of sample 3. Assuming equal numbers of domains of each kind and using the measured index of refraction of $n \sim 2.9$ at frequency ω_2, Eq. (11) predicts a strength of 47 cm^{-2} which, like χ_{bb}, should be nearly independent of temperature.

This discrepancy may be analogous to the *apparent* violation of Eq. (9) which occurs for the simple easy-axis antiferromagnets like MnF_2. There $\chi_{\parallel}$ is approximately proportional to T, but no antiferromagnetic resonance absorption is seen when the rf magnetic field is along the c axis. Equation (8) is satisfied (as it must be) by a spread-out region of absorption at higher frequencies which arises from second-order processes.[27]

An alternative explanation of both difficulties could be that the domains were predominanty of one type at low temperatures, but approached a more symmetrical distribution as the temperature increased.

V. CONCLUSIONS

The theory of magnetism in NiF_2 outlined above, originally due to Moriya[4] and extended by Joenk and Bozorth,[12] is adequate for a quantitative description of the measured magnetic-resonance modes of NiF_2. The parameters $E = 1.66$ cm^{-1} and $8JD = 482.2$ cm^{-2} are obtained directly from the measured frequencies at $T \approx H = 0$. We must choose $g_{\perp} = 2.35$ in order for the theory to fit $\omega_1(H)$. This value is in good agreement with the $g_{\perp} = 2.32$ and 2.33 obtained from other experiments and adequately predicts $\omega_2(H)$. One further datum is required to separate the exchange parameter $8J = 125$ cm^{-1} from the out-of-plane anisotropy $D = 3.86$ cm^{-1}. This can be either the susceptibility $\chi_{bb} = \chi_{cc}$ or the net ferromagnetic moment M. The quantitative agreement with the theory is most clearly indicated by the fact that these two approaches lead to values of $8J$ and D which agree within a few percent.

ACKNOWLEDGMENTS

The author is indebted to Dr. R. G. Shulman and Dr. J. Ferguson, Jr., for supplying samples for these measurements, and to Dr. B. Cohen for furnishing the GaAs thermometer. Thanks are also due to A. B. Schaafsma for constructing the magnetic-field apparatus and for assistance with the measurements.

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[27] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **7**, 539 (1952).

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Vibrational Spectra of Lithium-Oxygen and Lithium-Boron Complexes in Silicon

R. M. Chrenko, R. S. McDonald, and E. M. Pell*
General Electric Research Laboratory, Schenectady, New York

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Vibrational spectra of lithium-oxygen and lithium-boron complexes in silicon have been studied using enriched boron and lithium isotopes. The absorption bands in the 300–4000 cm^{-1} region are due to vibrations of interstitial oxygen atoms perturbed by lithium ions, and substitutional boron ions, also perturbed by lithium ions. The 517-cm^{-1} band of interstitial oxygen is displaced to 525 cm^{-1} by Li^7 and to 537 cm^{-1} by Li^6, and the 1106-cm^{-1} band is displaced to 1006 cm^{-1} by both lithium isotopes. (Frequencies are for 78°K except for the 1106- and 1006-cm^{-1} bands which are for 300°K.) No counterpart of the 1203-cm^{-1} band of interstitial oxygen is detected for the lithium-oxygen complex, and on this basis the 1203-cm^{-1} band is reassigned to a combination of the asymmetric SiO stretching vibration with the librational motion of oxygen around the $\langle 111 \rangle$ axis rather than to the symmetric SiO stretching fundamental. This new assignment provides a value of 67 cm^{-1} for the frequency of the vibrational mode associated with the libration. The 623-cm^{-1} triply degenerate vibration of isolated substitutional boron ions is split into two bands at 567 and 656 cm^{-1} by interaction with lithium, indicating axial symmetry for the lithium-boron complex. (These frequencies are for the B^{11} isotope.) The precipitation of lithium from the lithium-oxygen complex is inhibited in the presence of boron, probably because in the absence of free electrons the precipitation nuclei develop a positive charge which repels the diffusing lithium species (Li^+).

I. INTRODUCTION

VIBRATIONAL infrared spectra of light impurity atoms in elemental semiconductors which crystallize with the diamond lattice are of interest for many reasons, not the least of which is that the defects seem simple enough to be understood in considerable detail.

The present study was undertaken to learn more about the defect which is formed when dissolved lithium interacts with interstitial oxygen in silicon.

Oxygen forms an uncharged interstitial defect in silicon, the spectrum and chemical behavior of which have been the subject of a number of papers.[1–7] This

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* Present address: Xerox Corporation, Rochester, New York.

[1] W. Kaiser, P. H. Keck, and G. F. Lange, Phys. Rev. **101**, 1264 (1956).

[2] H. J. Hrostowski and R. H. Kaiser, Phys. Rev. **107**, 966 (1957).

[3] W. Kaiser, H. L. Frisch, and H. Reiss, Phys. Rev. **112**, 1546 (1958).

[4] H. J. Hrostowski and R. H. Kaiser, J. Phys. Chem. Solids **9**, 215 (1959).

[5] W. L. Bond and W. Kaiser, J. Phys. Chem. Solids **16**, 44 (1960).

[6] H. J. Hrostowski and B. J. Alder, J. Chem. Phys. **33**, 980 (1960).

[7] J. P. Suchet, J. Chem. Phys. **58**, 155 (1961).

defect is of interest, among other reasons, because it appears to be a simple quantum-mechanical system in which a single atom moves in the sixfold potential well around an axis fixed in the lattice.[6] A lithium ion interacts with an isolated interstitial oxygen atom to form a charged defect[8]:

$$\mathrm{O}+\mathrm{Li}^+ \leftrightarrows \mathrm{OLi}^+. \qquad (1)$$

The lithium ion apparently traps the oxygen atom in one of the six equivalent potential minima. The spectrum of the resulting defect gives information about isolated interstitial oxygen as well as about the OLi^+ defect itself.

Pell studied the lithium-oxygen complex through the effect of oxygen on the kinetics of precipitation of lithium,[8,9] and the effect of lithium on the 1106-cm^{-1} absorption band of interstitial oxygen.[8] He found the dissociation energy of the complex to be 0.42 eV.[9] Free-carrier absorption due to ionization of the complex prevented him from measuring the absorption spectrum below 900 cm^{-1}.

We have extended the spectrum to about 300 cm^{-1}. Free-carrier absorption at lower frequencies was eliminated by forming the complex in boron-doped silicon. This has permitted observation of an absorption band of the lithium-oxygen complex which corresponds to the 517-cm^{-1} band of interstitial oxygen.

In the spectra of these samples (which contained considerably more boron than oxygen), we have also observed three pairs of absorption bands due to boron vibrations, one band of each pair being due to the B^{11} isotope and the other to the B^{10} isotope. One pair of these bands which is due to isolated substitutional boron ion has been reported by Smith and Angress.[10] The other two pairs coincide in frequency with bands reported by Balkanski and Nazarewicz[11] for silicon containing boron, lithium, and oxygen. We have assigned the latter bands to boron vibrations of a lithium-boron ion pair with axial symmetry (point group C_{3v}).

We report here frequencies of the above-mentioned bands for samples prepared with enriched B^{10} and Li^6, as well as with boron and lithium of natural isotopic abundance. The frequencies mentioned in the text are 78°K values, except that the 1006- and 1106-cm^{-1} values are for 300°K.

TABLE I. Estimated impurity content of silicon samples.

	Sample 3 ($\mathrm{Li}+\mathrm{B}$)	Sample 4 ($\mathrm{Li}^6+\mathrm{B}$)	Sample 5 ($\mathrm{Li}+\mathrm{B}^{10}$)
Oxygen	0.73×10^{18}/cc	0.70×10^{18}/cc	1.1×10^{18}/cc
Boron (total)	4.4×10^{18}/cc	4.4×10^{18}/cc	9.5×10^{18}/cc
$\mathrm{B}^{10}/\mathrm{B}^{11}$	18/82	18/82	92/8
Li^+ (compensated by B^-)[a]	4.4×10^{18}/cc	4.4×10^{18}/cc	9.5×10^{18}/cc
$\mathrm{Li}^6/\mathrm{Li}^7$	8/92	94/6	8/92
Resistivity	710 Ω-cm (*n*-type)	420 Ω-cm (*n*-type)	260 Ω-cm (*p*-type)
Li^+(not compensated by B^-)	4.5×10^{12}/cc	8.5×10^{12}/cc	···
B^-(not compensated by Li^+)	···	···	3.5×10^{13}/cc

[a] No estimate is available for amount of precipitated lithium.

II. EXPERIMENTAL

Samples were prepared by diffusing lithium into crucible-grown, boron-doped silicon by procedures reported by Pell.[8] Concentrations and isotopic abundances are given in Table I. The boron concentrations were determined by electrical measurements before counter-doping with lithium. The compensation procedure yielded samples transparent to at least 250 cm^{-1}, with effective carrier concentrations of the order of 10^{13} cm^{-3}. In view of the equivalence of the lithium and boron concentrations implied by the conductivity data, the lithium *ion* concentrations have been taken equal to the boron concentrations.

The oxygen concentrations have been estimated by combining: (1) the calibration data of Kaiser and Keck[12] for the 1106-cm^{-1} band of interstitial oxygen and (2) Pell's observation that at 300°K the molar absorption coefficient of the 1006-cm^{-1} band of OLi^+ is equal to that of the 1106-cm^{-1} oxygen band.

Samples were examined optically with a Perkin-Elmer model 21 spectrophotometer with CsBr prism from 300 to 715 cm^{-1}, and a Beckman IR-7 spectrophotometer from 670 to 4000 cm^{-1}. Precise frequencies were determined with a Perkin-Elmer model 112 monochromator equipped with appropriate grating-prism combinations for each region. Calibration was by

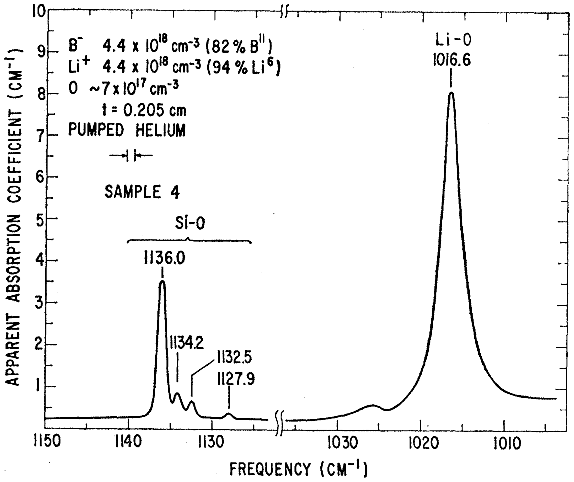

FIG. 1. Infrared spectrum at approximately 4°K of silicon containing oxygen together with boron of natural isotopic abundance and lithium enriched with Li^6. (Sample No. 4.) The bands between 1125 and 1140 cm^{-1} are due to the asymmetric stretching vibration of residual interstitial oxygen. The band at 1016.6 cm^{-1} is due to the corresponding vibration of the oxygen-lithium complex.

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[8] E. M. Pell, *Symposium on Solid State Physics in Electronics and Telecommunications* (Academic Press Inc., New York, 1960), Vol. VI, p. 261.

[9] E. M. Pell, J. Appl. Phys. **32**, 1048 (1961).

[10] S. D. Smith and J. F. Angress, Phys. Letters **6**, 131 (1963).

[11] M. B. Balkanski and W. Nazarewicz, J. Phys. Chem. Solids **25**, 437 (1964).

[12] W. Kaiser and P. H. Keck, J. Appl. Phys. **28**, 882 (1957).

TABLE II. Infrared absorption frequencies for oxygen, lithium, and boron in silicon.

Band assignment	Isotopic species	Frequency (cm^{-1})			Remarks
		300°K	78°K	4.2°K	
ν_r(O)	O^{16}	514.4±0.5	517.6±0.4		Interstitial oxygen
		$(513.5\pm2)^a$	$(517.3\pm0.5)^a$	$(517.3\pm0.5)^a$	
$\nu_r(OLi^+)$	Li^7	522.1±0.5	524.8±0.5		
		$(522)^b$			
	Li^6	534.6±0.4	537.3±0.4		
		$(534)^b$			
(?)			548		
B(1)	B^{11}	564.3±0.4	567.3±0.3		$\nu_1(a)$ or $\nu_3(e)$ for (B^-Li^+)
		$(564)^b$			
	B^{10}	584.8±0.4	587.7±0.3		
		$(585)^b$			
B(2)	B^{11}	620.8	622.8±0.3		probably $\nu_1(B^-)$
		$(617)^c$	$(619)^c$		
	B^{10}	643.6±0.4	645.8±0.3		
		$(641)^c$	$(644)^c$		
B(3)	B^{11} Li^7	653.6±0.4	656.5±0.3		$\nu_1(a)$ or $\nu_3(e)$ for (B^-Li^+)
		$(657)^b$			
	Li^6	656.7±0.4	659.5±0.3		
	B^{10} Li^7	680.3±0.4	683.0±0.3		
		$(684)^b$			
	Li^6	682.4±0.4	685.2±0.3		
$\nu_z(OLi^+)$	Li^7	1006.5±0.6	1014.9±0.4		no boron
	Li^7	1006.5±0.3	1014.9±0.3		with boron
	Li^6	1006.6±0.3	1015.5±0.3	1016.6±0.3	with boron
(?)				1026	with boron
ν_z(O)	O^{16}	1107±1		1127.9±0.3	interstitial oxygen
		$(1106\pm1)^a$		$(1127.8\pm0.3)^a$	
				1132.5±0.3	
				1134.2±0.3	
				1136.0±0.3	
				$(1136.0\pm0.3)^a$	

[a] H. J. Hrostowski and B. J. Alder, J. Chem. Phys. **33**, 980 (1960).
[b] M. Balkanski and W. Nazarewicz, J. Phys. Chem. Solids **25**, 437 (1964).
[c] S. D. Smith and J. F. Angress, Phys. Letters **6**, 131 (1963).

means of the usual narrow absorption lines of gaseous materials.[13–15]

Observed frequencies are listed in Table II, and intensities in Table III. Spectra are shown in Figs. 1–5; spectral slit widths are shown in the figures. All samples were measured at 300° and 78°K. One sample was measured in the 300–1200-cm^{-1} region at helium temperature and, except for the 1106-cm^{-1} band of residual interstitial oxygen, only minor changes in frequency, intensity, and bandwidth were noted below 78°K.

III. RESULTS

In this section, we summarize the experimental results and comment on their meaning insofar as this can be done without citing models for the structure of the defects. Later, we will discuss the spectra in terms of vibrations of specific models of three independent defects: interstitial OLi^+, substitutional B^-, and a boron-lithium ion pair.

TABLE III. Infrared absorption intensities for oxygen, lithium, and boron in silicon.

		Apparent integrated intensities at 78°K (cm^{-2})[a]		
Frequency	species	Sample 3 ($Li+B$)	Sample 4 (Li^6+B)	Sample 5 ($Li+B^{10}$)
525.3	OLi^7	33.5 (31 000 D)[b]	4.4	69.0 (41 000 D)
537.3	OLi^6	1.2	45.3 (42 000 D)	2.0
567.3	$B^{11}Li$	45.4 (9000 D)	41.0 (8100 D)	8.0 (7200 D)
587.7	$B^{10}Li$	10.0 (8900 D)	8.4 (7500 D)	108.0 (8400 D)
622.8	$(B^{11})^-$	5.6	8.0	···
646	$(B^{10})^-$	2.8	1.5	28 (14 300 D)
656.5	$B^{11}Li^7$	44.2 (8800 D)	···	10.0 (9000 D)
659.5	$B^{11}Li^6$	···	50.7 (10 000 D)	···
683.0	$B^{10}Li^7$	14.8 (13 200 D)	···	163.0 (12 800 D)
685.2	$B^{10}Li^6$	···	14.5 (13 500 D)	···

[a] Absorption intensities were calculated using $\ln_e$.
[b] Values in parentheses are molar integrated intensities in Darks based on concentrations estimated in the text for the various species. (D = Darks = cm/millimole).

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[13] *Tables of Wavenumbers for the Calibration of Infrared Spectrometers* (Butterworth, Inc., Washington, D. C., 1961).
[14] E. F. Barker, Phys. Rev. **52**, 170 (1937).
[15] K. Kakshmi, K. N. Rao, and H. H. Nielsen, J. Chem. Phys. **24**, 811 (1956).

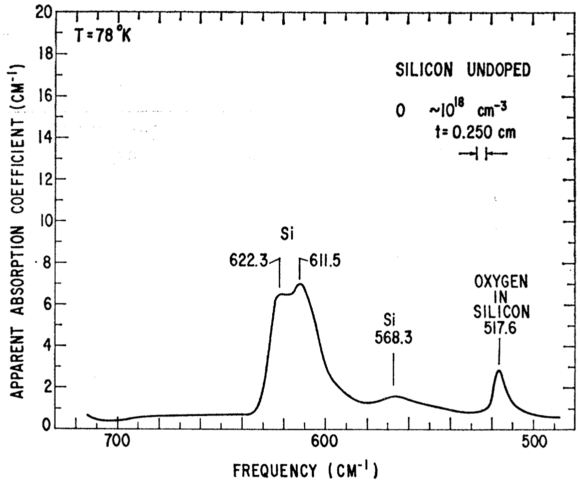

FIG. 2. Infrared spectrum at 78°K of silicon containing approximately 10^{18} oxygen atom/cm^3.

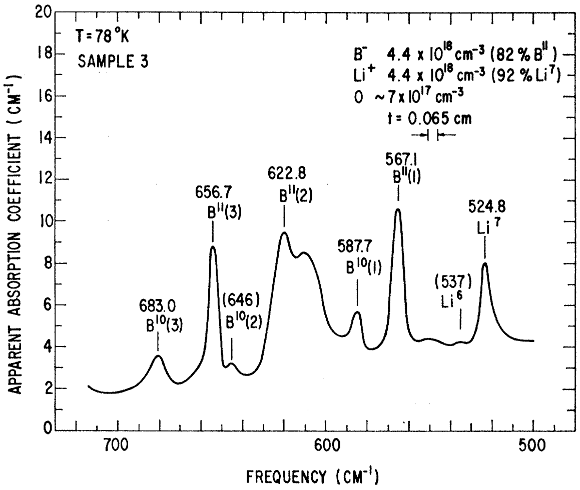

FIG. 3. Infrared spectrum at 78°K of silicon containing oxygen together with lithium and boron of natural isotopic abundance. (Sample No. 3.)

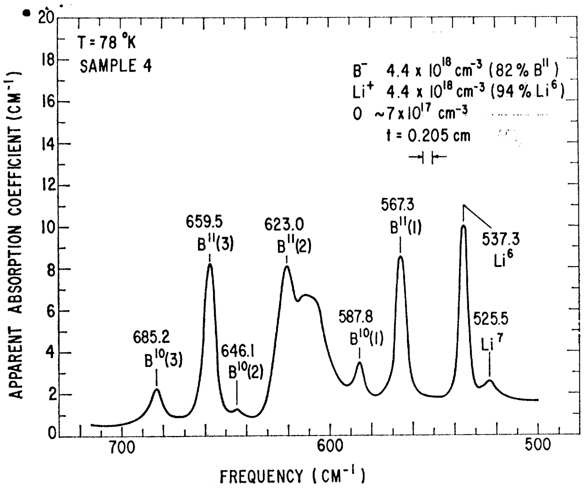

FIG. 4. Infrared spectrum at 78°K of silicon containing oxygen together with boron of natural isotopic abundance and lithium enriched in Li^6. (Sample No. 4.)

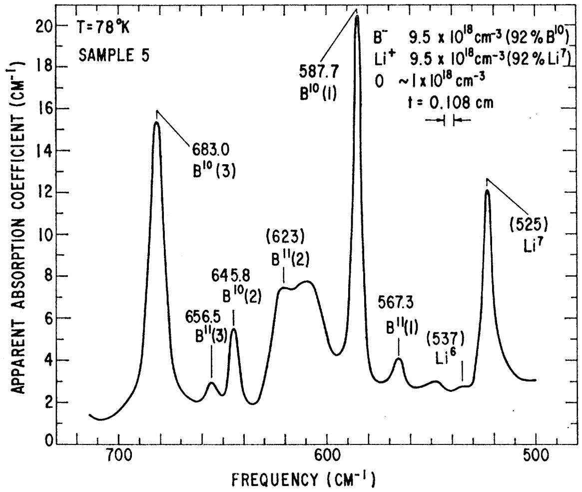

FIG. 5. Infrared spectrum at 78°K of silicon containing oxygen together with boron enriched in B^{10} and lithium of natural isotopic abundance. (Sample No. 5.)

In anticipation of the model for OLi^+, we will label the 1006-cm^{-1} band: $\nu_z(OLi^+)$, and the 525(537)-cm^{-1} band: $\nu_r(OLi^+)$. The three pairs of boron bands will be designated: B(1), B(2), and B(3), as indicated in Table II and Figs. 3–5.

Vibrational Origin of Absorption Bands

All of the absorption bands are vibrational in origin. For all but $\nu_z(OLi^+)$ this is clearly indicated by the effects of boron and lithium isotopes on the frequencies. The evidence for vibrational origin of $\nu_z(OLi^+)$ is less direct, as discussed later.

Li^6:Li^7 frequency shifts: For $\nu_r(OLi^+)$, the Li^6:Li^7 frequency ratio is 1.023±0.001. The magnitude of the frequency shift is about 40% of what one would expect for a pure lithium vibration. Evidently, the motion of lithium is strongly coupled with that of oxygen and perhaps with the lattice.

For the B(3) band, the Li^6:Li^7 frequency ratio is 1.005±0.001. The frequency shift is less than 10% of what one would expect for a pure lithium vibration. Clearly, the boron mode responsible for the B(3) band is coupled to a lithium mode, but the coupling is weak.

For $\nu_z(OLi^+)$, the Li^6:Li^7 frequency ratio is 1.001±0.001, hardly distinguishable from unity. Evidently, the vibrational amplitude of lithium in this mode is very small.

The frequencies of the B(1) and B(2) bands are independent of the lithium isotope used, and we conclude that the amplitude of lithium is negligible for the vibrations responsible for these bands.

B^{10}:B^{11} frequency shifts: For the B(1), B(2), and B(3)

bands, the B^{10}:B^{11} frequency ratios are 1.0360, 1.0369, and 1.0390[16] (±0.001), respectively. The magnitude of the frequency shifts indicates that these bands are due to vibrations which are primarily boron modes. For comparison, 1.039 is the frequency ratio calculated by Dawber and Elliot[17] for substitutional boron in silicon.

We observe the same frequency for $\nu_z(\mathrm{OLi}^+)$ regardless of whether or not samples contain boron, and regardless of the boron isotope. For $\nu_r(\mathrm{OLi}^+)$, we find the same frequency for both boron isotopes. These results indicate that the OLi^+ complex is not directly bonded to boron, and we will assume that OLi^+ and boron form independent defects in silicon.

As the temperature is lowered, all of the observed absorption bands become narrower and shift to higher frequency in the normal manner for vibrational absorption bands. There are no changes in intensity or frequency which would suggest "hot" bands and no fine structure which could be attributed to boron-boron or lithium-lithium coupling.

We have found no band that we could satisfactorily attribute to the analog of the 1203-cm^{-1} band of interstitial oxygen. We do not know the origins of the bands at 548 and 1026 cm^{-1} (see Table II), but we do not assign them to the analog of the 1203-cm^{-1} band for reasons of frequency and intensity.

IV. DISCUSSION OF THE SPECTRUM OF THE OLi^+ COMPLEX

Assignment of Bands to The Lithium-Oxygen Complex

The smallness of the lithium isotope shift for $\nu_z(\mathrm{OLi}^+)$ casts some doubt as to whether this band is due to a vibration of a complex containing lithium. However, Pell[8] reported that the 1006-cm^{-1} band, $\nu_z(\mathrm{OLi}^+)$, increased in intensity while the 1106-cm^{-1} band of oxygen, $\nu_z(\mathrm{O})$, diminished in intensity as the concentration of Li^+ was increased by diffusing lithium into silicon. The intensities changed in the reverse order as the concentration of Li^+ was lowered by permitting the lithium to precipitate. We consider this sufficient evidence to assign the 1006-cm^{-1} band to the OLi^+ complex. The vibrational origin of the 1106-cm^{-1} band was established by Hrostowski and co-workers[2,6] by use of oxygen isotopes, and we conclude that $\nu_z(\mathrm{OLi}^+)$ is primarily an oxygen vibration, also.

In establishing the correspondence between $\nu_r(\mathrm{OLi}^+)$ and $\nu_r(\mathrm{O})$, we have compared the spectrum of a silicon sample which contained oxygen but no lithium or boron (Fig. 2) with spectra of our samples which contain sufficient lithium to ensure that most of the oxygen is in the form of the OLi^+ complex (Figs. 3–5). The reduction in intensity of the 517-cm^{-1} band, $\nu_r(\mathrm{O})$, in the presence of lithium is best seen in the spectrum of the sample containing enriched Li^6 (Fig. 4). This comparison leaves little doubt that the degree of freedom responsible for the 517-cm^{-1} band of oxygen is modified by the presence of lithium, and it is on this basis that we have assigned the 525(537)-cm^{-1} bands to a vibration of the OLi^+ complex.

Model for the OLi^+ Complex in Silicon

A model of the OLi^+ complex should be compatible with the following results: (1) The frequency of $\nu_z(\mathrm{O})$ is reduced 100 cm^{-1} by interaction of oxygen with Li^+; (2) the frequency of the resulting band, $\nu_z(\mathrm{OLi}^+)$, is insensitive to the mass of lithium; (3) the fine structure of $\nu_z(\mathrm{O})$ at low temperatures is absent for $\nu_z(\mathrm{OLi}^+)$; (4) $\nu_r(\mathrm{OLi}^+)$ replaces $\nu_r(\mathrm{O})$ when lithium and boron are introduced simultaneously into silicon, and (5) the frequency of $\nu_r(\mathrm{OLi}^+)$ is sensitive to the mass of lithium.

Presence of only two absorption bands for OLi^+ in the region between 300 and 4000 cm^{-1} suggests that we are dealing with only one type of defect containing both lithium and oxygen. The two absorption bands of the complex bear an obvious relationship to the two prominent bands of interstitial oxygen. We will assume a model in which a lithium positive ion is bound at short range (2–3 Å) by ionic forces to an interstitial oxygen atom. The latter probably has a formal charge of about one electron. The position of the oxygen atom relative to nearest-neighbor silicon atoms is practically the same as that in the absence of lithium. This structure seems reasonable in view of the strong binding of oxygen to the lattice (activation energy for diffusion = 2.55 eV[18]) relative to the binding of Li^+ to oxygen (binding energy = 0.42 eV[9]). The experimental results are in most respects consistent with this model.

Before discussing interpretation of the spectrum in terms of the model, we consider the assignment of the vibrational absorption bands of isolated interstitial oxygen in silicon.

Vibrational Assignment for Interstitial Oxygen in Silicon

Hrostowski and co-workers[2,6] adopted a model in which the oxygen atom and its two nearest-neighbor silicon atoms form a bent triatomic molecule suspended in the lattice. Hrostowski and Kaiser[2] considered this $\mathrm{Si_2O}$ molecule (point group C_{2v}) to have three vibrational fundamentals, as if it were an isolated gas molecule. They assigned the 1203-cm^{-1} band to $\nu_1(a_1)$, a symmetric SiO stretching vibration; the 517-cm^{-1} band to $\nu_2(a_1)$, a symmetric SiO bending vibration; and the 1106-cm^{-1} band to $\nu_3(b_1)$, an antisymmetric SiO stretching vibration. In this model, ν_1 and ν_3 are primarily oxygen vibrations and ν_2 is primarily a silicon vibration.

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[16] The B^{10}:B^{11} frequency shift for the $B(3)$ bands is 1.0390 for Li^6 and 1.0404 for Li^7.

[17] P. G. Dawber and R. J. Elliot, Proc. Phys. Soc. (London) **81**, 453 (1963).

[18] J. W. Corbett, R. S. McDonald, and G. D. Watkins, J. Phys. Chem. Solids **25**, 873 (1964).

Hrostowski and Alder[6] recognized the libration of oxygen around the ⟨111⟩ axis joining the centers of the two silicon atoms as an additional degree of freedom (symmetry class: B_2) responsible for the fine structure of the 1106-cm^{-1} band at low temperature. They estimated the fundamental vibration frequency associated with the libration to be approximately 100 cm^{-1}.

The frequency assignment for the antisymmetric SiO stretching vibration ν_3 is consistent with that for siloxane groups (SiOSi) of organosiloxanes.[19–21] However, it is somewhat of a departure to assign a frequency *above* that of the antisymmetric stretching vibration to the symmetric vibration.[22,23] Furthermore, the 1203-cm^{-1} band behaves in an unusual manner for a fundamental inasmuch as it appears only at temperatures below 50°K.[2,6] No counterpart of this band is observed for OLi$^+$. We will assign it as a combination band below.

We now continue our discussion from a point of view which facilitates correlation of the three degrees of freedom of the oxygen atom with the vibrations of the OLi$^+$ complex.

We will label the three mutually perpendicular vibrations of interstitial oxygen with the cylindrical coordinates: z, r, and ϕ. Symmetry coordinates based on the assumption of point group C_{2v} are shown in Fig. 6.[24] Thus, $\nu_z(\mathrm{O})$ is the antisymmetric SiO stretching vibration; $\nu_r(\mathrm{O})$ is a symmetric SiO vibration, and $\nu_\phi(\mathrm{O})$ is the libration of oxygen around the ⟨111⟩ axis in a sixfold potential well.

We have assigned the bands at 1106 and 517 cm^{-1} to $\nu_z(\mathrm{O})$ and $\nu_r(\mathrm{O})$, respectively. These assignments do not differ appreciably from those of Hrostowski and coworkers.[2,6] We attribute the small value of the O^{16}:O^{18} frequency shift (less than 3 cm^{-1}) for the 517-cm^{-1} band[6] to coupling of $\nu_r(\mathrm{O})$ with vibrations of the lattice (the highest of these has a frequency of 510 cm^{-1}). Most of the O^{16}:O^{18} frequency shift must be distributed among the interacting lattice modes. We have not described $\nu_r(\mathrm{O})$ as either a stretching or a bending mode because coupling with lattice modes makes it difficult to define the exact form of the vibration. We will continue to consider $\nu_r(\mathrm{O})$ to be an oxygen vibration because the 517-cm^{-1} band is observable only when oxygen is present and because it is displaced when lithium interacts with oxygen.

The main difference between our assignment and that of Hrostowski and co-workers[2,6] is that we assign the 1203-cm^{-1} band to the combination $\nu_\phi(\mathrm{O})+\nu_z(\mathrm{O})$. Fundamental absorption due to the libration, $\nu_\phi(\mathrm{O})$, has not yet been observed; we derive a value of 67 cm^{-1} from the difference between the frequency of the combination at 1203 cm^{-1} and that of $\nu_z(\mathrm{O})$ at helium temperature (1136 cm^{-1}). This value is in reasonable agreement with the estimate of 100 cm^{-1} due to Hrostowski and Alder.[6]

The first excited vibrational level of $\nu_\phi(\mathrm{O})$ seems to lie near the top of the rotational barrier, and this provides an explanation for the disappearance of the 1203-cm^{-1} band as the temperature is raised above 50°K. The proximity of the vibrational level to the top of the barrier makes it difficult to predict the effect of exchanging oxygen isotopes, but the frequency is so low that the isotopic frequency shift for the combination band is dominated by that for $\nu_z(\mathrm{O})$. Thus, the O^{16}:O^{18} frequency ratio, 1.046, for the 1203-cm^{-1} band is consistent with the assignment as $\nu_\phi(\mathrm{O})+\nu_z(\mathrm{O})$.

The assignment of Hrostowski and co-workers[2,6] implies a SiOSi angle of about 90° and the vector sum of the SiO bond moments should be approximately equal for the symmetric and asymmetric SiO stretching vibrations, $\nu_1(\mathrm{O})$ and $\nu_3(\mathrm{O})$. These vibrations should cause bands of about the same intensity except for the effect of coupling with the libration. For the asymmetric stretching vibration, coupling is small and should have little effect on the intensity. For the symmetric vibration, coupling with the libration may reduce the intensity appreciably. Thus, for interstitial oxygen, the observed intensities might be reconciled with the model of Hrostowski and co-workers. However, for the complex the symmetric SiO stretching band should appear with high intensity because the libration is quenched by interaction of Li$^+$ with the oxygen atom (as discussed later). Since no such band appears, the spectrum of OLi$^+$ supports the assignment of the 1203-cm^{-1} band as a combination.

Thus, the new assignment provides a reasonable explanation for the observed isotopic frequency shift of the 1203-cm^{-1} band and the unusual behavior of the band with changes in temperature. Furthermore, the frequencies of the various modes for interstitial oxygen in silicon are now comparable with those for siloxane groups in ordinary silicon-oxygen compounds.[19–21]

Vibrational Assignments for the OLi$^+$ Complex in Silicon

If we assume point group C_{2v} for the OLi$^+$ complex,[24] the six vibrational modes can be described in terms of the three symmetry coordinates for interstitial oxygen, together with three similar symmetry coordinates for lithium, as shown in Fig. 6. The symmetry coordinates fall into three classes: A_1, containing S_r and $S_{r'}$; B_1, containing S_z and $S_{z'}$; and B_2, containing S_ϕ and $S_{\phi'}$. While the description in terms of C_{2v} symmetry is not exact, we feel that it is reasonable to assume that the

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[19] A. Lee Smith, Spectrochim. Acta **19**, 849 (1963).

[20] Raimund Ulbrich, Z. Naturforsch. **9**, 380 (1954).

[21] Heinrich Kreigsmann, Z. Electrochem. **65**, 342 (1961).

[22] This assignment implies a SiOSi bond angle less than 90°. In most siloxane containing compounds, the symmetric stretching vibration has a frequency between 400 and 600 cm^{-1}, and the siloxane bond angle is 130°–150° (Ref. 23).

[23] C. Eaborn, *Organosilicon Compounds* (Butterworths Scientific Publications, Ltd., London, 1960), p. 253–4.

[24] To be strictly correct, the point group for interstitial oxygen is D_{3d}, and that for OLi$^+$ is C_s or C_2. However, the comparison of the vibrations of the two defects proceeds much more readily if we assume point group C_{2v} for both.

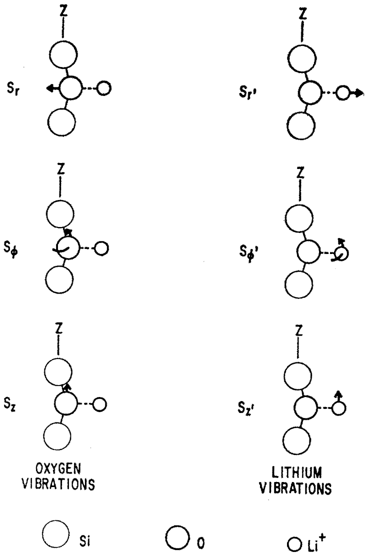

FIG. 6. Symmetry coordinates for interstitial oxygen in silicon and for the OLi^+ complex in silicon. The symmetry coordinates for the oxygen vibrations of OLi^+ are almost identical with those for interstitial oxygen.

two coordinates of each (pseudo) class tend to couple with each other more strongly than with coordinates of the other two classes.

We have already assigned the 525-cm^{-1} band of $O^{16}Li^7$ and the 537-cm^{-1} band of $O^{16}Li^6$ to $\nu_r(OLi^+)$, and the 1006-cm^{-1} band of both isotopic species to $\nu_z(OLi^+)$. The remaining vibrations probably have frequencies below 300 cm^{-1} and this accounts for our failure to observe them.

With only four observed vibrational frequencies and no information on bond lengths or angles from other sources, we have sufficient data to draw only qualitative conclusions about the structure of the complex.

The smallness of the lithium isotope shift for $\nu_z(OLi^+)$ implies that the form of the normal mode is very nearly the same as that of the corresponding mode of interstitial oxygen itself. Coupling between the $\nu_z(OLi^+)$ and $\nu_{z'}(OLi^+)$ modes is probably very small. This is because (1) to first order, there is no change in the OLi^+ distance for S_z and $S_{z'}$ which involve motion at right angles to the OLi^+ direction, and (2) the bending force constant for the ionic silicon-oxygen bond is negligible. The lithium mode $\nu_{z'}(OLi^+)$ probably has a very low frequency ($\sim$100–200 cm^{-1}).

The 100-cm^{-1} static lowering of the frequency from 1106 cm^{-1} for $\nu_z(O)$ to 1006 cm^{-1} for $\nu_z(OLi^+)$ is probably due to polarization of the SiO bond by the Coulomb field of the lithium ion.[25] This increases the negative charge of oxygen and reduces the covalent character of the bond, together with its force constant.

Since the fine structure (at low temperature) of $\nu_z(O)$ is due to the libration,[6] absence of the fine structure for the corresponding band of OLi^+ indicates that the librational motion of oxygen is quenched by lithium. This is consistent with a model in which Li^+ traps the oxygen atom in one of the six equivalent potential wells. We have not detected any band due to a combination of the asymmetric stretching vibration, $\nu_z(OLi^+)$, with the modes of OLi^+ which correspond to the libration, $\nu_\phi(OLi^+)$ and $\nu_{\phi'}(OLi^+)$.

The magnitude of the Li^6:Li^7 frequency shift for $\nu_r(OLi^+)$ indicates this vibration interacts strongly with $\nu_{r'}(OLi^+)$. On the basis of our model, one would predict this since a given change in the OLi^+ distance produces a maximum change in the symmetry coordinates S_r and $S_{r'}$. If we assume the 525(537)-cm^{-1} band is due to the high-frequency mode, and neglect interaction of these modes with lattice modes, we obtain an estimate of 200–300 cm^{-1} for the low-frequency mode on the basis of the Li^6:Li^7 frequency shift and the product rule.

We next rule out an alternate model for the OLi^+ complex. The large static lowering of the SiO stretching frequency is suggestive of the difference between the frequencies of the siloxane group (SiOSi) and the silanolate group (SiO^-Li^+).[26] The reduction in the SiO stretching frequency in the latter case is due to the disappearance of one of the SiO bonds. This model has what we consider to be a fatal weakness in that there is no compensation for the energy lost by breaking the SiO bond.

V. SPECTRUM OF SUBSTITUTIONAL BORON

Boron is well known to occupy a substitutional position in silicon. The magnitudes of the frequencies for the boron vibrations, $B(1)$, $B(2)$, and $B(3)$, together with the isotopic frequency ratios are consistent with a substitutional position for all boron atoms which are detected spectroscopically. The frequencies are all in reasonable agreement with those calculated by Dawber and Elliot[17] for the fundamental vibration frequencies of substitutional boron in silicon, 654 and 680 cm^{-1} for B^{11} and B^{10}, respectively.

The Spectrum of Isolated Substitutional Boron Ion in Silicon

The substitutional boron atom apparently occupies the normal lattice site of T_d symmetry. The spectrum of a single isolated impurity atom at such a site should consist of one (triply degenerate) absorption band. Frequencies of the $B(2)$ bands, 622.8 and 645.8 cm^{-1}, agree well with the frequencies reported by Smith and Angress[10] for isolated substitutional boron ion in silicon, 619 and 644 cm^{-1}.

Each OLi^+ ion is paired electrically with a boron ion, but there is no evidence for vibrational interaction of

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[25] Pell (Ref. 8) noted that the frequency shift from 1106 to 1006 cm^{-1} could be accounted for numerically by considering Li^+ to be bound very tightly to oxygen and at the same time assuming the force constants binding oxygen to the lattice to be unchanged. However, the absence of a frequency shift for different Li isotopes indicates beyond question that the effect of lithium is not to change the reduced mass as implied by Pell's model.

[26] William S. Tatlock and Eugene G. Rochow, J. Org. Chem. 17, 1555 (1952).

OLi^+ with boron. Evidently the compensating defects are somewhat removed from each other (probably beyond second-nearest neighbors). The concentration of the isolated boron ions should be nearly the same as the concentration of OLi^+, which we know from the intensity of the 1006-cm^{-1} band. Using this estimate of the concentration of isolated boron ions, together with the intensity of the $B(2)$ bands, we obtain a value of 2100-cm^2 $millimole^{-1}$ for the peak molar absorption coefficient. This is to be compared with the value of about 750-cm^2 $millimole^{-1}$ estimated from the published spectrum of Smith and Angress.[10] In view of possible differences in resolving power, uncertainties in concentrations, overlapping of the boron bands by lattice bands, and possible effects of strains and inhomogeneities due to rapid quenching of the samples, we do not consider the difference between these two estimates to be significant. We shall therefore assign the $B(2)$ bands to isolated substitutional boron in equilibrium with the lithium-boron complex.

Balkanski and Nazarewicz[11] did not detect the $(B)2$ bands in the room-temperature spectrum of silicon which, judging by the intensities of other absorption bands, contain approximately the same concentrations of boron, oxygen, and lithium as our samples. For boron of natural isotopic abundance, the $B(2)$ bands are quite difficult to distinguish from those of the silicon lattice, except at low temperature, and we believe that these bands were present but undetected in their room-temperature spectra.

Spectrum of Boron-Lithium Ion Pairs in Silicon

Boron and lithium are known to form a stable ion pair in silicon.[27–30] Pell concluded on the basis of diffusion measurements that the capture radius for Li^+ is 33–39 Å, and that the distance of closest approach is 2.5–2.7 Å.[29] We shall assign the $B(1)$ and $B(3)$ bands to boron vibrations of this complex.

We will assume that the complex consists of a substitutional boron ion which has captured a lithium ion. The Coulomb field of the lithium ion displaces the boron ion and the three vibrational degrees of freedom of the boron ion are no longer degenerate. If the equilibrium position is displaced along one of the threefold axes, the resulting defect has axial symmetry (point group C_{3v}) and the triply degenerate vibration is resolved into a nondegenerate vibration and a doubly degenerate pair. Two absorption bands should be observed in this case. For displacement of boron away from the geometric lattice site in any other direction, the degeneracy is completely lifted and three absorption bands should be observed.

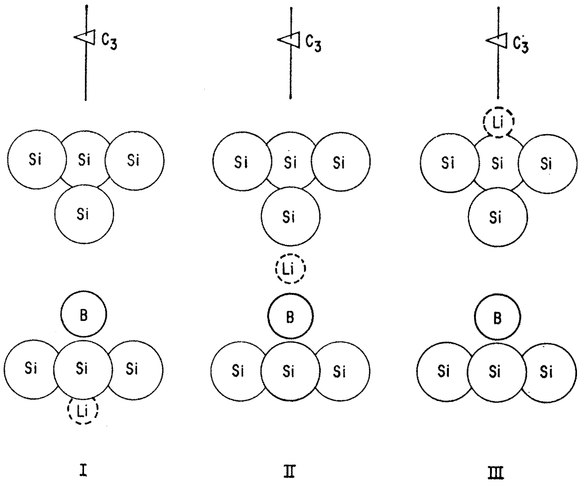

Fig. 7. Possible positions for lithium ion with respect to substitutional boron ion in the boron-lithium ion pair in silicon.

The observed spectrum of the boron-lithium ion pair seems to have two bands due to boron vibrations. This suggests that the defect has axial symmetry. There are three unique axial positions for Li^+ (Fig. 7) all of which have the same symmetry and selection rules. For each ion, there is one nondegenerate (A) vibration in which the ion moves parallel to the $\langle 111 \rangle$ axis, and a double degenerate (E) vibration in which the ion moves perpendicular to the $\langle 111 \rangle$ axis (Fig. 8). Selection rules permit all four of the vibrations to absorb in the infrared. Since the vibrating particles are ions, the bands should be intense. We have observed only the bands due to the two boron vibrations. Presumably the lithium vibrations were not detected because their frequencies are below 300 cm^{-1}.

Model (I), in which Li^+ lies on the threefold axis between three silicon atoms which are nearest neighbors to boron, seems more likely than the others but it is difficult to explain all of the results on this model. The lithium-boron distance would be between 2 and 3 Å. This is consistent with Pell's estimate of 2.5 to 2.7 Å[29]

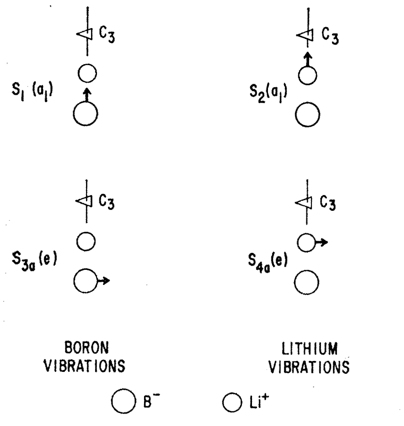

Fig. 8. Symmetry coordinates for the boron-lithium ion pair in silicon.

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[27] Howard Reiss, C. S. Fuller, and F. J. Morin, Bell System Tech. J. 35, 535 (1956).

[28] Howard Reiss and C. S. Fuller, J. Metals 8, 276 (1956).

[29] E. M. Pell, J. Appl. Phys. 31, 1675 (1960).

[30] E. M. Pell and F. S. Ham, J. Appl. Phys. 32, 1052 (1961).

on the basis of ion drift measurements, and also consistent with a binding energy of the order of 0.5 eV.

In model (II), the lithium ion lies between boron and one of its nearest-neighbor silicon atoms, forming a linear $SiLi^+B^-$ system. We do not favor this model because motion of the boron and lithium ions should be coupled strongly enough to produce considerably larger lithium isotope shifts than those observed.

For model (III), the lithium ion lies on the threefold axis between three silicon atoms which are next-nearest neighbors to boron. The minimum lithium-boron distance is approximately 4 Å, which seems too large. Thus, we will provisionally adopt model (I) for the lithium-boron ion pair.

We would predict coupling between lithium and boron vibrations to be larger for the A mode than for the E mode because a given change in either S_1 or S_2 produces a maximum change in the boron-lithium distance, whereas a change in S_3 or S_4 produces, to first order, no change in the boron-lithium distance. On this basis, the $B(3)$ bands, which show a small lithium isotope shift, would be assigned to $\nu_1(a)$, and the $B(1)$ bands, which show no lithium isotope shift, would be assigned to $\nu_3(e)$.

However, other arguments favor assignment of the $B(1)$ bands to $\nu_1(a)$ and the $B(3)$ bands to $\nu_3(e)$. Displacement of boron toward lithium lengthens the axial silicon-boron bond and shortens the other three silicon-boron bonds. The resulting change in the bond angles increases the contribution of the SiB stretching force constants to the normal mode force constant for $\nu_3(e)$ and vice versa for $\nu_1(a)$. This tends to increase the frequency of ν_3 relative to that of ν_1 even in the harmonic approximation in which the bond bending and stretching force constants do not change when boron is displaced toward lithium. Thus, if we neglect anharmonic effects, we would predict $\nu_1(a)$ to have a lower frequency than $\nu_3(e)$. The two main anharmonic effects, which we will not attempt to evaluate, are: (1) the Coulombic force between lithium and boron, which tends to lower ν_1, and (2) repulsive forces between boron and the three nearest silicon atoms which tend to raise ν_1. It would be desirable to have information on overtone and combination frequencies since this might permit the assignment to be made on the basis of anharmonic effects.

The relative intensity of the $B(1)$ and $B(3)$ bands might under some circumstances be used to arrive at an assignment on the basis of the twofold difference in statistical weight of the degenerate and nondegenerate vibrations. Such an assignment would be suspect in the present case. It is clearly indicated by isotopic frequency shifts that the motion of boron is coupled with that of lithium for the $B(3)$ band and not for the $B(1)$ band. This could have a large effect on the intensities.

For the present, we consider the assignment based on the magnitude of the lithium isotope shift to be the more reliable, and on this basis we tentatively assign the $B(3)$ bands to $\nu_1(a)$ and the $B(1)$ bands to $\nu_3(e)$.

VI. DISCUSSION

Intensities of Absorption Bands

Table III lists the specific integrated absorption intensities for all of the observed major bands. The corresponding molar integrated absorption coefficients are given for the bands whose intensities permit accuracy of ±10%. We have excluded the value for the $B(2)$ bands except in one case because the overlapping lattice bands of silicon prevent accurate measurements.

Our model represents OLi^+ and B^- as separate chemical species and the molar absorption coefficients should be invariant for corresponding bands from sample to sample.

On the whole, agreement is not as good as would be expected on the basis of the estimated experimental accuracy. In view of the very heavy doping, the discrepancies may well be due to variations among the samples. For example, long-range interactions which do not produce outright splitting of absorption bands may be responsible for the difference in intensity of the $\nu_r(OLi^+)$ band for the two samples which were doped with Li^7 (Figs. 3 and 5).

Equilibrium between the Lithium-Oxygen and Lithium-Boron Complexes

With oxygen and boron present simultaneously, there has been no detectable precipitation of lithium from the OLi^+ complex (as measured by intensity of the 1006-cm^{-1} band) for over a year at 300°K. In the absence of boron, the lithium would have precipitated in a matter of hours at this temperature. This might suggest that the OLi^+ defect is directly bonded to the boron ion with which it is paired electrically. However, as indicated above, there is evidence that the two defects are not bonded to each other.

Previously, we have written an equation for the formation of the lithium-oxygen complex, Eq. (1). Formation of the lithium-boron complex can be expressed in a similar manner, Eq. (2).

$$B^- + Li^+ \rightleftarrows B^-Li^+ . \qquad (2)$$

Eliminating the lithium ion concentration from the expressions for the equilibrium constants K_{OLi^+} and $K_{B^-Li^+}$ for these two reactions, we obtain

$$K_{OLi^+}/K_{B^-Li^+} = (OLi^+/O)/(B^-Li^+/B^-) . \qquad (3)$$

Our best estimates of the concentrations of the four species on the right of Eq. (3) give $(OLi^+/O) = (B^-Li^+/B^-) = 10 \pm 5$. Thus, the equilibrium constants for OLi^+ and B^-Li^+ seem to be nearly equal, and it is surprising that one of these defects, OLi^+, seems to be so much less stable than the other.

Let us consider the effect of free-carrier concentration on the precipitation rate or the solubility of lithium. Pell[8] has shown that the transport of lithium is mainly by the charged species Li^+. In view of the positive charge, equilibria and rates of reactions which involve this species might be expected to be sensitive to the free carrier concentration. However, Pell finds that the diffusion rate of Li^+ is no more than a factor of 10 less in compensated than in noncompensated silicon. This difference in diffusion rate is insufficient to account for the difference in the apparent stability of the OLi^+ complex. In view of the very long lifetime of the OLi^+ complex in compensated silicon, it seems possible that we are dealing with a change in the equilibrium between the precipitate particles and dissolved lithium rather than a change in rate. The precipitation can be written as follows:

$$Li^+ + Li_m{}^{n+}(\text{ppt}) \rightleftarrows Li_{m+1}{}^{(n+1)+}(\text{ppt})\,. \qquad (4)$$

The charge n of the precipitate particles is undoubtedly dependent on the free-carrier concentration:

$$Li_m{}^{n+}(\text{ppt}) + ke^- \rightleftarrows Li_m{}^{(n-k)+}(\text{ppt})\,. \qquad (5)$$

The equilibrium (5) is shifted to the right by the presence of a high concentration of free carriers. Thus, the precipitate particles should be considerably less positive (i.e., $k \cong n$) in uncompensated than in compensated silicon. The positive charge of the precipitate particles offers a barrier to the approach of Li^+ ion, and in compensated silicon it may be sufficiently large to prevent the capture of Li^+ ions. This can account not only for the apparent difference in stability of the OLi^+ complex with respect to precipitation of lithium, but also for the enhanced solubility of lithium in the presence of acceptors.[28]

Buffering of Isotopic Frequency Shifts by the Lattice

One of the main diagnostic tests for identifying the atoms responsible for various vibrational absorption bands is the frequency shift due to exchange of isotopes. When the vibrational modes of isotopic species are coupled to other modes, the isotopic frequency shift is distributed among the interacting modes as described quantitatively by the Teller-Redlich product rule. For defect atoms in a crystal lattice, the number of possible interacting lattice modes is very large. If conditions are favorable for coupling to lattice modes, the isotopic frequency shift of the vibrational mode of the defect may be quite small. As an example, we cite $\nu_r(O)$ for which the $O^{16}:O^{18}$ isotopic displacement is only about 10% of the value which one would expect for an oxygen vibration in the absence of coupling effects.

Dawber and Elliot[17] have made calculations that show that for a substitutional defect atom whose mass is approximately 90% of the mass of the lattice atoms, the isotopic frequency shift may be vanishingly small.

The situation is more complex in the case of interstitial defects like oxygen or the lithium-oxygen complex because the coupling constant between the lattice modes and the defect modes is not known as it is in the case of a substitutional impurity. In a general way, we can see that similar effects are likely to be found when the unperturbed frequency of the defect atom is very close to a lattice fundamental, and when the direction of motion of the defect atom is such that it can couple to motion of the nearest-neighbor lattice atoms. Both requirements are met by $\nu_r(O)$, and it is found experimentally that this frequency is relatively insensitive to the mass of oxygen.

Thus, care must be exercised in interpreting the isotopic frequency shifts when the vibration frequency of the defect is close to a lattice frequency. Interactions of this sort produce smaller isotopic frequency shifts than predicted from the difference in masses. The spectrum of OLi^+ offers an interesting opportunity to investigate this problem because the frequency of $\nu_r(OLi^+)$ is close to the silicon lattice frequency. We would expect the $O^{16}:O^{18}$ frequency ratio to increase appreciably in the order $\nu_r(O)$, $\nu_r(OLi^7)$, and $\nu_r(OLi^6)$.

VII. SUMMARY

The present attempt to interpret the absorption bands due to oxygen, lithium, and boron in silicon is necessarily qualitative. The principal absorption bands have been assigned to three isolated defects: interstitial OLi^+, a substitutional boron ion, and a boron-lithium ion pair.

A structure for the OLi^+ complex is proposed in which the oxygen atom occupies substantially the same position as that of isolated interstitial oxygen in silicon. The lithium ion is bound to oxygen at short range (2–3 Å) by ionic forces.

Vibrational assignments for interstitial oxygen have been modified to make them compatible with the observed spectrum of OLi^+. The new assignment provides a more satisfactory explanation of some of the features of the spectrum of interstitial oxygen itself and it is consistent with assignments for SiOSi groups in organosiloxanes and silicates. Thus, the structure of interstitial oxygen in silicon seems to be similar to the structure of SiOSi groups in other silicon-oxygen containing materials.

An axial (C_{3v} point group) structure for the boron-lithium ion pair is proposed. The boron ion occupies a substitutional position displaced slightly from the geometrical lattice site toward the lithium ion. The latter occupies an interstitial position on the threefold axis 2–3 Å distant from the boron ion and between three of its nearest-neighbor silicon atoms.

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