{*3})^{-1/2} \exp[-r/a^*], \tag{1.5}$$

where

$$a^* = \hbar^2 \kappa / m^* e^2. \tag{1.6}$$

Using the value of κ and the scalar approximation of m^* appropriate

to silicon, we obtain for the first Bohr radius a^* and the ground state

energy respectively the values

$$a^* = 25A \tag{1.7}$$

and

$$E(0) = 29 \text{ mev (milli-electron volts)}. \tag{1.8}$$

In comparing the first Bohr radius a* with the silicon lattice constant of 5.43 A, we see that this is at least consistent with our assumption that the electron spends most of its time in the region where (1.1) is appropriate.

Although the preceding analysis has given us some insight into the problem of shallow donor impurities in semiconductors, we must go further to obtain quantitative results for such donor impurities in the silicon lattice. Specifically, we take into consideration the detailed structure of the silicon conduction band and the resulting anisotropy of the effective mass of an electron within the band. In silicon there are six equivalent conduction band minima in k-space located at the points $(k_o,0,0)$, $(-k_o,0,0)$.....$(0,0,-k_o)$. Near any one of these minima, the energy of an electron may be expressed in the form (5)

$$E = \frac{\hbar^2}{2m_\ell} (k_z - k_o)^2 + \frac{\hbar^2}{2m_t} (k_x^2 + k_y^2). \tag{1.9}$$

The longitudinal and transverse effective mass parameters m_ℓ and m_t have, in terms of the free electron mass m, the following values (5):

$$m_\ell = 0.98 \, m,$$

$$\tag{1.10}$$

$$m_t = 0.19 \, m.$$

Using the effective Hamiltonian corresponding to (1.9) we obtain for the donor impurity an equation of the type

$$- \left[\frac{\hbar^2}{2m_\ell} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2}{2m_t} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{e^2}{\kappa r} \right] F(r) = EF(r) \qquad (1.11)$$

which is valid under the same assumptions used to justify (1.3). The anisotropic effective mass equation (1.11) has been solved (11, 15) by variational methods using trial functions derived from the hydrogenic eigenfunctions. For example, the hydrogen ground state eigenfunction is proportional to $\exp\left[-A\sqrt{(x^2 + y^2 + z^2)} \right]$ while the corresponding trial function for (1.11) is proportional to $\exp\left[- \sqrt{(B^2 x^2 + B^2 y^2 + D^2 z^2)} \right]$, where B and D are variable parameters chosen to minimize the energy. Although the solutions are rather different from the hydrogenic ones due to the large difference in m_ℓ and m_t, the solutions are labeled by the atomic notations which indicate the hydrogenic functions into which they go when $m_\ell = m_t$. These solutions of course exhibit a six-fold degeneracy due to the existence of the six equivalent minima of the silicon conduction band. Kohn and Luttinger (16) have shown that this six-fold degeneracy is reduced in the case of substitutional impurities when corrections are made to the potential for small r and symmetry arguments are considered. Their calculations indicate the existence of singly, doubly, and triply degenerate levels associated with the lowest eigenvalue of (1.11).

In Figure 1 the donor energy levels theoretically predicted by Kleiner (11) are compared with those observed by Bichard and Giles (2). For each listed donor, all other energy levels were placed relative to the 3P,$^\pm$ level (n=3, ℓ=1, m=$\pm$ 1) for which the shallow donor theory was
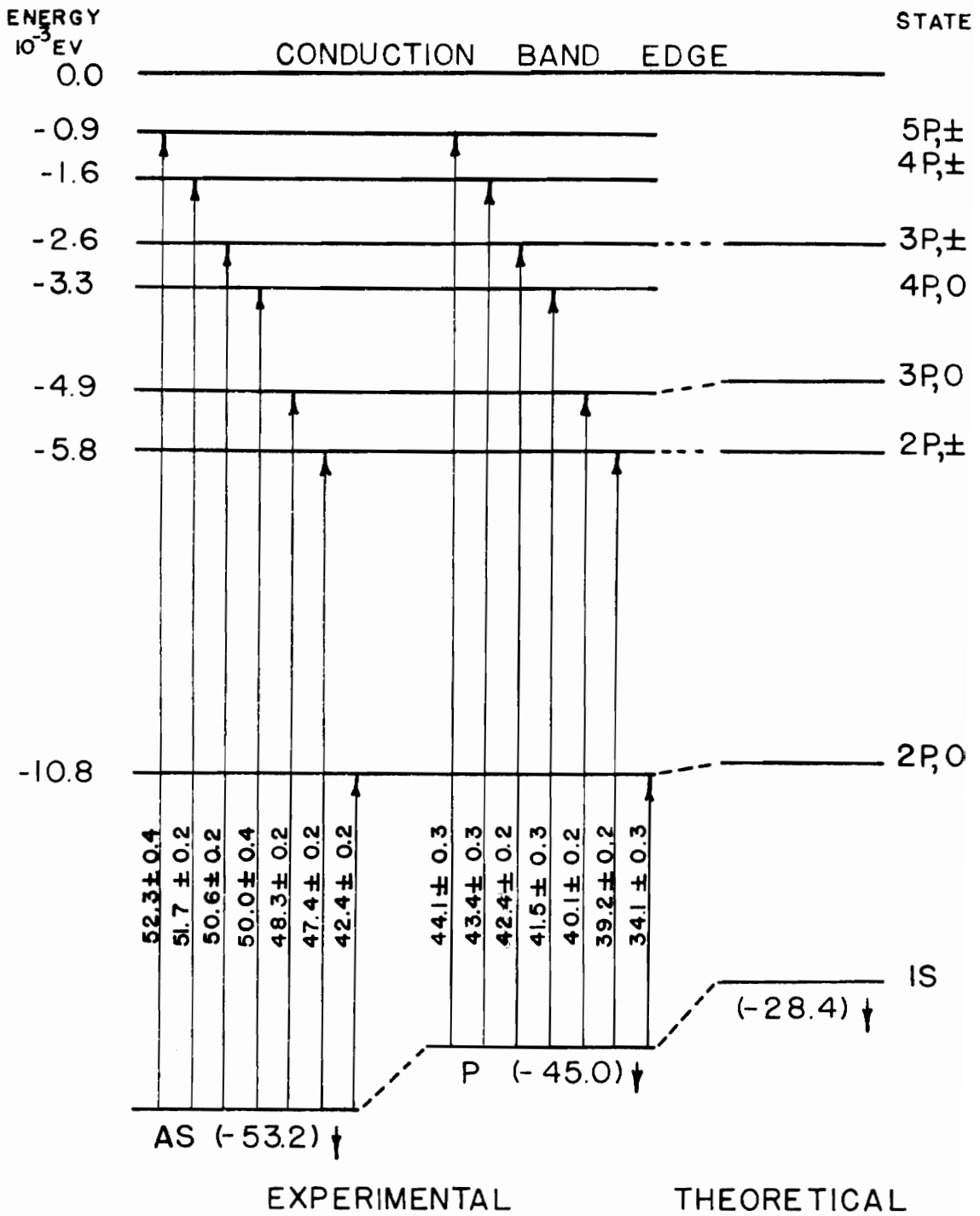
Figure 1. Energy level diagram for arsenic and phosphorus in silicon. Experimental levels due to Bichard and Giles (2). Theoretical predictions due to Kleiner (11).

assumed valid. The $4P,\pm$ and $5P,\pm$ level assignments were made in deference to Zwerdling, Button, and Lax (26) and their study of the Zeeman effect on impurity levels in silicon. The observed energy levels of the excited states are in good agreement with theory. We can attribute the disparity between the predicted and the observed ground state energies to our neglect of effects in the immediate vicinity of the donor nucleus. The form of the potential near the donor nucleus has relatively little effect upon the excited states examined, both due to the large radii of the electrons in these states and to the odd parity of the wave functions which requires that the wave functions vanish at the donor nucleus.

Of all the known shallow donors in silicon, the lithium donor best matches the assumptions made in the effective mass theory of shallow donors in silicon for the following reasons:

1. The limiting deviation from the theoretically assumed form of potential is relatively small due to lithium's small atomic number ($Z = 3$).

2. There exists only a very small volume about the donor ion in which the potential cannot be considered as that due to a point charge of + e at $r = 0$, due to the small radius of the lithium ion ($r = 0.60A$ (18)).

3. Consideration of the small size of the lithium ion, the interstitial lattice position occupied by the ion, and the relatively high diffusion coefficient of lithium in silicon

(19) indicates a minimal lattice disturbance of the silicon
lattice.

For the reasons stated, we expect a study of the lithium donor to
provide an appropriate test to the validity of the anisotropic effec-
tive mass theory of shallow donors in silicon.

Lithium-Oxygen Interactions in Silicon

Since lithium-oxygen interactions are suspected of introducing
complications into the study of the lithium donor in silicon, it is
necessary that we review the results of some experiments which shed
some light on the nature of these interactions in order to determine
a plan of investigation.

Using silicon samples having oxygen concentrations of the order
of 10^{17}/cc or greater, Pell (20) measured donor concentrations as a
function of temperature and time subsequent to the addition of the
lithium impurity. His results indicated a lithium-oxygen interaction
in silicon which tends to an equilibrium distribution described by
the expression

$$[LiO]C = [O][Li] , \qquad (1.12)$$

where the bracketed expressions indicate the lithium oxide, lithium,
and oxygen concentrations respectively, and C represents a dissociation
constant. The dissociation constant has the same temperature depen-
dence as does the equilibrium solubility of lithium in silicon and
has a room temperature value of 1×10^{15}/cc. For samples having

substantially higher donor concentrations than oxygen concentrations, his results indicated an oxygen concentration dependence of the lithium precipitation time constant. This indicates a role for oxygen in the formation of precipitation centers. Pell suggests that this relation may be useful for determining oxygen concentrations in silicon samples which are less than the 10^{17}/cc value which is the minimum to be reliably determined by the nine micron resonance absorption method of Kaiser and Keck (10).

The results of Feher (7), derived from paramagnetic resonance experiments on donors in silicon, tend to substantiate the conclusions of Pell as expressed in (1.12). Feher doped each of two silicon samples, one pulled from the melt and one prepared by the floating zone method, with lithium by a diffusion process to a donor concentration of 3×10^{16}/cc. Electron spin resonance signals indicating that the responsible donors did not occupy centers of tetrahedral symmetry were observed in the sample pulled from the melt, however no signal was observed for the sample prepared by the floating zone technique. The primary difference in pulled and floating zone crystals is in the amount of oxygen present; pulled silicon crystals usually have oxygen concentrations of about 10^{18}/cc while floating zone crystals characteristically have oxygen concentrations of the order of 10^{16}cc or lower. These results indicate that the donors observed in the two samples are not the same and that the donors in the pulled sample are most likely lithium-oxygen complexes of one or more types.
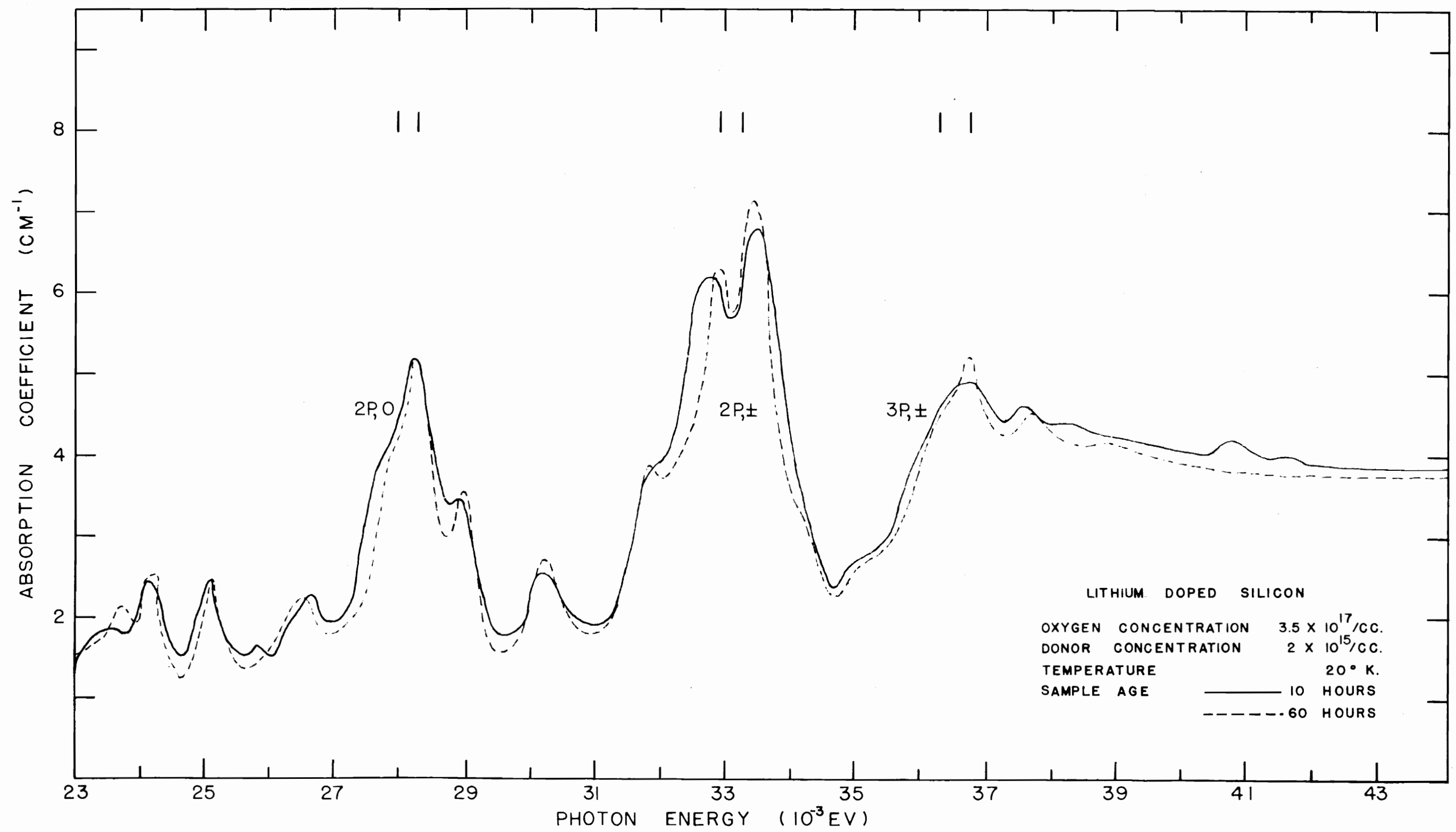
FIGURE 2. ABSORPTION SPECTRA, DETERMINED BY BELL (I), OF SILICON SAMPLE SE-I-D

Bell's absorption spectra (1) of a silicon sample containing lithium and a large amount of oxygen are shown in Figure 2. The principal absorption peaks correspond to a donor with its ground state located thirty-nine mev below the bottom of the conduction band. The absorption spectra of another sample with a lower oxygen concentration and with the lithium impurity mainly concentrated at the sample surface was also determined by Bell. This spectrum was essentially a typical donor absorption spectrum, i.e. no apparent splitting of the absorption peaks, with an indicated ionization energy of thirty-nine mev. Bell concludes that oxygen probably plays a significant role in the formation of the donors responsible for the complexities of the observed absorption spectra. The questions raised by the appearance of the complex structure of Figure 2 led to the present investigation.

We conclude from this review that the oxygen concentration must be considered in any study of the lithium donor in the silicon crystal. Specifically from (1.12) we see that the oxygen concentration should be much less than 10^{15}/cc if donor concentrations of the order of 10^{15}/cc are used since it is desirable to have an uncomplicated spectrum of the lithium donor. The room temperature dissociation constant was used in the preceding analysis since the temperature dependence of the lithium diffusion in silicon (19) indicates that the room temperature solution of (1.12) will be "frozen in" when the sample is rapidly cooled to liquid air temperatures or lower. We are also able

to conclude that a study of the donor spectra of lithium-doped
and oxygen-rich silicon samples might provide additional infor-
mation about the lithium-oxygen interaction in silicon since we
would expect to see different donor series corresponding to
different lithium-oxygen complexes.

III. EXPERIMENTAL DETAILS

Sample Characteristics

The pertinent data for each sample used in this investigation is listed in Table 1. The oxygen concentrations of the various silicon samples were determined by the nine micron resonance absorption method (10) for concentrations of the order of 10^{17}/cc or greater, and by precipitation time constant measurements as outlined by Pell (20) for lower concentrations. The impurity type for each sample was determined by the use of a thermoelectric probe as outlined by Dunlap (6). Resistivity measurements for the silicon wafers were made by the four probe method, due to Valdes (24), with a probe spacing of 4.25 mm. These resistivities were used in conjunction with the data of Irvin (9) to determine the donor concentrations of the silicon samples.

Sample Preparation

With the exception of sample SE-1-D, the diffusion of lithium into the silicon samples was accomplished in a dry helium atmosphere inside a fused quartz container at a temperature of 900° K. Quartz sinkers were used to hold the silicon wafers submerged in a tin bath containing 0.004% lithium by weight. Using the method outlined by Boltaks (3) and values of the diffusion coefficient and the solubility of lithium in silicon as determined by Pell (19, 21), diffusion times were calculated to insure a lithium concentration uniform to within five per cent for each sample. The introduction of appreciable

TABLE 1

Sample Data

Sample	Crystal Type	Thick. (mm)	Oxygen Conc. (cm^{-3})	Diffusion Data					
				Time (Hours)	Temp. (°K)	Before Diff. Donor Conc. (cm^{-3})	Type	After Diff. Donor Conc. (cm^{-3})	Type
M-1431-2	Floating Zone Refined	3.62	$<10^{14}$	42	900	$<10^{14}$	P	1×10^{15}	N
M-1431-3	Floating Zone Refined	3.68	$<10^{14}$	37	900	$<10^{14}$	P	1×10^{16}	N
SE-1-D	Floating Zone Refined	3.35	3.5×10^{17}	64	730	$<10^{14}$	N	2×10^{15}	N
SE-3-C	Floating Zone Refined	4.32	1.5×10^{17}	37	900	$<10^{14}$	N	4×10^{15}	N
SE-1051-2	Pulled From Melt	3.43	1.1×10^{18}	45	900	$<10^{14}$	N	2×10^{15}	N

amounts of impurities other than lithium into the silicon samples seems unlikely, considering the results of a spectroscopic analysis of the high purity tin, the small amount of reactor grade lithium used, and the relatively small diffusion coefficients of the other impurities involved.

Sample SE-1-D was doped with lithium by Bell (1). The procedure differed from that outlined above by the use of a pyrex glass container at 730° K and by the lithium content of the tin bath. The sample was first submerged for a period of 23 hours at a temperature of 730° K in a tin bath containing 0.25% lithium by weight. Subsequently the sample was submerged in a pure tin bath at the same temperature where out-diffusion of the lithium was allowed for a period of 41 hours. The resulting lithium concentration is estimated to be uniform to within 20%.

Prior to the transmission measurements, each sample was ground and polished to obtain parallel and mirror-like surfaces. A flat was ground into the periphery of each sample to facilitate contact with a germanium resistance thermometer.

Experimental Procedure

The arrangement of sample, germanium resistance thermometer, and mounting block is illustrated in Figure 3. The thermometer, calibrated in the range 4.2° K to 40.0° K, makes contact with the sample such that it indicates the average sample temperature. Sample temperatures in the neighborhood of 20° K were achieved by attaching the mounting block to the bottom of the liquid helium container of a cryostat. A thin

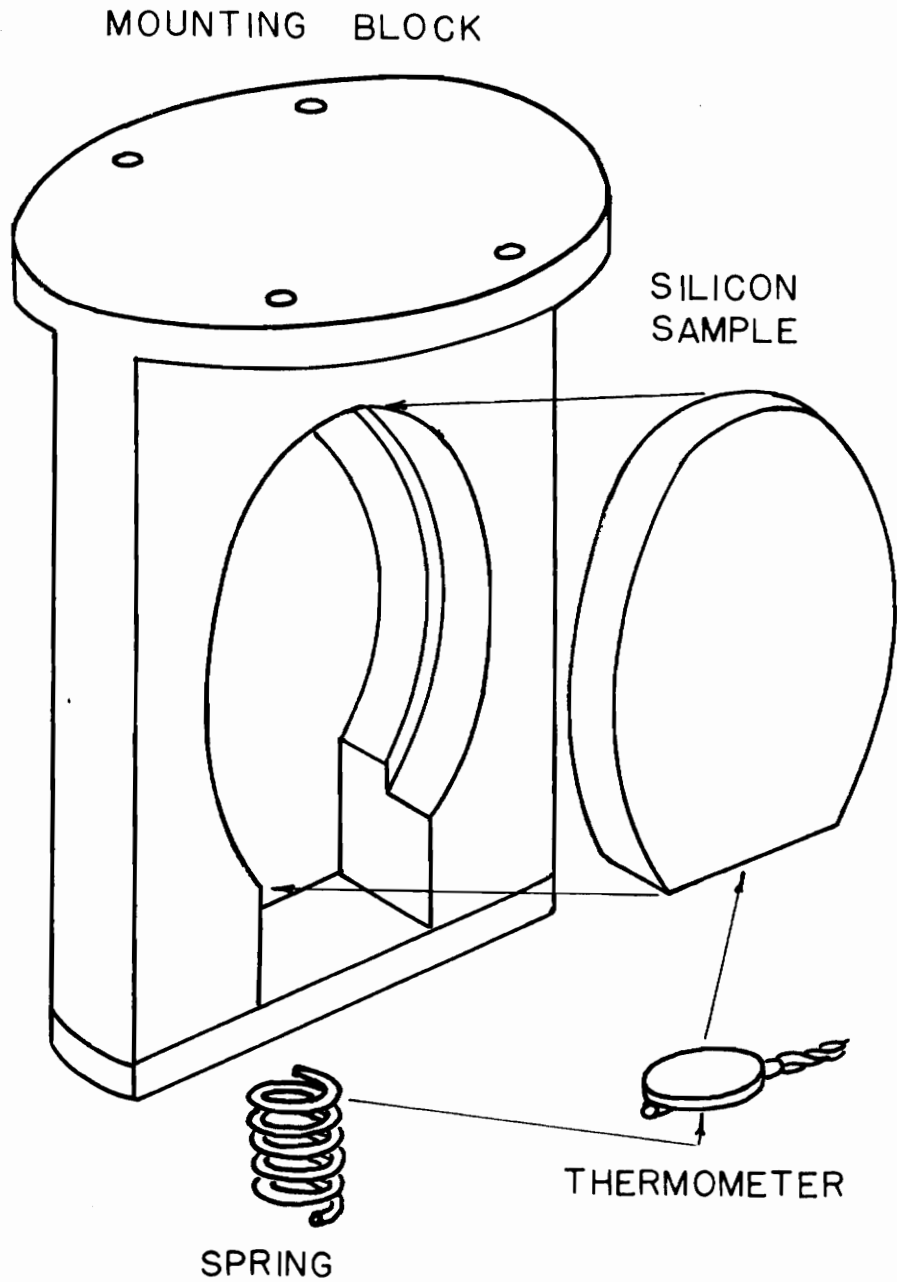MOUNTING BLOCK

SILICON
SAMPLE

THERMOMETER

SPRING

Figure 3. Assembly of Sample, Resistance Thermometer, and
Mounting Block.

film of silicone grease was used to enhance the thermal contact
between the various items mentioned.

A grating spectrometer, previously described by Bell (1), was
used in this investigation. The spectrometer was calibrated over the
energy range 23.0 mev to 45.0 mev using water vapor absorption lines
as determined by Randal, Dennison, Ginsburg and Weber (23). For use
in the computerized data reduction, the photon energy was expressed
as a fourth order polynomial in terms of the grating drive scale
reading with a standard error of 0.03 mev.

The cryostat, also described previously by Bell (1), was placed
so that the silicon sample faces were centered in and perpendicular
to the infrared beam of the spectrometer. For the purpose of elimi-
nating water vapor absorption lines from the transmission measurements,
dry nitrogen (maximum moisture content 0.0012% by weight) was con-
tinually admitted into the spectrometer housing both during and for
two hours prior to transmission measurements. Transmission measurements
were taken both before and after addition of the lithium impurity to
the silicon samples.

Data Reduction

We may express the intensity I of the spectrometer beam after it
has passed through a sample as

$$I = I_o \frac{(1 - R)^2 \exp[-\alpha t]}{1 - R^2 \exp[-2\alpha t]} \qquad (2.1)$$

where I_o, R, α, and t are the initial beam intensity, the sample

surface reflectivity, the sample absorption coefficient, and the sample thickness respectively. We thus obtain

$$\frac{I_d}{I_s} = \frac{1 - R^2 \exp[-2\alpha_s t_s]}{1 - R^2 \exp[-2\alpha_d t_d]} \exp [\alpha_s t_s - \alpha_d t_d] \qquad (2.2)$$

for the ratio of the intensities I_d and I_s of the spectrometer beam passed through the lithium doped and undoped silicon samples respectively. Since

$$\alpha_d = \alpha_s + \alpha_i, \qquad (2.3)$$

where α_i is the absorption coefficient due to the added impurity, we may rewrite (2.2) as

$$\alpha_i = \frac{\ln[I_s/I_d]}{t_d} + \alpha_s \frac{t_s - t_d}{t_d} - \frac{1}{t_d} \ln \left[\frac{1 - R^2 \exp[-2\alpha_d t_d]}{1 - R^2 \exp[-2\alpha_s t_s]} \right]. \qquad (2.4)$$

Over the energy range of interest the absorption coefficient α_s as determined by Bell ([1]) and the reflectivity R as determined by Yoshinaga ([25]) are nearly constant and have the values of approximately 0.12/cm and 0.3 respectively. The second term of (2.4) is negligible for $t_s \approx t_d$, while the third term introduces a maximum correction of - 0.3/cm for the sample thickness used in this investigation. We used only the first term of (2.4) since the contributions from the other terms are quite small in every case.

The absorption coefficients were calculated for energy increments of 0.05 mev, using an I B M 1620 computer. A determination of the error involved in these calculations, other than that due to the above approximations, would be so complicated as to demand a point by point analysis for each spectrum. This is due not only to the form of the calculations, but also to the necessity of making measurements in some energy ranges where either I_s and/or I_d were not much larger than the uncertainty due to the background signal. Fortunately, the uncertainties in the determination of the absorption coefficient have little effect upon the energy placement of the principle absorption resonances. This is because the resonance form exhibits a rather sharp dependence upon the photon energy. However, the uncertainties in the determination of the absorption coefficient do introduce substantial uncertainty into the determination of the area under a resonance curve, and therefore into the relative intensitities of the absorption lines.

IV. RESULTS AND CONCLUSIONS

General

For the sake of clarity, the results of this investigation are
presented in two parts; first we discuss the lithium donor in silicon,
and later the lithium-oxygen interaction in silicon. We present here
a discussion of information which is common to both aspects of the
problem.

The data is presented in the form of absorption spectra in which
the absorption coefficients are due only to the absorption centers
introduced into the silicon samples during the diffusion process.
The instrumental band width (full width at half maximum) is indicated
in each case for the energy regions in which the principal absorption
resonances occur.

The donor energy levels are compared in Table 2 with the theoreti-
cal (11) and other observed (2) donor energy levels. For each listed
donor, all other energy levels were placed relative to the 3P,± level,
for which the shallow donor theory was assumed valid. Identification
of the resonant absorptions with the appropriate electronic transitions
is simplified by the following considerations:

1. Only transitions from the ground state, or those states very
    near by, will be observed at the sample temperatures achieved,
    since only these states will be significantly populated.

2. Transitions from the even parity ground state to the odd

TABLE 2

Energy levels for donor impurities in silicon, relative to the bottom of the conduction band. Theoretical predictions due to Kleiner (11), phosphorus and arsenic data due to Bichard and Giles (2). Energies in mev.

State	Energy Levels				
	Theoretical	Phosphorus	Arsenic	Lithium	LiO*
6P,±				-0.3	
5P,±		-0.9	-0.9	-0.9	
5P,0				-1.4	
4P,±		-1.6	-1.5	-1.6	-1.6
3P,±	-2.6	-2.6	-2.6	-2.6	-2.6
3P,0	-4.7	-4.9	-4.9	-4.9	-5.0
2P,±	-5.8	-5.8	-5.8	-5.2	-5.9
2S	-7.1			-7.3	
2P,0	-10.6	-10.9	-10.8		-11.0
1S	-28.4	-45.3	-53.5	-32.5	-39.2

*See page 33

parity excited states will predominate since these are the
only transitions allowed in the first order approximation.

3. The observed transition energy differences and relative
absorption intensities should be in reasonable agreement with
theory.

The observed relative absorption intensities are compared with
the theoretical (13) and other observed (2) relative absorption in-
tensities in Table 3. The theoretical absorption intensity is
calculated in terms of the oscillator strength which is proportional
to the integrated absorption coefficient for the corresponding
transition (4). In calculating the integrated absorption coefficients
for the various transitions, allowances were made for the overlap of
the absorption resonances.

The Lithium Donor in Silicon

Absorption spectra of the lithium donor in silicon are shown in
Figures 4 and 5. The spectrometer range does not allow a determination
of the resonance absorption due to the 1S to 2P,0 transition. In view
of the differences in impurity concentrations between the two samples,
we attribute the broadening of the resonances of Figure 5 to inter-
actions between neighboring impurity centers, i.e. concentration
broadening. In these samples the oxygen content is so small that the
lithium oxide concentration should be negligible. A comparison of
these spectra with the spectra of Figure 2 shows that there are no
common absorption resonances. This is just what we should expect from

TABLE 3

Relative absorption intensities. Theoretical predictions due to Kohn (13), phosphorus and arsenic data due to Bichard and Giles (2).

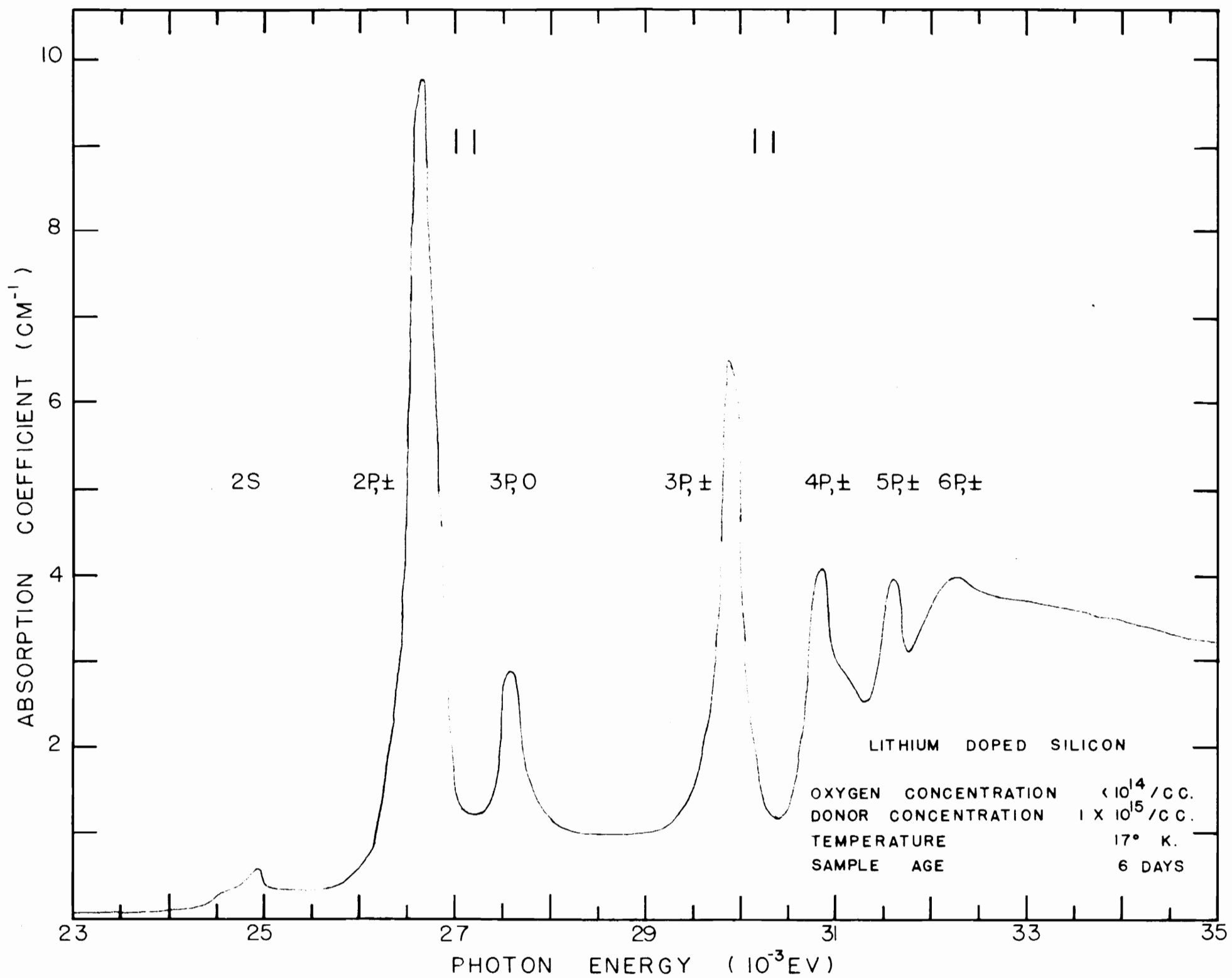| Transition	Theoretical	Relative Absorption Intensities			
		Phosphorus	Arsenic	Lithium	LiO*
1S - 2P,0	0.38	0.43±0.10	0.34±0.10		0.35±0.03
1S - 2P,±	1.00	1.00	1.00	1.00	1.00
1S - 3P,0	0.04	0.17±0.04	0.13±0.04	0.17±0.04	0.10±0.03
1S - 3P,±	0.29	0.66±0.16	0.56±0.10	0.55±0.10	0.45±0.10

*See page 33

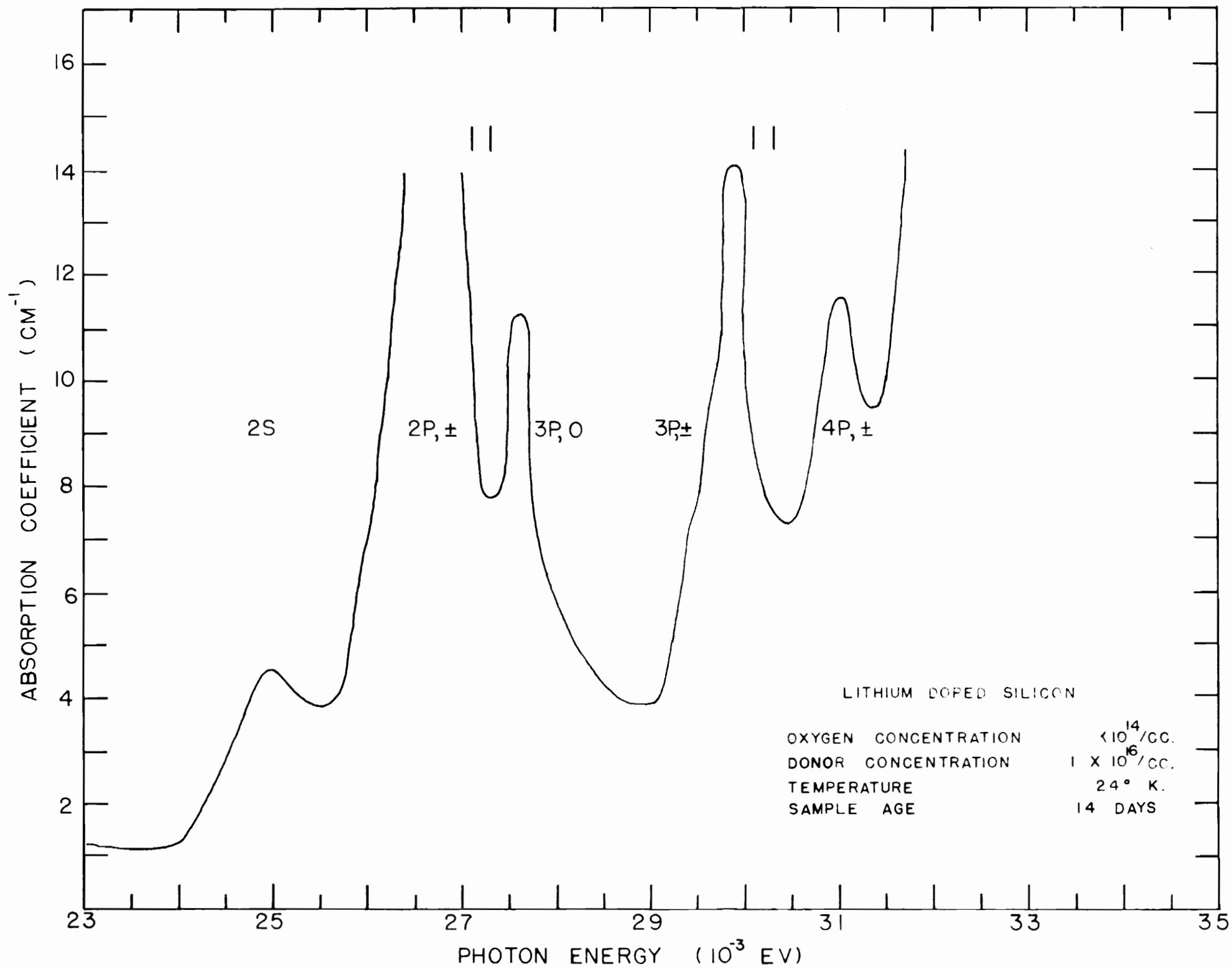FIGURE 4. ABSORPTION SPECTRUM OF SILICON SAMPLE M-1431-3

FIGURE 5. ABSORPTION SPECTRUM OF SILICON SAMPLE M-1431-2

a consideration of the sample donor and oxygen concentrations and the relation (1.12).

In Table 2 we compare the energy levels of the lithium donor with energy levels observed for other donors and with the energy levels predicted by theory. While the excited state levels of all donors listed show good agreement with theory, only the lithium ground state is in reasonable agreement with the predicted ground state energy. This is as we expected since, as we discussed in Section II, the deviation of the lithium ionic potential from that assumed in theory is not so severe as that for the other donor ions.

We see in Table 3 that the observed relative absorption intensities are in poor agreement with the theoretically predicted values, but are in reasonable agreement with previously determined experimental values. The disagreement between the predicted and observed relative absorption intensities is not disturbing since Kohn (13) has indicated that only limited reliance should be placed on the predicted values.

We have no knowledge as to the symmetry of the lithium donor's position within the silicon crystal. Feher's (7) electron spin resonance experiments on the donors contained in lithium-doped oxygen-rich silicon samples indicated that these donors did not occupy positions of tetrahedral symmetry. It now seems clear that the donors observed by Feher were not monatomic lithium atoms.

It is of some interest to note that there is no indication of a lifting of the six-fold 1S state degeneracy. Sample temperatures

during the experiment were high enough that states having energies
within several mev of the ground state energy would be significantly
populated. The existence of other 1S levels near the ground state
would produce secondary series of donor resonances or, if within 0.3
mev of the ground state, introduce a broadening and/or asymmetries
of the observed ground state resonances. Though no split in energy
of the 1S state has been specifically predicted for interstitial
impurities, large splits have been predicted by Kohn (14) in the
case of substitutional impurities in germanium and silicon, and
experimentally observed in the case of antimony in germanium (8).

Lithium-Oxygen Interactions in Silicon

We now turn our attention to the absorption spectra of silicon
containing lithium and rather large amounts of oxygen. From the data
of Bell (1), shown in Figure 2, and additional data obtained during
the present research and shown in Figures 6, 7, 8, and 9, we are able
to reach some conclusions about the lithium-oxygen interaction in
silicon.

The main structure of the spectra of Figures 6, 7, and 8 is
almost certainly due to a donor impurity having an ionization energy
of about thirty-nine mev. In deference to Pell (20), we shall assign
the responsibility for these resonant absorptions to lithium oxide.
The energy levels and relative transition intensities of these
principal resonant absorptions are compared with the theoretical and
other observed experimental values in Tables 2 and 3. Some of the
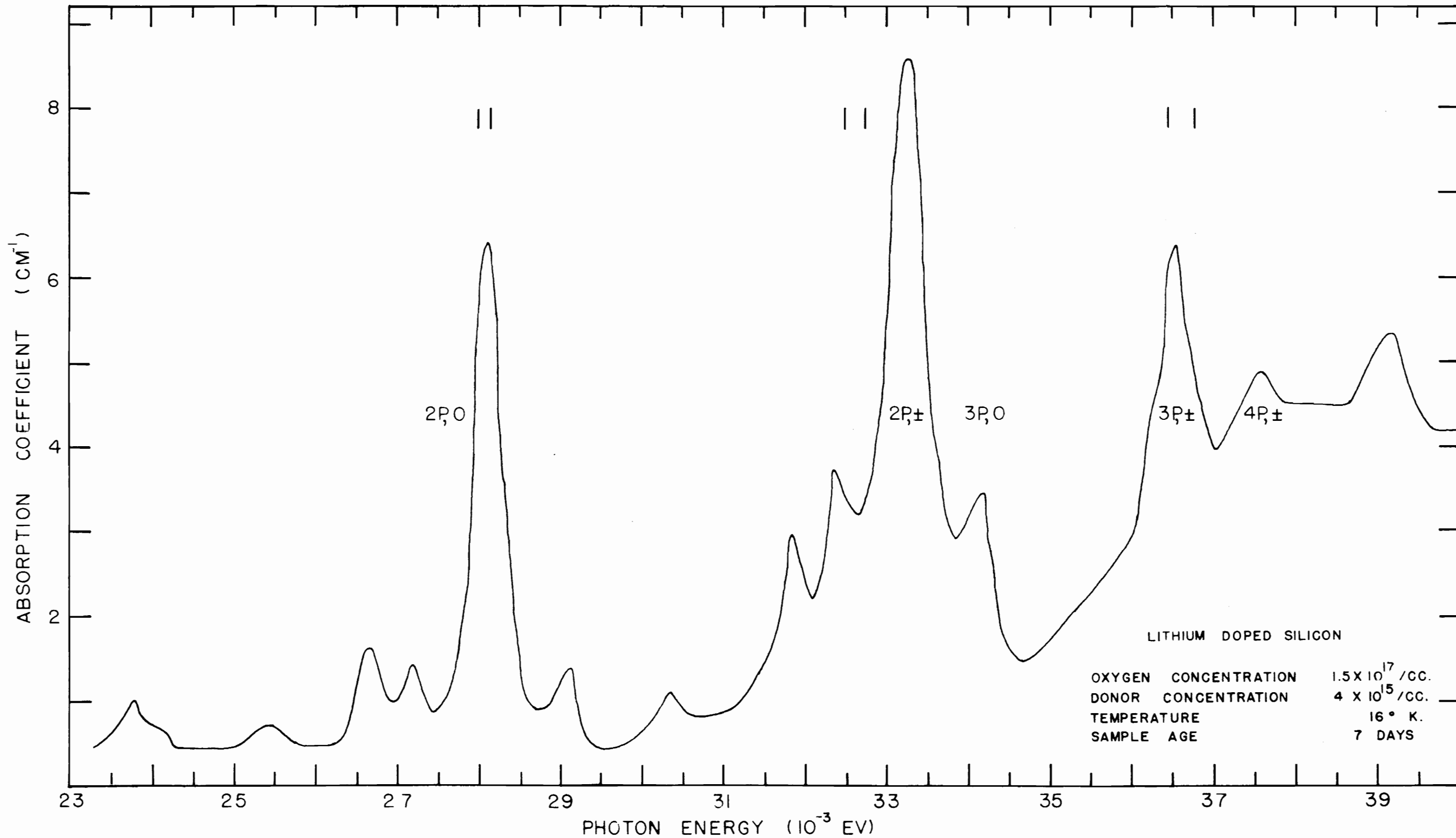other absorption resonances may be accounted for by donor transitions

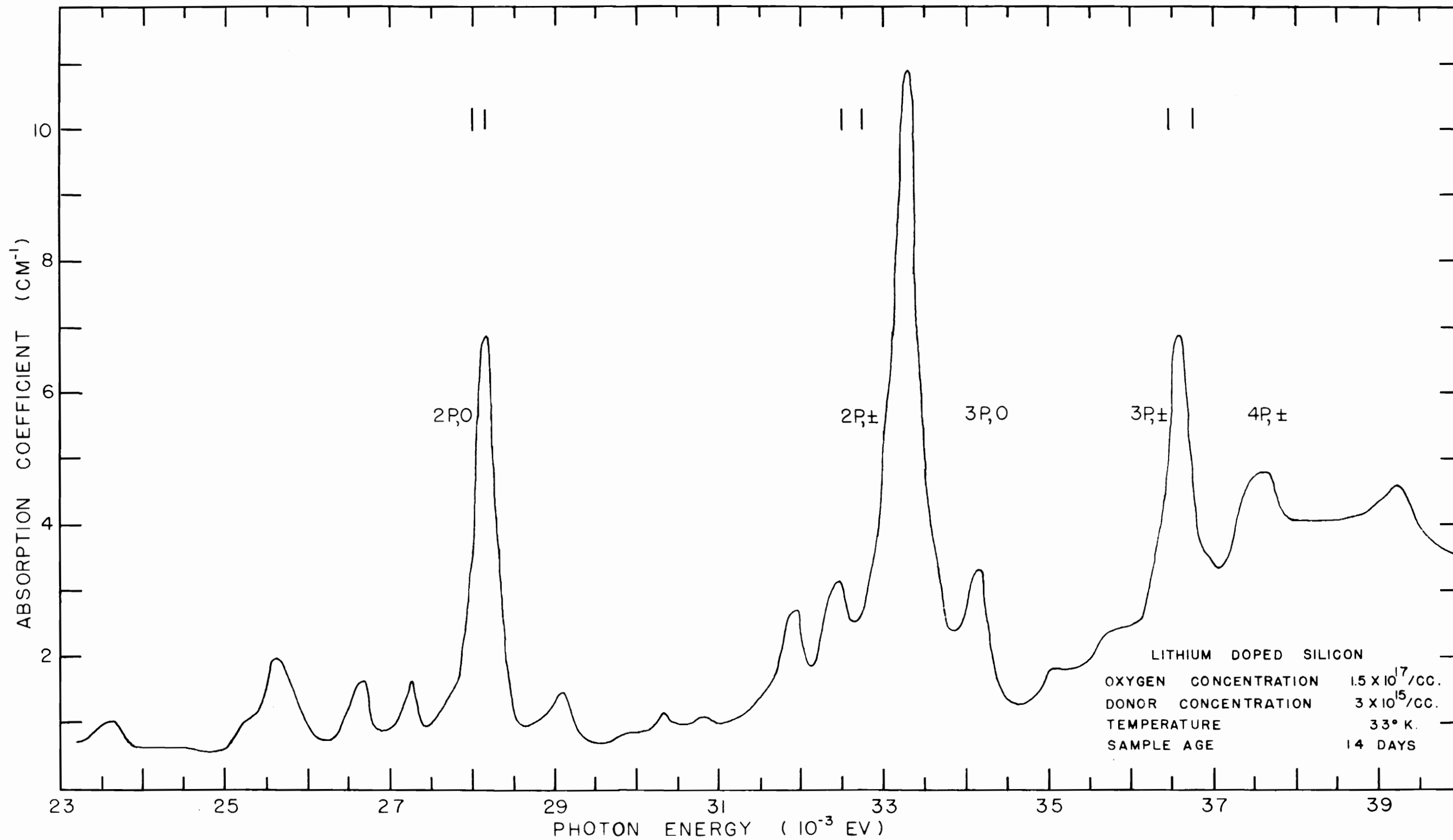FIGURE 6. ABSORPTION SPECTRUM OF SILICON SAMPLE SE-3-C

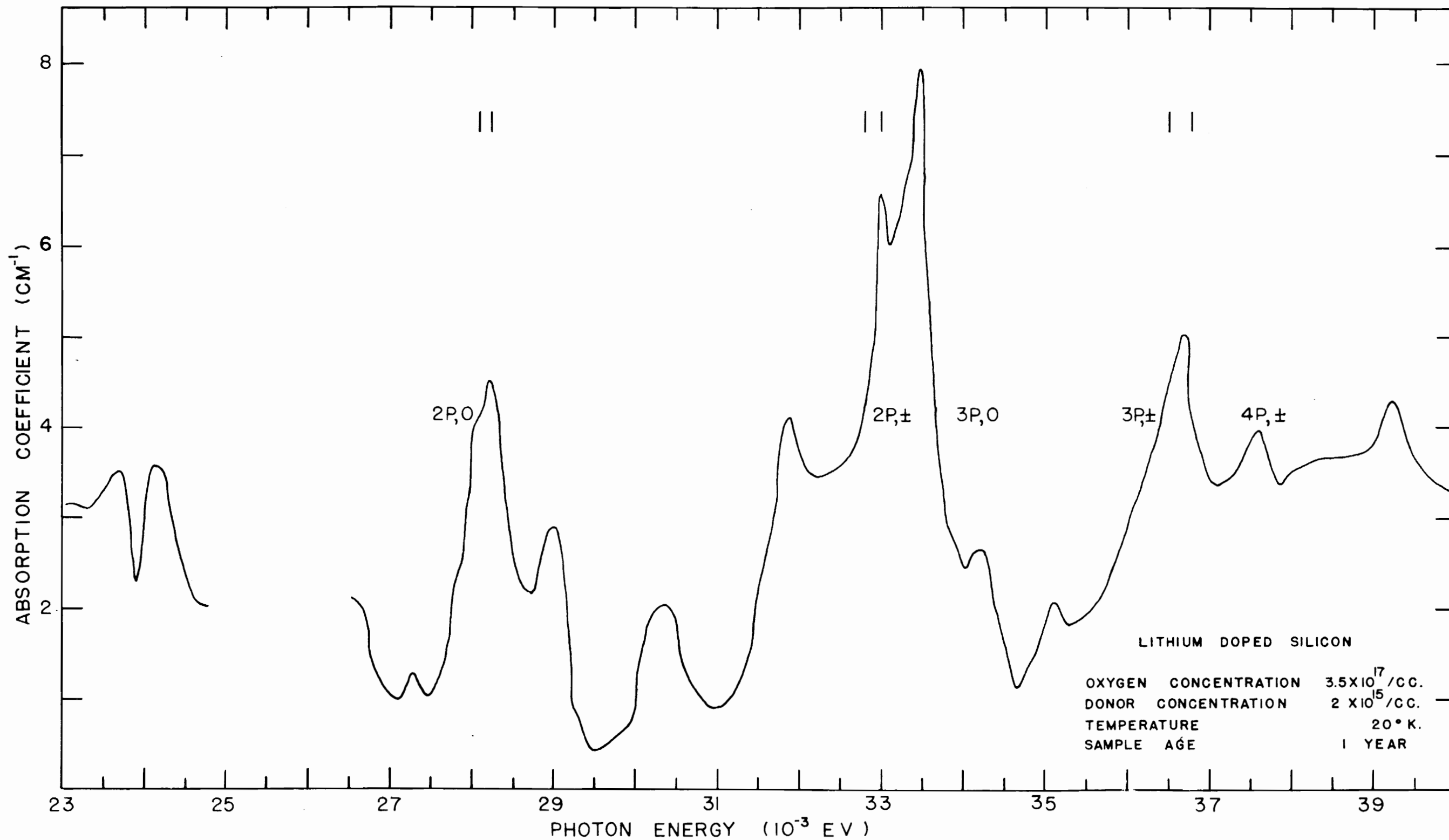FIGURE 7. ABSORPTION SPECTRUM OF SILICON SAMPLE SE-3-C

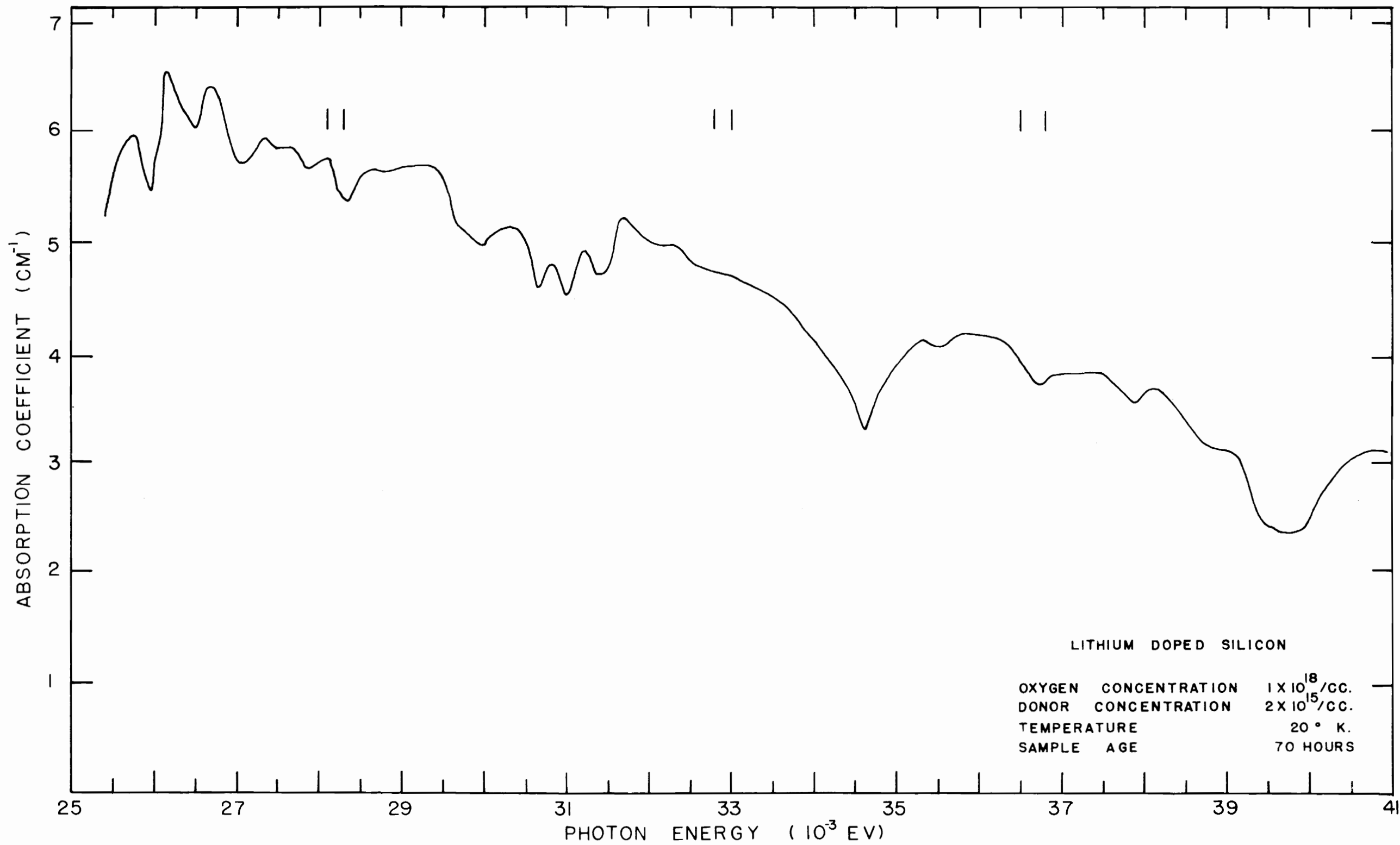FIGURE 8. ABSORPTION SPECTRUM OF SILICON SAMPLE SE-1-D

FIGURE 9. ABSORPTION SPECTRUM OF SILICON SAMPLE SE-1051-2

TABLE 4

Donor like series appearing in absorption spectra of silicon
containing lithium and large concentrations of oxygen.

Series	Transition Energies to Listed State from 1S State (mev)					Energy of 1S State Relative to Conduction Band Edge (mev)
	$2P,0$	$2P,\pm$	$3P,0$	$3P,\pm$	$4P,\pm$	
A	28.1	33.3	34.2	36.6	37.6	-39.2
B	28.0	33.0		36.2		-38.8
C	27.2	32.4		35.8		-38.2
D	26.7	31.9		35.1		-37.7
E	25.2	30.3		33.5		-36.1
F	24.1	29.1		32.3		-34.9

as indicated in Table 4. The various series of donor transitions
will be referred to according to the designations used in Table 4
for the remainder of this discussion.

We have good reason to believe that the several series of donor
transitions arise from different types of donors rather than from
different 1S levels of a single type donor. At low temperatures we
may treat all similar donors as a system having highly degenerate
discrete energy levels. This system will obey Boltzmann statistics
(17) and the occupation index of level i relative to level j will be
given by (N_i/N_j) exp $[(E_j - E_i)/kT]$, where N, E, k, and T are the
level degeneracy, level energy, Boltzmann's constant, and the sample
temperature respectively. If we assume the existence of a single
type donor with several 1S levels we would expect the magnitudes of
the absorption peaks in series C and D to increase with respect to
series A by seventy per cent and thirty four per cent respectively
upon a rise in temperature from 16° K to 33° K. Comparison of the
spectra shown in Figures 6 and 7 indicates that no such changes
occur.

We see an interesting time dependence of the absorption spectra
of the donors resulting from the lithium-oxygen interaction in
silicon. The sample used to determine the spectra of Figure 2 was
maintained at room temperature for twelve months prior to its use in
determining the spectrum shown in Figure 8. From these spectra we

observe a time dependence of the widths, and perhaps of the energy placements of the resonant absorptions. Spectra of a common sample taken seven and fourteen days after addition of the lithium impurity are shown in Figures 6 and 7 respectively. The dominance of series A in these spectra allows fairly accurate measurements of its transition widths. After correcting for instrumental broadening, we find that the full width at half maximum for the $1S \rightarrow 2P_{,\pm}$ transition decreases from 0.3 mev to 0.05 mev within the seven day period, in spite of the increase in sample temperature. The decrease in the resonance absorption widths with time can be at least partially accounted for in the last mentioned example by precipitation of the lithium and the corresponding reduction in the donor concentration broadening. However, in the first example of the reduction with time of the absorption widths, there was no measurable decrease in donor concentration over the one year period.

The lithium-oxygen interaction in silicon is apparently not limited to the production of LiO. We see in Figures 7, 8, and 9 a tendency for the smaller series of resonances to increase in magnitude relative to series A with increasing oxygen concentrations, thus indicating a relative increase in population for the associated donors. From this we might speculate about the formation of lithium-oxygen complexes in which the oxygen atoms are in the majority.

We can conclude with conficence only that the lithium-oxygen interaction in silicon is quite complex and produces several different

donor-like absorption resonance series whose relative populations

depend upon the time elapsed from the addition of the lithium and

upon the sample oxygen concentration in some complicated and as yet

undetermined manner.

V. ACKNOWLEDGEMENTS

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ABSTRACT

In the anisotropic effective mass theory of shallow donor impurities in silicon, we assume (3) that a shallow donor impurity ion and its loosely bound electron can be adequately described by a Schroedinger equation of the type

$$
-\left[\frac{\hbar^2}{2m_\ell} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2}{2m_t} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) + \frac{e^2}{\kappa r} \right] F(r) = EF(r), \qquad (1)
$$

where the effects of the crystal upon the system are concealed in the static dielectric constant κ of the silicon and the effective mass parameters m_ℓ and m_t of the donor electron within the silicon crystal. This equation has been solved by variational methods (2) using trial functions derived and labeled in analogy with the solutions of the hydrogen atom wave function into which (1) goes when $m_\ell = m_t = m$ and $\kappa = 1$. The binding energies so obtained are, in units of mev (milli-electron volts):

State	1S	2P,0	2S	2P,$\pm$	3P,0	3P,$\pm$
Binding Energy	28.4	10.6	7.1	5.8	4.7	2.6

The solutions of (1) are six fold degenerate due to the existence of the six equivalent minima in the silicon conduction band.

For sufficiently low temperatures the donor electrons are found in significant numbers only in the ground state, from which transitions to excited states may be induced, say by infrared radiation. The resonances observed in optical absorption spectra may then be used

to determine the excited state energy levels relative to the ground state level, the level widths, and the relative transition probabilities. By assuming the validity of the anisotropic effective mass theory for one of the excited donor states, we can determine the energy level of the donor ground state and the observed donor excited states relative to the bottom of the silicon conduction band.

Results of optical studies of donors in silicon are in good agreement with theory for the excited states; however the observed ground state binding energy is always larger than that predicted by theory by at least eleven mev (1). We may attribute the disparity in the observed and predicted donor ground state energies to our neglect of effects in the immediate vicinity of the donor nucleus.

Due to lithium's small ionic radius, small atomic number, and interstitial lattice position, the lithium donor best matches the assumptions made in the anisotropic effective mass theory of shallow donors in silicon. For this reason we expect the study of the lithium donor in silicon to provide an appropriate test to the validity of the shallow donor theory.

An analysis of absorption spectra obtained from lithium-doped silicon samples indicates the existence of several different types of donor impurities which range in ionization energy from 32.5 mev to 39.2 mev. The relative magnitudes of the corresponding donor series show a strong dependence upon the oxygen content of the silicon.

For silicon samples having oxygen concentrations less than 10^{14}/cc, the only absorption series observed is that due to the lithium donor. The observed lithium donor ionization energy of 32.5 mev is in much better agreement with the theoretically predicted value than that of any other donor impurity studied in silicon. This offers support to the validity of (1) for all regions except the immediate vicinity of the donor nucleus.

Absorption spectra of lithium-doped silicon having oxygen concentrations greater than 10^{17}/cc contain several donor-like absorption series, but show no trace of the lithium donor. The absence of significant quantities of monatomic free lithium in lithium-doped oxygen-rich silicon samples has been predicted by Pell (4). However, the results of this investigation indicates the formation of several types of lithium-oxygen complexes; while Pell predicted that only LiO would exist in significant quantities when the donor concentration is exceeded by the oxygen concentration of the silicon sample.

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