DYNAMICS OF LITHIUM IN GERMANIUM AND COMPENSATED SILICON

> Thesis for the Dagree of Ph. D. MICHIGAN STATE UNIVERSITY Eric Alexander Dounce 1972





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This is to certify that the

thesis entitled

DYNAMICS OF LITHIUM IN

GERMANTUM AND COMPENSATED LITHIUM

presented by

ERIC ALEXANDER DOUNCE

has been accepted towards fulfillment of the requirements for

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ABSTRACT

DYNAMICS OF LITHIUM IN GERMANIUM AND COMPENSATED SILICON

By

Eric Alexander Dounce

A study of the dynamics of lithium in germanium and silicon is important in helping to establish practical limits on the drift rate of lithium ions in silicons or germanium during the fabrication of nuclear detectors. The systems of lithium in germanium and lithium in silicon have been studied with this goal in mind. Isotopic diffusion studies of lithium in germanium have been made at relatively low diffusion temperatures, <u>i.e.</u>, 200-400°C. Measurements of the ratio of ⁶Li to ⁷Li diffusion constants provide evidence for the significance of quantum effects in the diffusion process at these temperatures. We have proposed a tunneling mechanism as the probable explanation and we compare our measurements with the results predicted by a general diffusion theory which includes tunneling effects. Our results, when extrapolated to detector drift temperatures, show that the lighter ⁶Li isotope drifts only 12% faster than 7 Li.

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The detector fabrication process requires drifting lithium ions into the silicon or germanium to form pairs or complexes with negatively charged trap sites. The dynamics of the lithium-acceptor complexes then becomes important in fully understanding the compensation process. We have found the present model describing pair dynamics in a crystal lattice to be inadequate. A modification of the existing model is proposed which takes into account the actual C_{3,} symmetry of the complex. The possibility of interactions between different local modes at the same physical site is also considered. Our analysis is, however, only approximate and a more rigorous formalism is indicated by comparison with measurements of line width and centroid variations with temperature. These measurements have allowed us to determine the coefficients of anharmonic terms in the local-mode potential.

If a local mode of free lithium exists in silicon or germanium it is important to locate its frequency so that it may be excited directly. We did not find a local mode of free lithium in silicon and expect that the free lithium exhibits only resonant modes in silicon. A review of the literature indicates a probable free lithium local mode in germanium near 364 cm^{-1} for ⁷Li.

Finally, the effects of uniaxial stress on the lithiumboron local modes in silicon have been studied. We observed that uniaxial stress near the fracture limit did not produce a detectable splitting of the two-fold degenerate lithium

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or boron local modes. Similarly, it did not produce a measurable shift in the local-mode centroids. It is unlikely then, that uniaxial stress will produce significant variations in the lithium drift rate in silicon.

DYNAMICS OF LITHIUM IN GERMANIUM AND COMPENSATED SILICON

By

Eric Alexander Dounce

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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I would like to thank: Dr. William Hartmann for his help with the theoretical interpretations, my committee co-chairman Dr. David Fisher for his critical reviews of the manuscript, Dr. Gary Cloud for his help with the birefringence work, and to Mrs. Marcella Williams for typing the final draft.

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CHAPTER 1

INTRODUCTION

The work described in this thesis began with the specific goal of establishing limits on the practicality of increasing the diffusion rate for lithium ions in a semiconductor matrix. Two questions were fundamental to this goal: can some means of selectively heating the lithium ion in the semiconductor lattice be found? Or, in a more direct approach, is an advantage gained if a lighter isotope of lithium is used?

Our interest in the motion of the lithium ion in a semiconductor matrix was initially generated by the role played by lithium in the fabrication of nuclear detectors. This fabrication involves a low-temperature drift of lithium ions through silicon or germanium to compensate negatively-charged trap sites. Low drift temperatures are used so as to reduce the precipitation of lithium on nucleation sites. This drifting process consequently requires considerable time and is limited by the lowtemperature diffusion constant. Therefore, any increase in the diffusion rate of lithium ions may be directly translated into a more efficient detector fabrication.

In an effort to answer the question on selectively heating the lithium ion in the semiconductor lattice, we set out to study the local-vibrational-modes of lithium in germanium and silicon by means of infrared absorption.

The introduction of lithium into silicon or germanium results in approximately equal concentrations of free electrons and lithium local modes. The free electrons have a much greater absorption coefficient than the local. modes and, therefore, mask them. The systems actually studied were electrically compensated with equal concentrations of acceptors and donor ions. The acceptors and donors generally form pairs which tend to complicate the local-mode spectrum. Of these systems, lithium and boron in silicon has been the most extensively studied. 1-10 However, relatively little has been done to evaluate the effects of lattice coupling on these local modes. Lattice coupling to the local modes is, however, fundamental to the question of selectively heating the lithium ion in a semiconductor lattice. The measurement of second harmonics by Waldner¹⁰ does give an indicator of lattice coupling effects; but, no indication of the lithium-boron pair dynamics is evident. We have, therefore, set out to learn about how the lithium ion reacts with its surroundings through measurements of the centroid shifts and line widths of the local modes as a function of temperature.

The spectrum of lithium-boron local modes in silicon has one uncertain feature; that is, the designation of the local mode at 522 cm⁻¹ as a singly or doubly-degenerate local mode of lithium in a paired configuration. It is generally thought to be a doubly-degenerate local mode of lithium paired with boron.^{3a,3b,9a,9b} However, Hayes⁸

in a review as isignation, a suggested^{7,8} Since we are lithium motio: the 522 cm^{-1} : stress. Prior to involved the : increased dif: diffusion cons isctopes. The li had alread Pell. 12 His me classical rate of the high te ratio of diff: advantage woul instead of 7 of tunneling e ratio at the 1 supporting thi of the low-ter Carium by Sher ^{decrease} in ac temperature me for by a tunne. in a review article raises some questions as to its designation, and the application of uniaxial stress is suggested^{7,8} to determine the degeneracy of this mode. Since we are primarily interested in local modes due to the lithium motion, we set out to determine the degeneracy of the 522 cm⁻¹ mode through the application of uniaxial stress.

Prior to our infrared absorption studies, our work involved the more direct approach to the problem of an increased diffusion rate; we studied the difference in diffusion constant (or mobility) between 6 Li and 7 Li isotopes. The ratio of diffusion constants of ⁶Li to ⁷Li had already been measured in silicon at 800°C by Pell.¹¹ His measurement showed no variation from the classical ratio. This result is not unexpected in view of the high temperature of measurement. The classical ratio of diffusion constants is only 1.080, and little advantage would be gained by drifting detectors with ⁶Li instead of ⁷Li. But for such light ions, the possibility of tunneling exists which may substantially increase this ratio at the low drift temperature involved. Evidence supporting this possibility was available in measurements of the low-temperature diffusion constant of ⁷Li in germanium by Sher.¹² These measurements showed about a 15% decrease in activation energy in the range of the lowtemperature measurement; such an effect might be accounted for by a tunneling mechanism. The parameter of greatest



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uncertainty in subsequent diffusion-ratio calculation turned out to be the lithium local-mode frequency; this uncertainty further motivated our infrared absorption studies which followed.

In order to make the account of these experiments more meaningful, the details of the necessary background material will first be presented. The sample preparation and instrumentation are then described, followed by a description of the local-mode experiments and their results. These results are then discussed in terms of theoretical calculations. Finally, the isotopic diffusion studies are presented and discussed.

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CHAPTER II

THEORETICAL HISTORY

2.1 Lithium and Germanium Diffusion Studies

The lithium atom enters a silicon or germanium lattice as a singly-ionized donor impurity. Most of the lithium is ionized for temperatures above 50° K.¹³ The diffusion constant for natural lithium as a function of temperature has been well studied.^{11,12,14} These studies show that the lithium ion must move among interstitial lattice sites to account for the high mobility observed. Both silicon and germanium have a basic diamond structure, so that interstitial equilibrium sites can have only a tetrahedral (T_d) or hexagonal symmetry. Various studies, including stress effects on electron excitations, show that the lithium must be in a T_d-symmetry site.^{3,15}

The potential well in which the lithium ion (Li⁺) is bound in the diamond-structure crystals is the key to understanding the motion of lithium in silicon or germanium. We have considered two methods for studying this potential. The first method involves a study of tunneling effects through the well as indicated by the diffusion constant at low temperatures. The second method involves the infrared absorption in a transition from the Li⁺ vibrational ground state to the first excited state.

Diffusion constants have been described classically by

$$D(T) = D_{o} exp(Q/kT), \qquad 2.1$$

where k is Ec in . Q rep the height of sites. D_o is where A depen for silicon a is the gas co mole of diffu sition state. the activatic sodulus at ab: du/dT = -6.0x Were first put the interstit: in the lattice of greatest up frequency of 1 mation it is a

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where k is Boltzmann's constant and T is the temperature in °K. Q represents the classical activation energy, i.e. the height of a sinusoidal barrier between equilibrium sites. D_0 is given by the expression¹⁶

$$D_{o} = \lambda d^{2} v \exp (\Delta S/R), \qquad 2.2$$

where λ depends on the unit-cell geometry, and equals 1/8 for silicon and germanium; d is the lattice constant; R is the gas constant, and ΔS is the change in entropy per mole of diffusing ions transferred to the activated transition state. ΔS is related to the elastic modulus μ and the activation energy by $\Delta S = -Q \frac{1}{\mu_0} d\mu/dT$; μ_0 is the elastic modulus at absolute zero, i.e. $\mu_0 = 4.2 \times 10^{-11} \text{ dyne/cm}^2$ and $d\mu/dT = -6.0 \times 10^7 \text{ dyne/cm}^2$ -deg. for germanium. These ideas were first put forth by Wert and Zener,¹⁷ who assumed that the interstitial diffusant jumped from one hollow region in the lattice to an adjacent hollow region. The parameter of greatest uncertainty in this formulation is the vibrational frequency of the lithium ion.² In a localized harmonic approximation it is given by

$$v = (Q/2Ma^2)^{1/2}$$
 2.3

where 'a' is the distance between adjacent interstitial sites, and M is the mass of the ion. This uncertainty in v further motivated our subsequent infrared absorption studies. The

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Li⁺ diffusion constant in silicon follows this classical expression (2.1) for all temperatures for which it has been measured;^{*} it is described by $D_0 = 23 \times 10^{-4} \text{ cm}^2/\text{sec}$ and $Q = 0.655 \text{ ev}^{12}$ In germanium, however, a somewhat smaller activation energy is found at temperatures below 155°C than at higher temperatures. The classical expression at higher temperatures is given by $D_0 = 13 \times 10^{-4} \text{ cm}^2/\text{sec}$ and $Q = 0.46 \text{ ev}.^{11}$

We have proposed that tunneling of the lithium through the activation energy barrier explains the low-temperature discrepancies of the Li⁺ diffusion constant in germanium. If this is indeed the case, the ratio of the diffusion constants of ⁶Li to ⁷Li at low temperatures should be larger than the 1.080 value predicted by the classical inversesquare-root mass ratio. We therefore set out to measure this ratio as a function of temperature. If this effect had turned out to be large, a time saving in detector fabrication would result if the drift were done with ⁶Li instead of ⁷Li.

A general diffusion theory,¹⁸ beginning with a sinusoidal potential and including tunneling through the barrier at low temperatures, is applicable to this problem. This sinusoidal potential is approximated by a harmonic potential well plus a parabolic barrier. The ion jump frequency $1/\tau$ is taken as proportional to a sum over all N oscillator levels

^{*}This includes temperatures down to 273°K.⁵²

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 E_{N} of a Boltzmann distribution times a tunneling probability $T(E_{N})$,

$$\frac{1}{\tau} = \sum_{N} \exp(-E_{N}/kT)T(E_{N}) \qquad 2.4$$

The resulting diffusion constant is

$$D(T) = B\{\exp(-\beta Q) \xrightarrow{\exp[\epsilon_{O}(\beta-1/kT)] - \exp[(2N-3)\epsilon_{O}(\beta-1/kT)]} + \frac{\exp[-(2N+3)\epsilon_{O}/kT]}{1 - \exp(-2\epsilon_{O}/kT)} \} 2.5$$

where $B = (2\epsilon_0/kT)D_0$, $\beta = (2\pi^2(0.35a)/h) \cdot (2M/Q)^{1/2}$, $\epsilon_0 = h\nu/2$ and h is Planck's constant. Q is the full height of the sinusoidal potential and (a) is the distance between interstitial sites. The number of oscillator levels N is determined from the barrier height by N = $(2Q/h\nu)-1/2$. The first term in brackets in eq. 2.5 represents the contribution to D due to tunneling; the second term reduces to the classical expression at high temperature. This expression for D(T) is compared with the full range of experimental diffusion constants in germanium; the ratio of diffusion constants for 6 Li to 7 Li is then simultaneously compared with measured ratios.

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2.2 The Boron Local Mode in Silicon

A local-vibrational-mode is a vibrational state of an impurity ion and its immediate surroundings. The ground vibrational state corresponds to the zero-point motion of the ion. Crystals with point impurities may have other vibrational modes, called band modes, with frequencies below ω_{M} .⁶ The first studies of local modes in silicon were theoretical, and they predicted reasonably well the local-mode frequency of the substitutional boron ion.¹⁹ The approximation was made that the silicon-boron force constants were the same as the silicon-silicon force constants; the results were a local-mode absorption coefficient $a(\omega)$ given by

$$\alpha(\omega) = \frac{2\pi^2 N e^2 \Lambda}{nc} |\chi(o)|^2 g(\omega) \qquad 2.6$$

where N is the number of impurities per unit volume, e is the charge of an electron, A is a local field correction of $[(n^{2}+2)/3]^{2}$, n is the refractive index, c is the velocity of light in vacuum, $|\chi(o)|^{2}$ is the vibrational amplitude of the impurity atom, and $g(\omega)$ is a normalized line-shape function. This work predicted that a localized-mode did not exist unless the impurity mass were less than 0.925 times the mass of the host atom. For very light impurities the localized impurity vibrations are much faster than those of the host lattice. One may then assume that these impurity ions vibrate in a rigid lattice, in which case the isotopic change should cause a frequency shift determined only by

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2.3 The Lithium Mode in Silicon

Bellomonte and Pryce did further theoretical work on the free interstitial lithium ion in a silicon lattice.^b They began with the assumption that the lithium ion occupied a T_d symmetry site. To calculate restoring forces on the Li⁺ they considered the primary energy contributions to be from overlap repulsion due to the exclusion principle, and from induced lattice polarization due to the charge on the lithium ion. The first of these effects stabilizes the ion in the Td site, and the second effect tends to destabilize it. The polarization energy falls off as the fourth power of the distance from the ion as expected. The overlap energy was found to be approximately proportional to the density of silicon electrons at the lithium nucleus. Slater wave functions were used to determine the silicon electron density. Bellomonte and Pryce found that the overlap repulsion exceeds the polarization attraction, causing them to believe that nearest-neighbor silicon atoms are displaced outward from the lithium by an amount of about 0.1A. Calculations were based on a numerical silicon phonon spectrum, and included lithium-silicon interactions to second nearest-neighbors. Results were presented in the form of a plot of the impurity mass vs. frequency relative to ω_m . The essential features are



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reproduced in Fig. 2.1. The calculations for a rigidlattice approximation are shown for comparison. These calculations predicted a critical mass of 12 AMUs above which no local mode would exist. Comparison of the theory with experimental data on isotopic shift in the 522 cm⁻¹ line gave a critical mass of about 8.1 AMU. The 522 cm⁻¹ line, however, is a Li⁺ mode perturbed by a paired boron ion and consequently does not represent the free interstitial lithium. The fact that no isolated Li⁺ local mode has yet been observed, even though samples studied by Spitzer at high temperature should have a significant number of unpaired lithium ions, suggests that the critical mass is less than 7 AMU. Hence, the effects of lattice coupling are apparently considerably different than these calculations predict.

2.4 Lithium-Boron Complexes

Experimental observations of local modes in silicon have most Often been made in compensated material in which Li⁺ and B⁻ ions are present in equal numbers. The oppositely charged ions have a strong affinity for each other, and the Li⁺ is captured by the boron at the radius of 33 to 39 Å;²¹ as a result, pairing or complexing occurs.^{22,23} The orientation of the Li⁺ - B⁻ pair axis has previously been found to be along a [111] direction with an equilibrium separation of 2.5 - 2.7 Å.^{11,21,23} The boron remains in a substitutional lattice site whereas the interstitial lithium is surrounded by three silicon atoms and the boron ion as nearest-neighbors. The effect of the Li⁺ ion on the boron local mode is to perturb



FIGURE 2.1 Interstitial mass M vs. relative localmode frequency in silicon, where (a) is the result of calculations made by Bellomonte and Pryce and includes anharmonic terms in the Hamiltonian and (b) is the result of calculations assuming a rigid-lattice i.e. no anharmonic terms.

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its T_d symmetry to C_{3v} axial symmetry. The three-fold degeneracy of the T_d symmetry is therefore split into an upper-frequency doubly degenerate band, and a lower-frequency singly-degenerate band. It is expected that the boron ion would have the same effect on the lithium local mode. However, only one peak at 522 cm⁻¹ can be attributed to the ⁷Li motion. This peak is just above the maximum lattice-phonon frequency ω_m , and is thought to be the two-fold-degenerate high-frequency perturbed lithium local mode.²⁴ The lower-frequency peak would then lie in the band of host lattice frequencies.⁶ The isotopic frequency shift in the 522 cm^{-1} line is observed to be approximately one third of the inverse-square-root mass ratio predicted in the rigid-lattice approximation. The boron peaks, on the other hand, have isotopic frequency shifts within 30% of the rigid lattice approximation. This may indicate a relatively strong anharmonic coupling of the lithium to the lattice.^{9a}

A Green's function treatment of free interstitial Li⁺, substitutional B⁻, and Li⁺-B⁻ pairs in silicon has been done taking into account variations in force constants.^{7,12} Accurate prediction of the boron local-mode frequencies required about a 10% decrease in force constants due to local deformation of the lattice. Calculations were made for an interstitial impurity (lithium) in a T_d symmetry coupled to its four nearest neighbors by a force constant β ; these calculations showed that the existence of a ⁷Li localmode required β >23 kerg/cm². Bellomonte and Pryce's calculations, however, showed coupling to second nearest-neighbors to be larger than to nearest-neighbors, but the sum of the

interactions w y Elliott and configuration constants arou constants & be reighbors, a+? the boron and and γ between bors. This mo accel to give should be kept force constant cormal coordi of the defect terms in the The lithium 1 ca² for which well with exfrequency shi , of the Siin the basic combination , borch local : to agree bes Peplaced by

interactions was in the range $20-30 \text{ kergs/cm}^2$. Calculations by Elliott and Pfeuty⁷ for boron and lithium in the paired configuration required considerable modification of force constants around the pair. The model used considered force constants B between the lithium and its three nearest-siliconneighbors, $\alpha + \beta$ between the lithium and boron, and ϕ between the boron and silicon pair co-linear with the Li-B axis, and γ between the boron and the three silicon nearest-neighbors. This model was chosen because it was the simplest model to give good agreement (0.3%) with experiments. It should be kept in mind, however, that second-nearest-neighbor force constants are important. In this model each of the normal coordinates of the defect space involves only one of the defect atoms. Only anharmonicity would result in terms in the hamiltonian which mix the atomic coordinates. The lithium line at 522 cm⁻¹ was fitted with a β of 23 kerg/ cm² for which the isotopic frequency shift agreed quite well with experiments. The boron local modes and isotopic frequency shifts were fitted by weakening the force constant • of the Si-B bond. Variations of other force constants in the basic six atom model above did not give the proper combination of intensity and isotopic shift of the paired boron local modes. Calculations of intensity were found to agree best with experiments when the lithium charge was replaced by an effective charge of 0.7e.



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2.5 Anharmonic Effects on a T_d Symmetric Local Mode

Line width and centroid shift with temperature are the result of anharmonic coupling of the free or paired ions to the lattice. Theoretical results for complexes in silicon have not as yet been presented, although residual line widths at zero °K have been discussed by Dawber and Elliott^{19a} for the free boron local mode. They conclude that the residual line width is "probably" determined by decay of the local mode into two band modes through anharmonic forces.

Anharmonic effects on local modes in ionic crystals have been studied theoretically by Elliott *et al.*²⁵ These calculations are for charged impurities in a T_d symmetry, but many similarities exist with the paired lithium and boron ions in silicon; the pertinent consequences of their theory are presented here. Their calculations begin with an expansion of the potential out to fourth order in atomic displacement divided by interatomic distance. The symmetry of the T_d site is used to determine which expansion coefficients are zero. Anharmonic thermal effects are the result of interactions between local modes (operators b, b⁺) and lattice modes (operators a(\vec{k})). Possible third-order interactions are represented by

$$(b+b^{+})^{3}$$

 $(b+b^{+})^{2}(a(\vec{k}) + a^{+}(\vec{k}))$
 $(b+b^{+}) (a(\vec{k})+a^{+}(\vec{k}))(a(\vec{k}^{*}) + a^{+}(\vec{k}^{*}))$
 $(a (\vec{k}) + a^{+}(\vec{k})) (a (\vec{k}^{*}) + a^{+}(\vec{k}^{*})) (a(\vec{k}^{**})+a^{+}(\vec{k}^{**})) 2.7$

In fourth (১+১⁺ (b+b⁺ (2+5 etc. where k i: The resul applicabl coordinat H₃ = E₄ = The numbe has a mag lattice-: The spat Perturba ieternin Droaden: وتتاتار قيرو In fourth order the combinations are

$$(b+b^{+})^{4}$$

 $(b+b^{+})^{3}$ (a(\vec{k}) + a⁺(\vec{k}))
 $(b+b^{+})^{2}$ (a(\vec{k}) + a⁺(\vec{k}))(a(\vec{k}) + a⁺(\vec{k}))
etc.,
2.8

where \vec{k} is the phonon wave vector and branch index.

The resulting third- and fourth-order anharmonic Hamiltonians applicable to displacements quadratic in the local-mode coordinates are

$$H_{3} = \sum_{\vec{k}} \mathcal{B} \frac{\hbar}{2M^{2}\Omega\omega_{M}} \left(\frac{\hbar\omega(\vec{k})}{2MN}\right)^{1/2} \left\{ \sum_{xyz} (b_{x}+b_{x}^{+})^{2} \right\} (a(\vec{k})+a^{+}(k)) 2.9$$

$$H_{4} = \sum_{\vec{k},\vec{k}} \zeta \frac{\hbar(\omega(\vec{k})\omega(\vec{k}^{-}))^{1/2}}{4M^{2}\Omega\omega_{M}^{2}MN} \left\{ \sum_{xyz} (b_{x}+b_{x}^{+})^{2} \right\}$$

$$(a(\vec{k})+a^{+}(\vec{k}))(a(\vec{k}^{-})+a^{+}(\vec{k}^{-})). 2.10$$

The number of unit cells is given by N. The silicon atom has a mass M, and the impurity atom mass M'; $\omega(\vec{k})$ is the lattice-mode frequency and Ω is the local-mode frequency. The spatial coordinates x,y and z refer to the local modes. Perturbation theory is applied to these Hamiltonians to determine thermal shifts of the local modes and linebroadening effects due to elastic scattering of band phonons. In the ionic crystal CaF₂ the expansion coefficients ζ and \mathfrak{B} have been measured to be $\zeta = 10^{21} \text{ erg/cm}^4$ and $\mathfrak{B} = 2 \times 10^{12}$ erg/cm^3 and similar orders of magnitude are expected for



homopolar crystals. Elliott *et al* found that the thermal shift in local-mode frequency is the result of fourthorder effects i.e. H_{μ} . H_{μ} was averaged over band modes, leaving local-mode operators unchanged to give

$$H_{\mu} = \sum_{\vec{k}} \zeta \frac{\hbar \omega(\vec{k})}{4MM^{2}N\Omega\omega_{M}^{2}} \sum_{xyz} (b_{x}b_{x}^{+}+b_{x}^{+}b_{x}) < a(k)a^{+}(\vec{k}) + a^{+}(\vec{k})a(\vec{k}) > 2.11$$

where terms like $a(k) a^{+}(k^{-})$ have averaged to zero. Comparison of eq. 2.11 with the ordinary oscillator Hamiltonian given by $\frac{1}{2}\hbar\Omega\sum_{x}(b_{x}b_{x}^{+}+b_{x}^{+}b_{x})$ gave a relative frequency shift of

$$\frac{\Delta\Omega}{\Omega} = \frac{\zeta}{M^2 \Omega^2 M \omega_M^2} \left\{ \frac{1}{N} \sum_{\vec{k}} \tilde{m} \omega(\vec{k}) [n(\vec{k}) + 1/2] \right\}, \qquad 2.12$$

where n(k) is the phonon number operator. This expression becomes linear in temperature at high temperature i.e. above $\theta_d/2$.

Line width may also be explained in terms of anharmonic coupling to the band modes. Spontaneous decay of the excited local mode into several band modes requires that the band-mode frequencies satisfy the energy-conservation requirement that $\sum \omega(\vec{k}) = \Omega$, where the sum includes the energies of the several band modes created. The local-mode frequencies of lithium and boron in silicon are between $\omega_{\rm M}$ and $2\omega_{\rm M}$, so that decay into two band modes through the third-order anharmonic potential is likely. This is represented by the product $(b+b^+)(a(\vec{k})+a^+(\vec{k})(a(\vec{k}')+a^+(\vec{k}'))$. The resulting Hamiltonian given by Elliott *et al.* is

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 $\frac{1}{\tau} = \frac{3^{-2}\pi}{4M^{-2}\tau}$

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 $\frac{1}{\tau} = 2\pi \left(\frac{1}{\tau}\right)$

$$H_{3} = \sum_{\vec{k},\vec{k}} \mathcal{B}' \frac{\tilde{h}}{2MN\omega_{11}^{2}} \left(\frac{\tilde{h}\omega(\vec{k})\omega(\vec{k}')}{2M'\Omega} \right)^{1/2} \sum_{xyz} (b_{x}+b_{x}^{+})$$

$$\{a(\vec{k})+a^{+}(\vec{k})\}\{a(\vec{k}')+a^{+}(\vec{k}')\}$$

$$(b_{x}+b_{x}^{+})$$

$$\{a(\vec{k})+a^{+}(\vec{k})\}\{a(\vec{k}')+a^{+}(\vec{k}')\}$$

$$(b_{x}+b_{x}^{+})$$

Perturbation theory with this Hamiltonian gives rise to a two-phonon-decay line width of

$$\frac{1}{\tau} = \frac{\mathfrak{Z}^{-2} \pi \hbar \nu}{4M \cdot \Omega M^{2} \omega_{M}^{4}} \sum_{\vec{k}, \vec{k}} \frac{1}{N^{2}} \omega(\vec{k}) \omega(\vec{k}') \{ [n(\vec{k})+1] [n(\vec{k}')+1] - n(\vec{k})n(\vec{k}') \} \delta(\omega(\vec{k})+\omega(\vec{k}')-\Omega)$$

$$2.14$$

where v is the local-mode oscillator level, taken as one for decay from the lowest excited state to the ground state. At low temperatures $\frac{1}{\tau}$ becomes constant, whereas at high temperatures it varies linearly with temperature. In the ionic crystals the dominant line-width broadening was found to be due to elastic scattering of band phonons in transition $|v,n(\vec{k}), n(\vec{k}') > + |v,n(\vec{k}) + 1, n(\vec{k}') + 1 >$ with conservation of energy requiring $\omega(\vec{k}) = \omega(\vec{k}')$. The resulting width is

$$\frac{1}{\tau} = 2\pi \left(\zeta - \frac{2\mathfrak{B}^2}{M \cdot \Omega^2} \right)^2 \left(\frac{\hbar (2\nu + 3)}{4M \cdot \Omega M \omega_M^2} \right) \sum_{\vec{k}, \vec{k} - N^2} \frac{1}{\omega^2} (\vec{k}) n(\vec{k})$$

$$[n(\vec{k}) + 1] \delta(\omega(\vec{k}) - \omega(\vec{k})) \qquad 2.15$$

This elastic s st high temper One of th tating the allo he through mea marbon local m substitutional basic conditio 1.8 Experimen Observati is silicon or test serious c associated wit can satisfy er or emission of tion of a phot coefficient pr as v-1.9 from m^{-1}/cm^3 at 8 Varies as v^{-2} m^{-1}/cm^3 at 8 is assumed to of lithium-to 10x10-19 cm-1 absorption co Tese absorpt factor e-ax,

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This elastic scattering line width goes to zero as T', and at high temperatures it varies as T^2 .

One of the best experimental means of further validating the above line width and centroid expression may be through measurements of line width and centroid of carbon local modes in silicon. Carbon enters silicon substitutionally; hence, it has a T_d symmetry, and all basic conditions of the theory are satisfied.

2.6 Experimental Difficulties in the Observation of Local Modes

Observation of the free_interstitial-lithium local mode in silicon or germanium presents several difficulties. The most serious of these is the presence of free electrons associated with the ionized lithium. These free electrons can satisfy energy and momentum conservation by the absorption or emission of a lattice phonon simultaneously with the absorption of a photon.²⁷ The resulting experimental absorption coefficient per unit lithium concentration in germanium varies as $v^{-1.9}$ from 1.1×10^{-16} cm⁻¹/cm³ at 500 cm⁻¹ to 7.0×10^{-17} cm^{-1}/cm^3 at 800 cm⁻¹. In silicon²⁸ the absorption coefficient varies as $v^{-2.0}$ from 1.1×10^{-16} cm⁻¹/cm³ at 500 cm⁻¹ to 7.0×10^{-17} cm^{-1}/cm^3 at 800 cm⁻¹. If the free interstitial local mode is assumed to have an absorption intensity similar to that of lithium-boron-pair local modes then a value of approximately 10×10^{-19} cm⁻¹/cm³ would be expected. The free-electronabsorption coefficient would then be about 170 times larger. These absorption coefficients are additive in the attenuation factor $e^{-\alpha x}$, so that making the sample thin enough to transmit an optical signal reduces the local-mode absorption strength

to undetectabl to the free-el the absorption higher wave no lower wave nut Soling would below about 4 innized lithin We have o through the cl junction where depletion regi intensity leve The star absorption is of an accepto: fectly compenthe compensat free-carriercarriers may the compensat are holes in a found, which -2.0x10-16 cm⁻¹ A perfec. Borption bac nicon and gr to undetectable levels. There is a temperature dependence to the free-electron absorption in germanium. At 700 cm⁻¹ the absorption is constant with temperature, whereas at higher wave numbers it increases with temperature; at lower wave numbers, it decreases slightly with temperature. Cooling would therefore be of little benefit until temperatures below about 40°K where the lithium re-ionizes,¹³ but the unionized lithium represents a different problem.

We have considered the possibility of shining light through the charge-depleted region of a reverse-biased diode junction where lithium was used as one of the dopants. The depletion region is so small, however, that the resulting intensity levels would not be detectable.

The standard method for reducing the free-carrier absorption is the introduction of an equal concentration of an acceptor impurity. Ideally this addition would perfectly compensate the lattice electrically; in practice, the compensation is usually not complete, and a residual free-carrier-absorption background remains. These free carriers may be either electrons or holes, depending on the compensation processing. If the remaining free-carriers are holes in silicon, a wavelength dependence²⁹ of $v^{-2.2}$ is found, which varies from 9.2×10^{-16} cm⁻¹/cm³ at 500 cm⁻¹, to 2.0×10^{-16} cm⁻¹/cm³ at 1000 cm⁻¹.

A perfectly-compensated lattice will still have an absorption background, due primarily to the lattice itself. Silicon and germanium are covalent or homopolar crystals,

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and have no net dipole moment per unit cell. In these crystals lattice absorption is a two-phonon process which can be visualized as follows: A first lattice-vibrational mode induces charge on the lattice atoms. A second mode simultaneously causes the charge to vibrate, thus producing an electric moment which couples to the radiation field.³⁰ The structure of this absorption spectrum then varies according to the two phonon density of states, and represents sums or differences of two or more lattice phonon interactions. The main absorption peak in silicon, at 610 $\rm cm^{-1}$, is the twophonon summation band of TA and TO phonons; similarly, the maximum absorption band in germanium at 360 cm^{-1} is a summation of TA and TO phonons. The dispersion relations obtained from neutron spectrometry³¹ show these branches to have the highest density of states. Typical peak lattice absorption coefficients for both silicon and germanium are about 10 cm^{-1} . In a doublebeam spectrophotometer, the lattice absorption can be subtracted out by placing an equal thickness of undoped crystal in the reference beam.

The system of lithium in silicon differs from that of lithium in germanium in two important respects. The Debye temperature in silicon is 658°K, in germanium 362°K. As a result, thermal broadening of the local-mode peaks occurs at much lower temperatures in germanium than in silicon. The germanium system must therefore be cooled below 200°K in order to observe the local modes. The two systems also differ in the diffusion constant of lithium. Hence, in



the rate of precipitation of lithium from super-saturated germanium is faster than that from super-saturated silicon, by approximately the inverse ratio of diffusion constants. The precipitation of lithium in germanium continues at temperatures down to room temperature; consequently, lithium compensated germanium must be maintained at a low temperature until all measurements on the sample are complete. The precipitation of lithium would otherwise leave large concentrations of uncompensated acceptors, and hence an unacceptable free-carrier background absorption. More will be said about the precipitation process later.

The two systems are similar in several important ways. Lithium occurs in both silicon and germanium as a singlyionized donor in an interstitial lattice site. Both lattices have the basic diamond structure with lattice constants of 5.43Å for Si and 5.66Å for Ge. Furthermore, the outer electronic shells of silicon and germanium both contain two s electrons and two p electrons, hence similar repulsive forces on the lithium ion due to the exclusion principle may be expected. Many aspects of the local-mode studies on silicon can therefore be generalized to germanium through appropriate frequency or temperature shifts.

2.7 Complexing of Donors with Acceptor Ions

The introduction of acceptor compensating ions into the lattice gives rise to the formation of positive and negative ion pairs or complexes. Calculations of the relative percent of complexed ions, for any fixed temperature and substitutional acceptor concentration, have been done

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by Reiss *et al.*²² They assumed that paired and unpaired ions were in dynamic equilibrium hence, a law of mass action could be written down. Thus, if P represents the concentration of paired ions, N_A -P, the concentration of unpaired acceptor ions, and N_D -P the concentration of unpaired donor ions, the mass action expression is

$$\frac{P}{(N_A - P)(N_D - P)} = \Omega(T)$$
, 2.17

where $\Omega(T)$, an equilibrium constant independent of concentration, is given by

$$\Omega(T) = 4\pi \int r^2 \exp\left(\frac{e^2}{\epsilon k T r}\right) dr . \qquad 2.18$$

These calculations included only the effect of coulomb interaction between ions. The fraction of paired donors (P/N_D) was then a function of the acceptor concentrations and $\Omega(T)$. In the case of nearly equal concentrations of donors and acceptors, (P/N) is given by

$$P/N = (1 + \frac{1}{2N\Omega}) - (\frac{1}{N\Omega} + \frac{1}{4N^2\Omega^2})^{1/2}$$
. 2.19

Appendix B contains a somewhat modified form of this expression evaluated as a function of temperature for equal concentrations of lithium and boron in silicon. As would be expected, the fraction of paired ions increases rapidly with impurity concentrations (N) for a given temperature. For a fixed N,

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the fraction paired decreases with temperature. The possibility of observing the unassociated Li⁺ or B⁻ local mode in a compensated system must subsequently be considered. That is, is it possible to quench a compensated sample from a high temperature fast enough to prevent pair formation? Reiss *et al.*²² have made calculations of the average lifetime of an unpaired ion, and denoted it as the relaxation time τ_p for ion pairing. They found τ_p to be closely approximated by

$$\tau_{\rm p} = \frac{\epsilon k T (N-M)}{4 \pi e^2 N^2 D_{\rm o}(T)}, \qquad 2.20$$

where

$$M = \frac{1}{4\pi} \int_{a}^{L} r^{2} \exp(\frac{e^{2}}{\epsilon k T r}) dr . \qquad 2.21$$

The distance of closest approach (a) between oppositelycharged ions can be taken as 2.6Å. The Debye length L is given by L = $(\epsilon kT/8\pi e^{2}N)^{1/2}$, and D_o(T) is the lithium diffusion constant. For impurity concentrations of N = $10^{19}/cm^{3}$, M is small compared to N so that τ_{p} varies as $T/ND_{o}(T)$. To freeze-in a sizable fraction of unpaired ions, i.e. 10% at 400°K, it would be necessary to quench the sample in a time small compared with the relaxation time τ_{p} at that temperature. At 400°K, τ_{p} has a value of 1.3×10^{-3} sec.; at room temperature τ_{p} is 0.76 seconds. Hence, a quench fast enough to freeze-in unpaired ions is unlikely. At room temperature about 1% of the ions remain unpaired. As a result, the free-boron local mode

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has been observed in compensated silicon.^{4,5,9a,9b,10} However, a free-lithium local mode has not been observed, and it is thought that it must lie in the lattice continum.^{5,6,9a}



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CHAPTER III

SAMPLE PREPARATION

The infrared study of local modes in silicon and germanium required a sample uniformly doped with equal amounts of lithium and an appropriate acceptor impurity. Concentrations were required to be equal within 1% in order to eliminate the free-carrier absorption background. Impurity concentration and sample thickness were then of primary importance in determining the observed localmode absorption intensity.

3.1 Compensation Methods

Three basic methods for producing high-resistivity silicon doped heavily with lithium donors have been reported. These processes are all similar in that they introduce trapping sites for the donated lithium electron. The earliest method involved a radiation of the sample with nucleons.³² The silicon would first be diffused with lithium at high temperatures to produce the desired concentration.^{*} The samples were then irradiated with nucleons to produce lattice defects. The defect site then captures one of the lithium donor electrons. In this manner the silicon was compensated to give resistivities near that of pure silicon. Spitzer⁵ later described a similar compensation technique using electron irradiation in the neighborhood of 1 Mev. This method is thought to leave a larger number

[°]For solubility of Li in Si see E. M. Pell, J. Phys. Chem. Solids, <u>3</u>. 77 (1957)

funpaired ic diffusion of 1 because the nu randomly distr sarily near a other hand, is an accelerato: reported by S; with a substisuch that the the acceptor achieved by a give uniformly mde of the s to be heavier lethod 34 star such as boron the material. the sample, t More will be The diffusior ^{associated} wi other technic to the lattic ^{generally} fev orystal growt a result, aigue was cho

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of unpaired ions than techniques based on a final thermal diffusion of lithium to achieve compensation. This is because the nucleons, e.g. neutrons, will leave defects randomly distributed throughout the silicon and not necessarily near a lithium ion. The irradiation method, on the other hand, is not so convenient because of the need for an accelerator. A second method of compensation has been reported by Spitzer.^{5,33} It consists of growing the silicon with a substitutional donor and a substitutional acceptor such that the donor concentration is about 10% less than the acceptor concentration. The final compensation is then achieved by a diffusion of lithium. This is reported to give uniformly-compensated samples; furthermore, no local mode of the substitutional donor will occur if it is chosen to be heavier than the host silicon atom.⁷ Another early method³⁴ starts with silicon uniformly doped with an acceptor such as boron. Lithium is then diffused in excess throughout the material. The final compensation is produced by annealing the sample, thereby causing the excess lithium to precipitate. More will be said about the precipitation process later. The diffusion-precipitation technique has many problems associated with it, but requires less apparatus than the other techniques. It does not cause nearly as much damage to the lattice as the irradiation methods and involves generally fewer uncertainties. The double-doping during crystal growth involved technologies not available to us; as a result, the diffusion-precipitation compensation technique was chosen. These techniques apply equally as well for the compensation of germanium.
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Additiona the surfa samile co this is cussed 3.2 Material, Mechanics and Preparation

The initial material was single-crystal silicon grown in the [111] direction and doped with 10¹⁹ atoms of boron per cm³. A concentration of 10^{19} was chosen because it was reported²⁴ to produce local-mode coefficients on the order of 10 cm⁻¹ which could be readily observed. Higher concentrations would produce larger absorption coefficients, but were not as readily available. The three symmetry axes of the [111] direction were evident along the sides of the crystal, and the orientation could be readily ascertained. X-ray diffraction photographs were taken in order to confirm the orientation, and show that the material was singlecrystal. The sample was then sliced in the desired orientation on a diamond saw. The resulting wafers were typically 0.7 to 1.5 mm thick. The infrared radiation is attenuated while traveling through the silicon by $e^{-\alpha x}$, where α is the absorption coefficient and x is the sample thickness. The maximum attenuation of the signal "that we could easily work with and also the maximum sample thickness that didn't require excessive preparation time, techniques, and cost was 1.5 mm. The thinner samples, although easier to make, gave smaller signal variations between the local-mode peaks and the background.

[&]quot;Purchased from Materials Research Corporation.

^{**} Additional signal losses were caused by reflection from the surfaces and the small cross-sectional area of the sample compared with the spectrometer beam.

^{***} This is primarily due to thermal surface effects discussed later.



3.3 The Lithium Deposition

⁷Lithium^{*} was deposited on the boron-doped silicon by an evaporation process. The silicon was first lapped with #600-grit carborundum, and then with aluminum oxide. It was finally cleaned in an ultrasonic cleaner containing methal alcohol just prior to the lithium deposition. The lithium metal was placed in a tantalum boat, which was then mounted in a bell jar. A tantalum boat was chosen because it wouldn't react rapidly with the lithium at the vaporization temperature (1609°K). A grounding path to the sample was provided to prevent a possible surface charge build up due to deposition of thermally-ionized lithium atoms. Figure 3.1 illustrates the evaporation system. The bell jar was pumped down to two microns or below before the lithium was heated. Vaporization of the lithium was achieved by adjusting a current through the tantalum boat until the boat began to glow a faint red. If the boat was allowed to get too hot, or if it was placed too close to the sample, the deposited lithium layer was likely to boil off, and the sample would have to be reprocessed. Samples were typically kept 2.25" or more from the lithium boat. We generally tried to get a thick lithium deposition, i.e. greater than 10 mils, during the evaporation. The heating current was then turned off, and argon was let into the bell jar. When atmospheric pressure was reached, the sample was quickly removed from the vacuum chamber and placed in xylene. The amount of time that the evaporated sample spent in the

The lithium isotopes were 99.99% pure obtained from Ortec.







atmosphere was kept to a minimum, because the lithium surface layer would react quickly with the N_2 , O_2 , CO_2 and especially water vapor in the air. Mineral oil was also tried as protection for the lithium surface, but it was found that cracks and peeling occured in the lithium surface when the sample was placed in the oven. If the mineral oil was burned off slowly at about 260°C, the surface remained quite good even though this temperature is above the melting point of lithium metal.

3.4 Diffusion and Lithium Solubility

The oven consisted of a quartz tube about 6 feet long and about 3.5" inner diameter. A joint allowed one end to be removed for insertion of samples. Gas-line connections were provided at both ends. At the high diffusion temperatures involved, lithium reacts readily with most substances except inert gases, consequently an argon atmosphere was provided during the diffusion. Three independent heating coils in the oven provide adjacent temperature zones of one foot in length and thermally regulated to +0.1°C. Insulation and electrical controls make up most of the main unit. This oven tube and the quartz sample mount were preheated to 375°C. The mounting pad was then withdrawn into the removable end of the furnace tube and the tube was opened. An argon flow of 25 kcm³/min was maintained over the pad. Then, the evaporated sample was removed from the xylene and placed on the hot pad. The furnace tube was quickly closed up again, and after allowing two minutes to vent



the atmospheric gases from the furnace, the argon flow was reduced to 10 kcm³/min. If the sample was not initially heated from the quartz pad, it would have to be heated very slowly: otherwise, the lithium surface has a tendency to heat faster than the bulk silicon, and the lithium film is likely to boil, thus leaving only small beads of lithium on the silicon. The sample was left at 375°C for ten minutes to form the initial lithium-silicon pre-alloy.³⁴ The lithium was then firmly attached to the silicon, and the oven temperature was then raised to its diffusion temperature of 550°C. The argon flow rate was maintained at 10 kcm³/min. throughout the diffusion.

Several factors had to be considered in the selection of the diffusion temperature. Perhaps the most important factor was the concentration of lithium desired in the sample. Clearly, the final lithium concentration must closely approximate the boron concentration. A compensation to within 1% of equal concentration would reduce the number of free carriers to a manageable level of $10^{17}/\text{cm}^3$. It is conceivable that the diffusion temperature could be chosen such that the solubility of lithium in the doped silicon was equal to the boron concentration. But, it is known^{22,35} that an indeterminate amount of lithium will precipitate upon cooling, leaving the sample strongly p-type. Thus, it was decided to use the technique of diffusing in an excess of lithium and annealing out the excess at a lower temperature following the diffusion.

• it has been s or germanium lithium. Thi analogy with sented by the chemical-equi free hole "h solubility of At the dopin is valid, ar. each reversi in a dilute concentratio centration c ^{constant}. S acceptors, t holes e h+. also the cha ^{solub}ility, results sho eorioo tioriog corcentrat: It has been shown²² that an acceptor impurity in silicon or germanium has a pronounced effect on the solubility of lithium. This effect may be understood by considering the analogy with impurity ions in an aqueous solution represented by the silicon. It can be seen in the following chemical-equilibrium expression that the presence of the free hole "h⁺" from the boron impurity greatly enhances the solubility of lithium;

$$B \iff B^{-} + h^{+}$$

Li ext. \iff Li \iff Li⁺ + $\stackrel{+}{e}^{-}$
 $\int_{h^{+}e^{-}}$

At the doping levels involved, the dilute-solution condition is valid, and mass-action relationships can be written for each reversible reaction. The mass-action law states that in a dilute solution, at equilibrium, the product of the concentrations of the unassociated ions divided by the concentration of initial associated reactant is equal to a constant. Such relationships can be written for the boron acceptors, the lithium donors and the associated electronholes e^-h^+ . Calculations based on these equations, including also the charge-neutrality condition, predict quite well the solubility of lithium in acceptor-doped silicon.²² These results show it to be a simple matter to match lithium and boron concentrations, but in order to reach uniform lithium concentrations significantly above the $10^{19}/cm^3$ boron level,

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a temperature near the eutectic point of the lithium-silicon system is indicated. At this temperature, lithium would diffuse away from a high concentration silicon-lithium surface-layer alloy. The temperature is high enough to allow sufficient lithium to remain in the silicon following precipitation caused by cooling to room temperature. However, it would not leave the very large precipitation sites and resulting local strain of a much higher diffusion temperature. The eutectic point is reported²⁴ to occur at 590 \pm 10°C and a lithium concentration of 58 \pm 5%.

The total diffusion time also had to be considered in selecting the diffusion temperature. The diffusion time t_d may be approximated by $t_d = d^2/4D(T)$, where "d" is the diffusion depth and D(T) is the temperature-dependent diffusion constant. D(T) has been measured at high temperatures, 14 and is found to closely approximate the temperature dependence given by the classical model $D(T) = D_e^{-Q/kT}$, where D_i is 23×10^{-4} cm²-sec, and the classical activation energy Q is 0.65 ev.² Unfortunately, the diffusion does not take place uniformly.^{3a,3b} This is partly due to non-uniform wetting of the lithium to the silicon during the pre-alloying phase, and partly due to oxygen impurities³³ in the original silicon material. Our own experiments show that 5td gives a reasonably uniform lithium distribution in the material that we used. During this time (5t $_d$), either a continuous and rather expensive argon flow must be maintained, or else the sample must be placed in a sealed argon atmosphere. The sealed vessel



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approach is reasonable, but somewhat difficult. It would be necessary to prepare a quartz vessel and a mount made of pure silicon. * If the sample were allowed to make contact with the quartz vessel, the quartz would tend to draw lithium from the sample at the point of contact. A sample coated with lithium and protected from the atmosphere with xylene could be mounted in a quartz vessel which is then evacuated. After allowing sufficient time for degasing, 1/2 atmosphere of argon would enter the tube. If the tube were left evacuated, the diffusion would be very difficult because of the evaporation of lithium.²⁴ The tube would then be sealed, and care taken not to overheat the sample or knock it out of its mount. The whole quartz vessel could then be placed in the diffusion oven. If required, quenching of the sample, though difficult, could be done. Of course, any errors in the sealing process, particularly gas leaks, would not show up until after the diffusion. This process was found to be troublesome, and as expensive as maintaining a continuous argon flow. Hence, a higher diffusion temperature and a subsequently shorter t_d is obviously advantageous in terms of cost.

High diffusion temperatures, above 600°C, introduce some new problems, however. Evaporation of the lithium²⁴ from the sample becomes serious, as does the increased reaction rate of lithium with impurities in the argon. The precipitation of lithium during cooling of the sample, is

^{*}SiC is also a good mounting material.³⁴

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also much more severe, ^{24,34,35} so that it is not at all certain that sufficient lithium remains dissolved in the sample. Furthermore, the presence of a large number of precipitation sites in the sample could cloud the interpretation of the data.

At a diffusion temperature of 550°C and an argon flow rate of 10 kcm³/min., we found that of the order of six hours was required for the surface layer of lithium to be depleted by evaporation, reaction with impurities in the argon, and diffusion into the sample. At this time and temperature, the lithium could potentially diffuse through a one-millimeter-thick sample. The sample was quenched by dropping it into room-temperature mineral oil. It was then prepared for another lithium deposition, by a coarse lapping with #600-grit carborundum to remove about 2-to-3 mils from the diffusion surface. This step was taken because the silicon immediately below the evaporated lithium layer came out of the diffusion as p-type material for a depth of 1- to-2 mils. This is thought to be the result of diffusion of vacancies into the silicon, which combine with the lithium. Best results in the final lithium distribution were obtained when the first, second, and all other evaporations were made on the same surface.

As mentioned earlier, most materials in contact with the sample in the diffusion oven tend to draw the lithium from the sample; furthermore, many materials will diffuse into the silicon. We also found, and it was reported by



others,⁵ that any free surface of the sample acted as a sink, or zero boundary condition, to the diffusion of lithium. Out-diffusion could occur as fast as in-diffusion, leaving unacceptably large lithium concentration gradients throughout the sample. Use of a piece of pure or lithiumdoped silicon turned out to be the simplest solution. If good contact was made between the sample and pure silicon, the sample came out sufficiently uniform in lithium concentration. Contact surfaces flat to within about one mil were found to be sufficient to remove the apparent zero boundary condition at the sample surface. The somewhat lower solubility of lithium in the pure silicon tended to prevent considerable lithium losses to the pure silicon mount. Another more expensive approach would have been to simply make the sample four to six times thicker than desired; then, when the diffusion process was complete, a piece of the desired thickness would be sawed off.

The samples were quenched upon removal from the oven by first being moved to a cool--about 350°C--section of the furnace tube for 15-30 seconds. They were then dropped immediately into room-temperature mineral oil. Precipitation of lithium in silicon cooled from 550°C is not severe, but the probability of ending up with strongly n-type material after three to five diffusions would be considerably reduced without the quenching. At the diffusion temperature of 550°C, most of the lithium and boronis unassociated.²² Some thought was given to the possibility of freezing in the unassociated

lithium ions process turn second relax Earther comp mecessity of result of th quenching ca on the ratio confirmed by in the local Much of the same as Because of 1 were not abl Concentratio pensated wit absorpt difficult to diffusion at 1.5 hours. ^{becau}se a si ^{showed} that 3.5 The Hot A check also dur theck was to lithium ions by rapid quenching. However, our quenching process turned out to be too slow compared with the millisecond relaxation times²² of the pair-formation process. Further complications would have been introduced by the necessity of annealing out the excess lithium. As a result of the short pair-formation relaxation times, the quenching can be safely assumed to have had little effect on the ratio of paired to unpaired ions. This was later confirmed by observation of relative absorption intensities in the local-mode spectrum.

Much of the germanium sample preparation was exactly the same as the silicon sample preparation just described. Because of lithium precipitation and lack of solubility, we were not able to compensate germanium doped to 2×10^{18} Ga/cm³. Concentrations of $2.5-3 \times 10^{17}$ Ga/cm³ germanium could be compensated with a lithium diffusion, but the subsequent localmode absorption coefficient would be less than 3 cm⁻¹ and difficult to detect. Samples were compensated by lithium diffusion at 420-460°C with total diffusion times of 1.25-1.5 hours. The relatively short diffusion time was possible because a signal-maximization technique (see Appendix A) showed that sample thickness should be typically 100-600 µ.

3.5 The Hot-Point Probe

A check of carrier type was necessary after the diffusion and also during the subsequent precipitation process. This check was performed with a simple hot-point probe. The probe



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was a small pencil-type soldering iron powered by a variac set to 64% of full output. The sample was placed on an etched metal plate, and the hot probe was placed on the surface of interest. The voltage between the probe and the metal plate was measured with a Keithley model 155 null-detector microvoltmeter with a minimum DC input impedance of 10⁶ ohms. A positive voltage reading, relative to the etched metal plate, indicated an n-type surface under the probe, and a negative voltage indicated a p-type surface. This measurement was found to be most sensitive for lightly-doped or nearly compensated semiconductors; it was, therefore, especially useful for our purposes. The magnitude of the thermal voltage was found to depend strongly on the contact pressure. As a result, a mechanicalprobe arm was constructed which allowed equal probe pressure for each measurement.

3.6 Precipitation Kinetics

The kinetics of the precipitation process have been reviewed for lithium in silicon, and for lithium and copper in germanium.³⁵ Only some of the highlights will be mentioned here. The precipitation kinetics for lithium in silicon is essentially the same as for lithium in germanium; the primary differences are in the rate at which precipitation occurs at any given temperature. Our main purpose was simply to remove all excess free carriers associated with the lithium ions in the silicon. It turned out, however, that one of our principal



spectroscopic background problems could be attributed to a precipitation effect at the surface of the sample.

The precipitation of lithium in silicon or germanium is a heterogeneous process in which the nucleation sites are lattice defects and lattice impurities. When lithium is diffused into silicon or germanium, and then quenched rapidly, the system is very much analogous to a supersaturated aqueous solution. The lithium tends to diffuse toward the nucleation sites and congregate about them. It is obvious that such a process is diffusion-limited, i.e. the precipitation time is primarily determined by the length of time that it takes for the bulk lithium to diffuse onto a nucleation site. Equally important in the precipitation process is the density of nucleation sites; this density may vary several orders of magnitude from one crystal to another. For crystals refined by the same process, the density of nucleation sites is approximately of the same order of magnitude. In the case of an equal number of nucleation sites in samples of silicon and germanium, the precipitation rates can be scaled as the ratio of diffusion constants. Furthermore, the rapid increase in lithium precipitation with diffusion temperature can be attributed to the increase in the diffusion constant with temperature. The precipitation of lithium continues until the solution is no longer supersaturated. That is, precipitation stops when the density of lithium in the solution becomes equal to the solubility of lithium in silicon at room temperature,

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or when the lithium concentration becomes equal to or slightly less than the acceptor (boron) concentration.

The principal nucleation site in silicon is thought to be a substitutional oxygen site.³⁵ Oxygen is one of the most abundant impurities in silicon, and also one of the most difficult to remove. It typically exists in the silicon lattice at interstitial sites. These sites will readily capture a lithium ion to form Li^+0 complexes, but these are not the nucleation sites for the precipitation of lithium. The substitutional oxygen (0_s) is formed by the reversible reaction of an interstitial oxygen (0_i) with a lattice vacancy (V) as follows:

$$[0,] + [V] <=> [0,]$$
. 3.1

The corresponding equilibrium mass-action relation can be written as

$$\frac{[O_{s}] N}{[O_{i}][V]} = \exp (\Delta S_{b}/k) \exp (-\Delta H_{b}/kT) = K = equilibrium 3.2$$
constant

where ΔS_b is the change in entropy of the oxygen, ΔH_b is the binding enthalpy of the vacancy, and N is the number of lattice sites/cm³. The concentration of vacancies has been given by $Logan^{37}$ for the condition of thermal equilibrium to be

$$[V] = 1.3 \times 10^{24} \exp(-2.0/kT) \text{ cm}^{-3}$$
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where C_o is the concentration ture concentration tration of list particles have or disk shapes etics follows case, all present theory during Then, by assuming that the number of nucleation sites N_s is equal to $[0_s]$, it is seen that

$$N_{e} = 39 [0] \exp(\Delta S_{b}/k) \exp(-(H_{b}+2.0)/kT) cm^{-3}$$
 3.4

Interstitial lithium then tends to congregate in a spheroid about the substitutional oxygen site with concentrations near ten atomic percent of lithium.

Other shapes are possible for the precipitation center and the rate at which precipitation occurs can be shown to depend on the shape of these sites. For the spheroidal precipitation particles, the kinetics of precipitation is approximated by

$$\frac{\overline{C} - C_{f}}{C_{o} - C_{f}} = \exp(-t/\tau)^{n} \qquad n = 3/2 \text{ for } \frac{\overline{C} - C_{f}}{C_{o} - C_{f}} > 0.5 ,$$

$$n = 1 \quad \text{for } \frac{\overline{C} - C_{f}}{C_{o} - C_{f}} < 0.5 , 3.5$$

where C_0 is the high-temperature (diffusion-temperature) concentration of lithium, C_f is the final annealing-temperature concentration of lithium, and \overline{C} is the average concentration of lithium at time t. In the case of precipitation particles having the shape of long rods growing only radially, or disk shapes only growing thicker, the precipitation kinetics follows a simple exponential decay with n = 1. In any case, all precipitation kinetics follow a simple exponential decay during the latter phase of the process. Measured

precipitation ra sites in silicor lithium precipit more, the rate of precipitation ha to the 2/3 power with the number pertional to the initial high-te: An addition mechanism occurs introduction of of stacking fau silicon. Photo precipitation o ing faults, alt may reduce cons sich a sample w After the miformly n-tyannealing to pa as a function Precipitation not require an the detection Sence, an ohrad resistivity.

precipitation rates³⁵ and optical observations³⁵ of these sites in silicon and germanium confirm that most of the lithium precipitation occurs on spherical sites. Furthermore, the rate constant τ governing the latter phase of precipitation has been measured to be inversely proportional to the 2/3 power of oxygen concentration. This is consistent with the number of precipitation sites being directly proportional to the oxygen content, and independent of the initial high-temperature lithium concentration.

An additional but relatively minor precipitation mechanism occurs in silicon but not in germanium. The introduction of lithium into silicon causes a high density of stacking faults which are not found in the original silicon. Photographic evidence exists³⁵.indicating the precipitation of lithium onto these faults. These stacking faults, although not important in precipitation kinetics, may reduce considerably the stress which can be applied to such a sample without causing fracturing.

After the lithium diffusion, our samples were usually uniformly n-type with low resistivity; they then required annealing to precipitate the excess lithium. The resistivity as a function of time was used initially to monitor the precipitation process. This resistivity measurement did not require an accurate measurement of resistivity, since the detection of a maximum of resistivity was sufficient. Hence, an ohmmeter was used to indicate relative changes in resistivity. The n-type sample was initially prepared for

the precipitati It was then pla placed in 162°C diffusion const to the diffusio Since lithium w tate in germani variations over observed, howev mersion into the from 289 ohms a creased steadil periment. The 1,100 ohms at 6 constant. The upon cooling to was then measur found to be p-t balk effect so remove approxichecked again. Without signif that the lithi centration of lithium near t This results i the out-diffu

the precipitation by lapping and cleaning in methanol. It was then placed in point-contact pressure clamps and placed in 162°C mineral oil. At this temperature the diffusion constant for lithium in silicon is about equal to the diffusion constant of lithium in germanium at 34°C. Since lithium was known to take several hours to precipitate in germanium at 34°C, it was expected that resistance variations over five-minute intervals would be small. We observed, however, that within the first minute after immersion into the hot mineral oil, the resistance increased from 289 ohms at room temperature to 890 ohms; it then decreased steadily to 746 ohms at four minutes into the experiment. The resistance then increased quite rapidly to 1,100 ohms at 6.5 minutes, where it remained relatively constant. The resistance did not change significantly upon cooling to room temperature. Charge-carrier type was then measured with the hot-point probe, and it was found to be p-type. This effect was not expected to be a bulk effect so the surfaces of the sample were lapped to remove approximately one mil and the carrier type was checked again. The bulk of the sample was still n-type without significant change in the resistivity. It is likely that the lithium was congregating on the high surface concentration of nucleation sites. The effective density of lithium near the surface would then be considerably reduced. This results in a lithium concentration gradient, hence the out-diffusion of lithium. The depth of this surface

effect would the onstant at the esting to compa had been etched the number of d in turn, should The resist sipitation phas n-type sample w in mineral oil lapped with #60 The resistivity and recorded. with the hot-po until the resis type began to c A four-poi ate difference from one measur the four-point ^{source} on the the same magni then contact p on surface eff Since the resi Value should r

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effect would then be determined by the lithium diffusion constant at the annealing temperature. It would be interesting to compare this effect in a similar sample which had been etched previous to annealing. This should reduce the number of defect nucleation sites on the surface which, in turn, should reduce the rate of out-diffusion.

The resistivity of the bulk material during the precipitation phase was measured in a multistep process. The n-type sample would first be heated for five to ten minutes in mineral oil at 200°C. It was then cooled, cleaned and lapped with #600-grit carborundum to remove surface effects. The resistivity was then measured with a four-point probe and recorded. Finally, the charge-carrier type was measured with the hot-point probe. This entire process was repeated until the resistivity became very large, or until the carrier type began to change.

A four-point probe was now needed, in order to eliminate differences in contact potential and surface effects from one measurement to the next. A switch was provided on the four-point probe to reverse the polarity of the current source on the two outer probes. If the voltage reading had the same magnitude after switching the current source polarity, then contact potentials were not a problem. Further checks on surface effects were provided by varying the source current. Since the resistivity is independent of current, the measured value should not change with current unless surface problems occur. For the actual determination of resistivity, the
aproximation for reasonably accu the sample edge The resistivity the point of me thin samples, a sample thicknes four-point prob spacing of .025 For samples of 1.57, giving a conducting sur: Sample res ically, eventua simple four-po: able measureme: for the best s or possibly be tance to be in precipitation he of the bea mental determi width and cent this good. So before reachin thought to be tifusion. t , these same

approximation for a thin infinite plane was used. This is reasonably accurate for measurement at more than 5d from the sample edges, where d is the spacing between probes. The resistivity ρ , in the case of all edges being far from the point of measurement, is given by $\rho = 2 \pi dV/I$. For our thin samples, a correction factor based on the ratio of sample thickness w to probe spacing d is needed. The four-point probe used was a Dumas model G-25-C with a point spacing of .025" and loaded for 25 grams of contact force. For samples of one millimeter thickness, w/d is equal to 1.57, giving a correction factor³⁸ of 0.85, assuming nonconducting surfaces.

Sample resistivities were found to increase monotonically, eventually becoming too high to be measured on our simple four-point probe system. Since we could make reasonable measurements of ρ up to 100 ohm-cm, the compensation for the best samples was comparable within one part in 10^5 or possibly better. Ohmmeter checks showed maximum resistance to be in the neighborhood of one megohm. The total precipitation time at 200°C generally was 15 to 30 minutes. One of the best compensated samples was used in our experimental determination of temperature dependences of linewidth and centroid. Unfortunately, not all samples were this good. Sometimes a sample would begin to turn p-type before reaching a very high value of ρ . This change is thought to be the result of non-uniformities in the lithium diffusion. If the compensation was better than one part in 100, these samples were still useful.

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The primary spectral background in the thermal studies experiment was an effect similar to the surface precipitation phenomenon described earlier. As the temperature was raised, lithium diffused toward the surfaces, leaving behind excess "holes" associated with the uncompensated boron. Since this effect was limited to a thin surface layer, the spectral signal was not totally blocked out, but instead was modulated with a free carrier type of absorption background. This background could, however, be readily subtracted out.

The germanium samples were precipitated at room temperature for convenience, hence several hours were required. To prevent the precipitation process from continuing past compensation, it was necessary to cool the sample immediately to -60°C or lower. Consequently, precipitation in the germanium was monitored by measuring the intensity of the spectrophotometer signal. The sample was mounted on a dewar cold finger in the spectrometer; when the intensity stopped increasing with time, the dewar was filled with liquid nitrogen. Samples, when not in use, were stored at -90°C to prevent further precipitation.

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CHAPTER IV

INSTRUMENTATION

4.1 The Spectrophotometer

Much of the initial exploratory work was done on a modified Perkin Elmer model 112G grating spectrophotometer. The original 112G spectrometer consisted of three distinct units; the source section, the fore-prism, and a doublepass grating monochromator. It was designed primarily for high-resolution work over a narrow wavelength region. For the narrow spectral-scanning ranges, the optical background variations were small, hence the single beam, without background cancellation, was sufficient. However, the localmode spectrum of interest covers a much wider spectral range and, furthermore, does not require the very high resolution provided. It was apparent, then, that some major modifications were in order.

4.1.1 The Fore-Prism

The fore-prism was intended to act as a sharply-tuned band-pass filter with a pass band on the order of two microns. Its function was to eliminate higher orders passed by the grating. This was done by passing the signal back and forth through a prism of KBr. The angle at which the signal struck the prism could be varied by means of an external drum; in this manner the central band-pass frequency could

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be varied. To avoid a large background effect from the fore-prism section, it would be necessary to change the fore-prism drum setting for nearly each micron scanned. Instead, the fore-prism section was removed and replaced with a set of three filters * covering the ranges 10.2 - 18μ , $14.3 - 24.3\mu$, and $24.3 - 40\mu$. The filters were constructed by deposition of thin films of selected filter materials;³⁹ they were consequently degradable by prolonged exposure to atmospheric water vapor. Most of the silicon local-mode spectrum could be covered with the 14- to-24µ filter. The remainder of the spectrum was covered by the 10.2- to- 18μ filter. The 24-to-40 μ filter allowed us to look for similar local modes in germanium. An additional benefit from the removal of the fore-prism section was a two-to three-fold gain in signal level. The increase was due to removal of the KBr prism, a decrease in the optical path length, and to lower atmospheric absorption and scattering.

4.1.2 The Source

The source section, shown in Figure 4.1, includes simply a black-body radiation source, viz., a Globar, a flat mirror m_1 , and a spherical mirror m_2 . The Globar source is heated to about 1600°K by an electrical power of 280 watts. The resulting radiated power is given by Planck's black-body radiation formula,⁴⁰

[&]quot;The filters were models number 221-1790, 221-2009, and 221-2010 obtained from Perkin Elmer, Inc.



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$$Fd\lambda = \frac{2\pi\hbar c^2}{\lambda^5} \left(\frac{d\lambda}{exp(\hbar\nu/kT)-1} \right) , \qquad 4.1$$

where F is the power per unit area in the wavelength interval λ to λ +d λ given in watts/m². The spectral background between 14 and 20µ is seen to decrease uniformly with wavelength, the total variation being a factor of 3.1. A single-beam spectrometer must, therefore, have a large background due to source variations. The Nernst glower is the other principal source of infrared radiation in this wavelength region; although somewhat greater intensities are possible, fluctuations in intensity make it less suitable for this work. The total optical power delivered between 17 and 17.2 μ from the Globar source is about F·A·d λ , where A is the area of the aperture at the source in square meters. This source area A, however, radiates into an area of 3300 cm^2 at the distance of mirror m_1 from the source; therefore, mirror m_1 with an area of 15.1 cm² collects and sends on to the sample a power of 4.6×10^{-3} F·A·d λ . This value comes out to be 14×10^{-5} watt, and will be reduced considerably by attenuation in the sample, monochromator losses, spectral-resolution requirements, and scattering. Attenuation through the sample is described by Lambert's law, for which the attenuation factor is given by $exp(-\alpha(\lambda)x)$. Here $\alpha(\lambda)$ is the absorption coefficient in cm⁻¹, and x is the sample thickness.

Alignmen sections were Elzer manual xas aligned s chromator sli minimum signa Similarly, th stattering lo 2.14 AM 1420 4.1.3 The Gr The grat of the Littro The mechanica in a Perkin E and Littrow m 4.1). Since local-mode ab ratio was nee teed of estim Losses. The infr trance slits width, and ar width of 2mm similar set o Mechanically ^{concohromator} intensity of Alignment procedures for the source and monochromator sections were simple and are well described in the Perkin Elmer manual for the 112G. Mirror m_2 in the source section was aligned so that the source image focused on the monochromator slits. A focus on the slits was necessary for minimum signal losses and for the most uniform slit dispersion. Similarly, the sample should be near a focal point to reduce scattering losses.

4.1.3 The Grating-Monochromator

The grating-monochromator section of the 112G is a design of the Littrow type intended as a high-resolution instrument. The mechanical layout and optical path are similar to those in a Perkin Elmer model-99 monochromator in which the prism and Littrow mirror have been replaced by a grating (see Figure 4.1). Since our germanium samples were expected to have small local-mode absorption coefficients, a maximum signal-to-noise ratio was needed. The expected low signal also points to the need of estimates of the monochromator efficiency and signal losses.

The infrared beam enters the monochromator through entrance slits S_1 . These slits have fixed height and variable width, and are controlled by an external drum; a maximum slit width of 2mm is provided with a precision of one micron. A similar set of slits S_2 is located near the output and is mechanically driven in parallel with the input slits. The monochromator generates a spectrum at the exit slits, the intensity of which depends linearly upon the signal passed

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by the entrance-slit area or slit width.⁴¹ The amount of this spectrum passed through the exit slits depends linearly on the exit-slit width. Hence, the power passed by the monochromator depends on the product of input and output slit widths. Observation shows that about 1/4 of the input beam is stopped by the entrance slits set at 2 mm. The output slits are observed to block approximately one third of the first-order spectrum. The variation of signal intensity with slit width W is then approximately $W^2/12$. The assumption here is that the slits are the principal factor determining resolution. This is true except for very narrow (less than 100µ) slit widths. Adequate resolution for the local-mode spectra was obtained with slits of 900µ or more. Calculations of resolution based on slit setting and grating parameters can be made, 42 but the standard procedure is, instead, to run a spectrum, often water vapor, and observe minimum peak separations.

The gratings were the echelette type in a Littrow mounting. The echelette grating consists of many parallel grooves or lines. Each line gives rise to a single-slit diffraction pattern, and the whole grating represents an interference of $l \cdot W_g$ such patterns, where l is the number of lines/mm and W_g is the grating width. In this type of grating the intensity of higher orders does not fall off as a single-slit pattern does. On the contrary, the intensity of higher orders is similar to that of the first order, with efficiencies generally greater than 60%. By



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changing the monochromator from a double-pass to a singlepass instrument, a signal gain of more than 60% was attained.

The monochromator efficiency E, from input slits to the detector, is approximated by E = $(W^2/12)(.60)$ where W is in mm. It has been assumed that there are no atmospheric losses and that the aluminum mirrors are perfectly reflecting. The power P_d delivered to the detector, in the wavelength region 17-to-17.2µ, is less than or nearly equal to P_d = 14×10^{-5} $(W^2/12)(0.6)$. The 0.2µ resolution occurs for a slit setting of about 1 mm, so P_d = $14\times10^{-5}(0.60/12) = 7\times10^{-6}$ watts without the sample in place. This will be further reduced by a factor of 4 as a result of the action of the external chopper.

The change from a double-pass to a single-pass mode also allowed the built-in chopper to be by-passed. Since this chopper was a large source of noise, a further gain in signal-to-noise ratio resulted. An external variable speed chopper, PAR model -222, was mounted at the monochromator input. The chopping speed was still set at 13 Hz because of the limited detector response time.

A few more details on the grating are in order to facilitate an explanation of the calibration. The grating equation describing wavelength vs. grating angle θ is 2d sin θ = n λ , where d is the distance between adjacent grating lines and n is an integer corresponding to the various "orders". A plot of grating angle vs. wavelength is shown in Figure 4.2 for n = 1,2,3, and 4. The cut-off wavelengths of the 14.3-



L

to -24.3µ filter are shown as dotted horizontal lines. This grating was blazed for 45μ i.e. the first order efficiency is a maximum at 45μ . The efficiency of the $n^{\mbox{th}}$ order is a maximum at $45\mu/n$. Thus for local-mode spectra in the range $14-to-20\mu$ the $14-to-24\mu$ filter should be used with this grating in second order. The grating should be driven through 7° from 16.8°-to-23.8°. Two gratings were selected to cover the range 2-to-50µ, with each grating requiring the use of three orders. The grating discussed above was blazed for 45μ and the other grating selected was blazed for 8μ . The orders were considered efficient for wavelengths within 33% of the blaze wavelength $\lambda_{\rm B}$ for the first order and within 23% of $\lambda_{\rm R}/n$ for higher orders. In practice, usable efficiencies were obtained within +70% of the blaze wavelength, although background effects became large. The grating is driven with a mechanical sine function so that a linear calibration of wavelength vs. drum setting could be obtained.

Calibration was necessary to adjust the grating angle θ and to determine wavelength vs. drum reading. This was done by placing a thin film of indene between two NaCl discs and running the spectrum. Indene has a known spectrum in the 14-to-20µ range, with absorption peaks located to a hundredth of a micron. The grating with 20 lines/mm blazed to 45µ was used in first order. One of the absorption peaks occurred at 16.95µ and a drum reading of 700. This drum setting corresponds to a grating angle of 15°. But 16.95µ corresponds to an actual grating angle of 9.75° from the grating equation.

Rotating the grating mount by 5.25° would give agreement between the measured angle and the actual angle. Seven indene peak centroids were recorded vs. drum setting; the results are given in Figure 4.3. This plot confirms the linearity of the drive mechanism.

4.1.4 The Infrared Detector

Infrared detectors are classified in one of two categories: thermal or photoelectric.⁴³ Thermal detectors include the thermocouple, bolometer, Golay cell, and the pyroelectric detector. The thermocouple depends on a thermo-electric effect at the junction of two different metals. The bolometer depends on a resistance change due to infrared heating. The Golay cell depends on the thermal expansion of a small volume of gas. These detectors all have similar thermal response times, i.e. they respond in tens of milliseconds or slower. The maximum chopping speed is therefore limited, allowing greater 1/f noise in the system. Their spectral response, on the other hand, is quite flat over the entire local-mode spectrum range. The photoelectric detectors employ a ferroelectric crystal which exhibits a spontaneous polarization that is temperature dependent. No bias current is required hence no 1/f detector noise. Chopping frequencies can be used out to 2 kHz without signal degradation; furthermore, they are generally more sensitive than the other thermal detectors and can also be operated at room temperature. The photoelectric detectors are generally characterized by their narrow spectral region and extremely high sensi-



tivity; they most often require cooling to liquid-nitrogen or liquid-helium temperatures. Chopping frequencies, however, are generally as high as 100 kHz. Their narrow spectral response and cooling requirements make them unacceptable for this local-mode study.

Infrared detectors are generally compared on the basis of a figure of merit called Detectivity D^{*}. Detectivity is equal to the square root of the sensitive area of the detector divided by the noise equivalent power, i.e. D^{*} = $A^{1/2}/NEP$. The noise equivalent power (NEP) is defined as the square root of the mean-square thermal noise of the detector per unit band width, divided by the detector sensitivity, i.e. NEP = $(v^{-2}/\Delta f)^{1/2}/sensitivity$.

A thermocouple detector with a CsI window was employed in the local-mode studies. The sensitivity was 4 microvolts/ microwatt with an active target area of 0.2 mm by 2 mm; the resistance was 12 ohms. The resulting NEP is then $(4kT(12))^{1/2}/4$ or $1.11x10^{-10}$ watts/ $(Hz)^{1/2}$. The Detectivity is then $5.7x10^{8}$ cm-watts/ $(Hz)^{1/2}$. A comparison of thermal detectors ⁴⁴ shows this detector to be one of the better detectors for this wavelength region. This detector was used in conjunction with a matched-input-impedance preamplifier built into the monochromator. Phase-sensitive electronics were connected to the plate of the preamp tube through an a.c. coupling capacitor to complete the measurement system.

There was still one serious defect in the system as it now stood; that was the single-beam aspect. A single-beam

instrument has large background variations, primarily due to source variations and grating efficiency variations. These effects are greatly reduced or eliminated in a doublebeam instrument.

4.2 The Double-Beam Modification

It was decided then to divide the beam into upper and lower halves. This division was done by designing a chopper blade with two apertures 180° out of phase and at different radii. The chopper blade is shown in Figure 4.4. Figure 4.4 also shows the chopped signal for both upper and lower beams along with the chopper reference output. The chopper reference signal is obtained by photoelectric feedback from a light mounted in the chopper. The chopper blade was constructed so that the reference light passed through only one of the apertures per cycle. The chopper reference signal then indicated the fundamental chopper frequency.

The lower half beam was assigned as a reference beam and the sample was placed in the upper beam. A black wedge was constructed which could be moved along a threaded rod back and forth across the lower beam. This allowed for the adjustment of an optical null at which the intensity of the upper and lower beams were equal.

4.3 The Measurement System

The key to this system was the lock-in amplifier. A PAR model-220 was used in conjunction with a PAR model-210 tuned amplifier. The lock-in amplifier was tuned to the chopper reference frequency. A glance at the monochromator detector output shown in Figure 4.4 will show that the only



FIGURE 4.4 Double beam modification.

signal available at that frequency is generated by the difference in intensity of the upper beam compared with the lower beam. Since the two beams have been optically nulled, the largest intensity differences are due to absorption in the sample.

The overall system is sketched in Figure 4.5. The d.c. "block" is simply an R-C filter to block the bias voltage, 15 volts, from the output of the preamp tube. The 213 preamp shown was operated at a gain of 1 primarily because of its ground-loop-isolation properties. The 212 amplifier was used for its variable-gain function; it was generally run at a gain of 200 or less. The tuned amplifier served to limit the noise bandwidth seen by the lock-in amplifier. It was generally run at a Q value of 10 and a gain of 1.

It should be pointed out that for the double-beam modification the necessity of decreasing the area of the lower beam to achieve an optical null had two undesirable effects on the system. First, it represented additional intensity losses. Secondly, it meant that the areas of the upper and lower beams striking the filter were different. This difference in areas, resulted in a background due to wavelength variations in the filter. Consequently, the optical-null condition was modified to mean a minimization of all background effects. This minimization was performed with the sample in place by first selecting equal beam



intensities and scanning the spectrum. The reference-beam area was then changed slightly and the spectrum was scanned again. After comparing the two backgrounds, the referencebeam area would be changed accordingly. A minimum background was soon obtained.

In addition to use of the lower beam as a simple reference, it may also serve to cancel out any material backgrounds. For example, if a piece of pure silicon of the same thickness as the sample is placed in the lower beam, the effects of lattice absorption can be canceled. This is especially useful for looking at the free-¹¹boron peak occuring on top of the twophonon lattice-absorption peak in silicon. Another possibility is to make up two samples, one compensated with ⁶Li, the other with ⁷Li. These samples could then be placed in the upper and lower beams and only the differences due to the lithium isotope observed.

4.3.1 The Lock-in Amplifier

The PAR model-220 lock-in amplifier is similar to the basic homodyne amplifier;⁴⁰ a sketch of this type of amplifier is shown in Figure 4.6. The reference tuned amplifier is tuned to the fundamental of the input reference signal. This is amplified and limited to give a bipolar square wave. This phase is adjusted to match that of the signal. This bipolar reference square wave can be thought of as the switch controls for a double-pole, double-throw switch. The switching action is illustrated in Part (b) of Figure 4.6. Parts



FIGURE 4.6 The phase sensitive amplifier.

(c) and (d) of Figure 4.6 show an input signal in phase with the reference signal. The switching then produces the signal V' shown in Part (e). The d.c. value of V is fed to the output meter and is proportional to the component of the input signal which has the same phase and the same frequency as the reference signal. Part (f) of Figure 4.6 shows what happens to a signal that is 90° out of phase with the reference. The resultant V' has a zero d.c. level, and no output is produced. The principal feature of such a system is its low-noise figure owing to the narrow effective bandwidth allowing considerable external amplification.

The system described above was used primarily in investigations of local-modes in germanium. With some additional modifications it was also used in some laser Raman experiments. The silicon samples did not require cooling, and hence considerably less time was involved with use of the spectrometer. For the decreased spectrometer time required for the silicon samples, a Perkin Elmer model-225 spectrophotometer was available. The main feature of the 225 are its ease in handling, its double-beam design, the degree to which it is automated, and its wide spectral range from 200 to 5000 cm⁻¹. It employs phase-sensitive detection with a Golay detector; D^{*} for the Golay detector is nearly the same as for the thermocouple detector. All data on local-modes in silicon were taken with the 225 spectrograph.

CHAPTER V

LOCAL-MODE EXPERIMENTS AND EXPERIMENTAL RESULTS

5.1 The Germanium System

Our initial work began with germanium doped with gallium and compensated with lithium. We were interested in locating either a free-lithium local mode, or the local mode of lithium in a paired configuration. The two lithium peaks of a paired configuration would have allowed a good estimate of the location of the free-lithium local mode. Once the lithium local modes were located, thermal and stress dependencies could have been studied. Local modes of gallium paired with lithium in germanium have been reported by Spitzer;³³ our preliminary work was intended to produce similar local modes. The absorption coefficient for these complexes were reported to be in the neighborhood of 2 - 4 cm⁻¹ for a lithium concentration of 3×10^{17} /cm³. Spitzer chose a double-doping compensation technique with Ga and P such that [P]≤[Ga]. Spitzer used a gallium concentration of 2x10¹⁸ atoms/cm³; the phosphorus concentration was about 1.7×10^{18} atoms/cm³. Our samples, with $2.5 - 3 \times 10^{17}$ Ga/cm³, were expected to give similar results when compensated with lithium. A sample compensated with ⁷Li was fastened to a copper plate which, in turn, connected to the cold finger of a liquid-nitrogen dewar. The sample, thus

mounted, was placed in the upper beam of the spectrograph and the optical background balanced to roughly 1%. A room-temperature spectrum was then recorded; all localmode peaks would be thermally broadened beyond distinction, serving as a background reference. Liquid-nitrogen was then poured into the dewar, and enough time was allowed for the system to reach thermal equilibrium. The spectrum was then rerun with all settings the same except for the amplifier gain and d.c. offset. The comparative results are shown in Figure 5.1. There is an indication of a Ga -'Li local-mode at 28μ on top of the lattice peak. This indication is, however, too small and too poorly defined for any meaningful studies. A similar spectrum of the sample compensated with 6 Li showed no indication of a peak at 26.3µ. Thin samples of pure germanium doped with lithium also showed no local-mode peak.

The local-mode absorption intensities of lithiumgallium complexes, observed by Spitzer, were small. Consequently, precipitation of lithium had to be held to a minimum in order to preserve the local-mode signal strength. Two possible explanations for the success of Spitzer's double-doping technique are apparent: first, Spitzer's germanium samples may have had a lower oxygen impurity concentration than our samples. Secondly, the phosphorus and gallium impurities are substitutional; hence, they do not have a strong tendency to form pairs. As a result, as much as 8 times more unpaired gallium may have been



FIGURE 5.1 Results of I-R absorption measurements in germanium.

available to pair with the lithium ions. Hence, the formation of lithium-gallium pairs was greatly enhanced.

5.2 The Silicon System

Our attention then shifted to the boron-doped lithiumcompensated silicon system for which the lithium site symmetry is the same as in germanium. The silicon system is, however, easier to study. Larger concentrations of lithium-boron complexes are attainable, hence larger localmode absorption coefficients result; furthermore, cooling is not required.

Thermal studies of the local modes in silicon were made for the purpose of exploring anharmonic terms in the local potential. Similarities and differences in the lithium mode at 522 cm⁻¹ compared with the boron modes were also of interest. A good measure of the effects of anharmonic terms is the change with temperature of the local-mode centroid and line width. Other measures of anharmonic effects already evaluated,¹⁰ are the position, width, and intensity of the second harmonic of the localmodes. Line widths and centroids have been measured for temperatures below 300°C, and variations are reported to be small. We have extended this temperature range up near 500°K where variations are expected to be larger.

5.2.1 The Temperature-Dependence Measurements

Measurements were done on the Perkin Elmer 225 spectrometer with a resolution of 0.8 cm^{-1} . The device for heating the sample is shown in Figure 5.2. This device is


FIGURE 5.2 The heating apparatus.

a block of brass with a hole in it to pass the infrared radiation. The sample is placed over the hole in good contact with all edges. A heating element, powered by a variac, was placed in another hole through the block as shown. A third hole passing very close to the sample contained a thermometer to record the sample temperature. Silicon grease insured a good thermal contact.

The measurement temperature was selected by adjusting the variac and monitoring the temperature until thermal equilibrium was reached. All spectrometer settings were maintained fixed for the entire temperature range of measurements. The resulting spectra are shown on Fig. 5.3. A scale is not indicated on absorption coefficient, but peak values can be estimated from the height of the lattice peak at 610 cm⁻¹, which is known to be approximately 9.5 cm⁻¹ at room temperature. Cross verification on the complex local-mode intensities can be made from work reported by Spitzer²⁴ in which absorption coefficient vs. doping concentration is plotted. Plots of the centroid shift and line width variations are shown in Figs. 5.4 and 5.5 respectively.

Error bars are shown to indicate errors from instrumental resolution, pen line width, and electronic-noise background.

There are four basic contributions, from the sample, to the background of these measurements; the first is the thermal generation of free carriers and the presence of free carriers due to incomplete compensation. As seen











earlier, the free-carrier absorption forms a relatively smooth background and can be readily subtracted out. Another background effect has been observed to occur at the surface of the sample. As the measurement temperature approaches 500°K, the surfaces tend to become p-type due to a loss of lithium compensation. This surface effect is the same effect observed in the precipitation process. Since the effect occurs in such a thin surface layer, less than one mil in depth, the sample remains transparent to the infrared but has a free-carrier type background due to the p-type surfaces. A third possible background effect is the thermal breaking of Li-B complexes, causing an increase in the free-boron local mode and subsequent decreases in the local modes of the complexes. Calculations show a maximum effect of about 22% at 500°K and doping levels of 10¹⁹/cm³. Calculations are given in Appendix B for the relative number of pairs as a function of temperature. This unpairing will not affect the local-mode centroid, but the decrease in amplitude will show up as a loss of accuracy in the line width. Finally, the background can be shifted by infrared emittance from the heated silicon; this effect is not expected to alter the local-mode spectrum.

Immediately after the temperature data was recorded, the sample was cooled to 351°K and the spectrum was recorded. The resulting background had a similar appearance to the background at 482°K. This background was the result of the non-reversible loss of lithium compensation at the surfaces.

The surfaces were later checked with the hot-point probe and found to be p-type. Removal of about one mil of surface by lapping restored the sample to nearly its previous level of compensation. The line-width and centroids of this final spectrum fit the plot of the rest of the data well within the limits of error, indicating that background effects had been effectively subtracted out. The total time at 482° K, the highest temperature, was only 16 minutes, so that the total surface effect was not large enough to prevent a good measurement. A plot of time vs. sample temperature is shown in Fig. 5.6. As a further control on background effects, a spectrum of pure silicon was run in the same temperature range. Calculations of a background normalization factor based on the ratio of the doped-silicon-lattice peak centroid divided by the centroid shift of the pure-silicon-lattice peak showed no appreciable slope with temperature, and therefore were not incorporated into the data.

Immediately prior to recording the temperature data, but with the same spectrometer settings and resolution, a spectrum of indene was run. This gave us a calibration of the spectrometer and showed the need of adding 1 cm⁻¹ to the wavenumber readings.

The area under the local-mode peaks was observed to be very sensitive to background effects. For this reason we adopted a normalization factor which is the product of two terms. The first term is the ratio of the pure-lattice peak area to that of the doped-lattice peak area. The



second term is the effect of thermal breaking of the complexes calculated in Appendix B. The normalized local-mode peak areas and normalization factors are shown in Fig. 5.7.

5.2.2 The Pressure-Dependence Measurements

The pressure measurements were made on the same spectrometer (P & E 225) with a resolution of 0.8 cm⁻¹. The pressure applicator is sketched in Fig. 5.8. The associated pressure meter was calibrated to an accuracy of ± 8 %. A slightly compressible backing, such as bakelite, was needed to allow a more uniform distribution of the load across the sample.^{*}

The pressure gauge on our stress-applicator device was calibrated with two strain gauges attached to the sides of a small aluminum cylinder of about 1/2" in diameter and one inch long. The two strain gauges were connected in opposite arms of a four-arm bridge. The cylinder was first loaded with 5-pound weights on the end of a 15-to-1 mechanicaladvantage lever system. A plot of pounds loaded on the aluminum cylinder vs. bridge reading was then made for loading and unloading of the cylinder. The aluminum cylinder was placed in the pressure-applicator device, and several plots of the pressure gauge reading in psi vs. the bridge readings were made. A sizable hysteresis was observed between loading and unloading of the cylinder. This hysteresis accounted for the +8% error in the pressure deter-

Pieces of bakelite 1/2" thick were necessary to prevent their breaking under pressure.





mination. Both the loading and unloading plots were found to be linear. From the above measurements a plot of actual pounds of applied force vs. the pressure-gauge reading was made. This is shown in Fig. 5.9. A scale of kg/mm² is also shown for a sample cross-sectional area of 10 mm², which was in the range of most of our experiments.

Our spectroscopic pressure experiments did not give us any conclusive results on line width or centroid variations. Centroids were found to be constant with stress perpendicular to the [111] direction or parallel to the [112] direction. The line width variations were inconclusive. A plot of line width vs. pressure is shown in Fig. 5.10 to illustrate this. The maximum pressure that we obtained in the [112] direction was 1.22x10⁹ dynes/cm² with unpolarized radiation propagating in the [111] direction. The sample was 10.5 mm in the [112] direction with a cross section of 9.65 by 0.74 mm. Another experiment was done with the applied pressure perpendicular to the [111] direction and a maximum value of 0.9×10^9 dynes/cm² was obtained. The sample dimensions were 15.0 mm in the direction of pressure with a cross section of 12.0 by 1.09 mm. In each case the experiment concluded with the fracturing of the sample.







CHAPTER VI

DISCUSSION OF LOCAL MODES

6.1 Local-Mode Assignments in Silicon

Before discussing the results of our local-mode measurements, we review the assignments of the local modes in the silicon system. A good discussion of these assignments is in a paper by Spitzer.^{9b} This paper includes a study of isotopic shifts in the local-mode frequency and a measurement of local-mode intensities as a function of the equal concentrations of lithium and boron. The free-substitutionalboron local mode had already been observed in silicon by Angress et al.;²⁰ no other constituents had been added to the silicon. Spitzer⁹⁶ observed this free-boron peak in reduced intensity at 620 cm⁻¹ for 11 B. This is between the two boron modes of the lithium-boron complexes, and is closer to the doubly-degenerate 654 cm^{-1} peak. When the boron isotope was changed from 11 to 10, the 564 $\rm cm^{-1}$ peak shifted to 584 cm⁻¹ and the 654 cm⁻¹ peak shifted to 681 cm⁻¹. When the lithium isotope was changed, these peaks shifted less than 3 $\rm cm^{-1}$. This identified these peaks as boron local modes. Their intensity was found to be directly proportional to the concentration of lithium-boron pairs. The degeneracy of the upper band was assigned as two-fold

degenerate, and the lower band as one-fold degenerate, on the basis of relative integrated intensities of 5 to 3. Axial symmetry of a paired configuration predicts an intensity ratio of 2 to 1, but local polarization due to atomic distortion may account for the difference. * The 522 cm^{-1} line was found by Spitzer to shift to 534 cm^{-1} when ⁶Li was substituted for ⁷Li. It is insensitive to changes in the boron isotope, and appears at 515 cm^{-1} for galliumdoped ⁷Li compensated silicon. The intensity of this mode is also directly proportional to the number of lithium-boron pairs. The isotopic shifts and intensity ratio identified the 522 cm^{-1} peak as a lithium mode. By analogy with the two boron local modes, the 522 $\rm cm^{-1}$ peak is expected to be the two-fold degenerate peak of a paired lithium ion in a C_{3v} configuration. Further studies on the breaking of the complexes with temperature have been done by Spitzer and Waldner.^{9a} They found that as the temperature was raised to 150°C, the peaks assigned to lithium-boron complexes decreased in intensity whereas the free-boron peak increased in intensity. This is in agreement with predictions on the thermal breaking of complexes given by Reiss et al.²² This comparison between experimental and theoretical thermal effects further reduced the possibility of the 522 cm^{-1} peak belonging to the free-interstitial lithium since such a peak would also have increased in intensity as the sample temper-

["]For example, carbon impurities in silicon are substitutional and un-ionized but they have an effective local charge of about e.⁴⁷

ature was raised. The experiment also confirmed the identity of the 654 and 564 cm⁻¹ as boron paired to lithium. The temperature at which the lithium is diffused into the silicon does not significantly alter the intensity of the observed local modes. Therefore, it is unlikely that the 522 cm⁻¹ peak could be a lithium-vacancy complex local mode. The small but finite shift in frequency of the 522 cm⁻¹ peak for different acceptor impurities confirms the designation of the 522 cm⁻¹ peak as a paired lithium local mode. The free interstitial lithium must then be a resonance mode within the band of allowed lattice frequencies. We did not observe any such resonance mode in our samples.

6.2 The Lithium-Gallium Complexes in Germanium

Our attempted measurements of lithium-gallium complexes in germanium were unsuccessful because of problems in sample preparation. However, some observations on work reported by A. E. Cosand³³ will be made.

The two local modes of lithium in a paired configuration have apparently been observed by $Cosand^{33}$ in germanium at liquid-nitrogen temperatures. The lithium is paired to gallium, and ⁷Li local modes occur at 356 and 380 cm⁻¹.^{*} When ⁶Li was used, these peaks occurred at 379 and 405 cm⁻¹ respectively. Cosand suggests, on the basis of integrated intensities, that the lower-frequency peak is the two-fold degenerate mode. His suggestion indicates that a free-

[&]quot;The maximum single phonon lattice frequency in germanium is 300 cm⁻¹.

lithium local mode does exist in germanium and should be between the two lithium complex local modes close to 364 cm⁻¹. It was not observed in Cosand's samples because the solubility of lithium in germanium limited the amount of lithium; in fact, sample preparation was the major problem in this work. The complex local modes had only a 2 to 4 cm⁻¹ absorption coefficient, and at the liquid-nitrogen temperature over 99.9% of the lithium was paired to acceptors. The location of the free-lithium local mode might be confirmed by slowly heating such a sample to break the complexes. However, it appears that thermal broadening may mask such an effect.

6.3 Temperature Dependences of Centroids and Line Widths in Silicon

Figures 5.5 and 5.6 show that thermal effects are most pronounced above room temperature. Centroids are observed to shift to lower wave numbers with temperature, as expected. The 482°K data point in the centroid shift of the 522 cm⁻¹ line seems to represent a rather sudden departure from the linear approximation. It is at about this temperature that the centroid has been shifted to the edge of the latticeband modes. Therefore, the effect of the lattice phonons on the centroid appears to account for the deviation from linearity of the 482°K point of this line. The data on centroid shifts can be fitted with a linear approximation

Low-temperature measurements of line width and centroids have been done with <u>+</u>lcm⁻¹ resolution by Balkanski and Nazarewicz^{3b}

by lines varying in slope by $\pm 10\%$ from the lines shown and still fall within the limits of the error bars. Variations in the fit to line-width data of $\pm 15\%$ in slope are within the corresponding error bar limits.

The paired substitutional-boron and interstitial-lithium ions are each in essentially a perturbed T_d symmetry. The resulting symmetry is C_{3y} , but the dynamics of the system are quite complex; the theory necessary to explain the centroid shifts and line-width variations with temperature has not as yet been fully developed. It is expected, however, that such a theory will take the form of the effects of anharmonic terms in atomic displacement described by Elliott et al.²⁵ for an isolated impurity, applied to the Green's function treatment of an impurity pair by Elliott and Pfeuty.⁷ A preliminary review of these ideas showed that such a correctly done formalism was likely to result in third-and fourthorder Hamiltonians having the same form as those presented by Elliott et al. The interpretation, however, would be quite different, i.e. the local-mode operators must be relabeled to apply to each local mode observed. The relabeling should also include a distinction between the possible one and two-fold degeneracies. Details of how such a relabeling of the local-mode operators occurs, and what the relabeling means, are given in Appendix D. In this new representation, the two-fold-degenerate boron local-mode operator is subscripted with Γ_{q}^{2} , and the singly-degenerate boron local-mode operator is labeled with Γ_1^2 . The 522 cm⁻¹ lithium local-mode operator

is labeled with $\Gamma_3^{\ 1}$. The superscripts 1 and 2 refer to lithium and boron respectively; Γ_1 and Γ_3 refer to the singly and doubly degenerate infrared-active representations of the $C_{3,*}$ symmetry.

With this interpretation and relabeling of local-mode operators, equation 2.12 approximates the centroid shifts. Since our own measurements did not determine the zero-temperature local-mode frequencies Ω_0 , this parameter was varied to obtain a best fit to our data. Equation 2.12 is reproduced here for convenience with the indicated labeling of the local-modes.

$$\frac{\Delta\Omega_{r_{j}}^{i}}{\Omega_{o_{r_{j}}}^{i}} = \frac{\zeta_{r_{j}}^{i}}{M^{1}(\Omega_{r_{j}}^{i})^{2}M\omega_{M}^{2}} \left\{ \frac{1}{N} \sum_{\vec{k}} \mathcal{H}_{\omega}(\vec{k})(n(\vec{k})+1/2) \right\} \quad 6.1$$

Evaluation of this expression requires a knowledge of the silicon phonon spectrum $g(\omega)$. This has been evaluated numerically by F. A. Johnson (unpublished) for a mesh of 61 points on the interval $0 \le \omega \le \omega_M$. A modification giving closer agreement with experiments has been presented by Dawber and Elliott.^{19b} These calculations represent one direction in the Brillouin, zone and all other directions are assumed to give the same density of states. The bracketed term of eq. 6.1 then becomes

$$6\int_{0}^{\omega_{M}} \frac{g(\omega)\hbar\omega[n(\omega)+1/2]d\omega}{\int_{0}^{\omega_{M}} g(\omega)d\omega}, \qquad 6.2$$

where the number operator $n(\omega)$ is given by $1/(\exp(h\omega/kT)-1)$. The factor of 6 occurs because the original sum over \vec{k} included the sum over the 3 optical and 3 accoustical lattice dispersion branches. This expression can be easily programmed to give the full range of temperature variations. The fortran program and further details are given in Appendix E along with the values of the silicon phonon spectrum taken from Dawber and Elliott's paper.

The expansion coefficients $\zeta_{\Gamma_j}^{i}$ and Ω_o were evaluated by requiring that the calculations agree in both magnitude and slope with the data. The results of these calculations are shown as dashed lines in Fig. 5.4. Calculations in the Debye approximation, for which $g(\omega) = 3\omega^2/\omega_D^{3}$, have also been done. The results in all cases were very close to the results based on the silicon phonon spectrum. Agreement with our experimental results is very good for the 522 cm⁻¹ lithium mode, and reasonably good for the two boron modes at 645 and 565 cm⁻¹. The resulting expansion coefficients $\zeta_{\Gamma_j}^{i}$ and zero-temperature local-mode frequencies Ω_o are summarized in Table 1.

These calculations have not included such possible effects as the interaction between the various local modes. It is expected that the interaction between the two boron local modes would be the largest of such interactions be-

[&]quot;The Debye frequency for silicon is 457 cm⁻¹ for a Debye temperature of 658°K.

Line-Width Coefficients for Two-Phonon Decay

Local Mode	$\zeta_{r_j}^{i}$ (erg/cm ⁴) x 10 ²¹	Ω _o (cm ⁻¹)
522 cm ⁻¹	$\zeta_{\Gamma_3}^{l} = 2.14$	525
564.5 cm ⁻¹	$z_{r_1}^2 = 3.62$	567.9
654 cm ⁻¹	$\zeta_{\Gamma_3}^2 = 5.00$	657.7

TABLE 1

cause both modes are at the same physical location. Interaction between the lithium mode and a boron mode would be a smaller effect because the ions are separated by 2.5 Å. These effects would then be small for the 522 cm⁻¹ line, possibly accounting for the good agreement of the data with the simplified theory. Similarly, such effects could account for some of the disagreement between the data and the calculations for the boron local modes.

The line-width processes also arise from the relabeled local-mode operators described in Appendix D. Again, although the interpretation is different, the expressions for line width take the form of eq. 2.14 for the two-phonon decay process, and eq. 2.15 for the elastic-scattering process. To evaluate eq. 2.14 as a function of temperature, we first converted the sum over \vec{k} to an integral over ω making use of the phonon density of states $g(\omega)$. The delta function allows this integral to be easily evaluated as the value of the integrand at $\omega' = \alpha_{\Gamma j}^{i} - \omega$. For example, $g(\omega)$ becomes $g(\alpha_{\Gamma j}^{i} - \omega)$. The sum over \vec{k} is then converted to an integral over ω by making use of $g(\omega)$. Equation 2.14 then becomes

$$\frac{1}{\tau} = \frac{\mathcal{B}_{\Gamma j}^{i} \mathcal{P}_{m n \nu}^{2}}{\mathcal{P}_{M n \nu}^{j} \mathcal{P}_{m n \nu}^{j}} \frac{36 \int_{0}^{\omega_{M}} \frac{\mathcal{P}_{M m}^{(\omega)} g(\Omega_{\Gamma j}^{i} - \omega)}{N_{P}^{2}} \omega(\Omega_{\Gamma j}^{i} - \omega) \times [(n(\omega) + 1)(n(\Omega_{\Gamma j}^{i} - \omega) + 1) - n(\omega)n(\Omega_{\Gamma j}^{i} - \omega)] d\omega . \qquad 6.3$$

The phonon density functions $g(\omega)$ and $g(\Omega_{\Gamma_j}^{i}-\omega)$ have been

normalized so that $\int_{p}^{M} (g(\omega)/N_p) d\omega = 1$. Since $g(\Omega_{\Gamma_j}^{i} - \omega)$ is zero for frequencies below $\Omega_{\Gamma_j}^{i} - \omega_M$, the lower limit on the integral in eq. 6.3 can be replaced by $(\Omega_{\Gamma_j}^{i} - \omega_M)$. The program for the temperature dependence of eq. 6.3 is given in Appendix E.

The elastic-scattering process has the form of eq. 2.15. The sum over \vec{k} and \vec{k}' can be replaced by the following integral:

$$36\int_{O}^{\omega_{M}} \left(\frac{g(\omega)}{N_{P}}\right)^{2} \omega^{2}n(\omega)[n(\omega)+1]d\omega \qquad 6.4$$

The fortran program for elastic-scattering temperaturedependent line width is also given in Appendix E. When the parameter $\zeta_{\Gamma_j}^{i} - 2(\mathcal{B}_{\Gamma_j}^{i})^2 / M\Omega_{\Gamma_j}^{i}$ is evaluated to give agreement with the magnitude of the experimental results, the calculated line width is found to cross the experimental data sharply. The elastic-scattering mechanism is therefore considered an unlikely explanation of the observed linewidth variations.

The results of the two-phonon-decay calculations are shown as dashed lines on Figure 5.6. The expansion parameter $\mathbf{g}_{\Gamma_j}^{i}$ was fitted to give reasonable agreement with the magnitude of the experimental results. The calculations give approximate agreement with the measurements at temperatures above 300°K. However, agreement is poor below 300°K. As mentioned earlier, there are likely to be interactions between the two boron local modes. This would give a line-width contribution to the 654 and 564 cm⁻¹ lines proportional to

 $\Delta\Omega[n(\Delta\Omega)+1][g(\Delta\Omega)/N_p][n(\Omega')+1]$,

where Ω' is the frequency of the boron local mode which is not decaying and $\Delta\Omega$ is the difference between the two boron local-mode frequencies. This expression has a T² dependence at high temperatures. However, the effects of the thermal population term $[n(\Omega')+1]$ are small below about 450°K or most of our temperature range of measurements. As a result the variations appear nearly linear in temperature between 300 and 450°K. This temperature dependence is similar to that of the two-phonon-decay calculations and therefore cannot account for the large low-temperature line widths. Accurate prediction of the observed line widths will have to wait for a formal treatment of the problem based on the anharmonic factors of the actual symmetry of the lithium-boron pairs.

6.4 Temperature Dependence of the Integrated Intensity

The relative integrated absorption intensity I/I_{o} is shown on Figure 5.7 as a plot of $(1.0 - I/I_{o})$ vs. temperature. In this form, the dependence is linear on a log-log plot. The integrated intensity has incorporated into it the correction factor mentioned in section (5.2.1). The relative integrated absorption intensity was evaluated by first plotting I vs. T on a linear scale. The zero-temperature

value I_0 was then extrapolated for each set of local-mode data. The dependence of $(1.0 - I/I_0)$ is approximately T^n where n = 4.2 through 5.1. This plot indicates that no local modes exist above a temperature of about 530°K. This temperature dependence is, however, the least accurate of our data because of the correction factors involved, and because of some uncertainty in I_0 . Nevertheless, we do believe that a non-linear decrease in integrated intensity occurs.

6.5 The Uniaxial-Stress Results

The results of the uniaxial-stress measurements were inconclusive. The centroid shifts were constant for stress applied in the [112] direction and perpendicular to the [111] direction. A similar experiment by Hayes and MacDonald²¹ on H⁻ and D⁻ ions in CaF₂ had shown a linear variation of singly-degenerate local-mode centroids with uniaxial stress, and a splitting of multiply-degenerate modes. Line-width variations were expected to be of a similar order of magnitude. It now appears that not enough stress can be applied to the lattice to shift the lithium-boron local-mode frequency by a measurable amount, i.e. more than 0.8 cm^{-1} . The limiting factor is, of course, the fracturing of the samples. Evidence supporting this conclusion can be found in a paper by Hayes.⁴⁸ Hayes has applied uniaxial stress to oxygen doped silicon with a resonance mode due to oxygen at 29.3 cm⁻¹. At stresses near the breaking point (24 - 30 kg/mm^2) he observed a frequency shift of only one cm⁻¹. This small

a variation in the lithium-boron local modes would remain essentially undetected by our system. On the other hand, if the frequency shift scales with the impurity vibrational frequency, the results of uniaxial stress should have been easily detected and the fact that we observed no shift would be paradoxial. It appears that uniaxial-stress effects on Li-B local modes will require a high-resolution spectrometer (.2 cm⁻¹ or better). The degeneracy of the local modes is unlikely to be determined by infrared-absorption techniques since the amount of splitting, near the fracture load, is much less than the local-mode line width.

CHAPTER 7 ISOTOPIC DIFFUSION STUDIES

Our isotopic studies on the mobility of lithium in germanium were initiated by a desire to obtain a faster drift rate of lithium in the fabrication of nuclear "charged-particle" detectors. ⁶Li will drift faster than ⁷Li because mobility is inversely proportional to the square root of the ion mass. Measurements on the ratio of diffusion constants "were made primarily by means of a diffusion type measurement, although some effort was also put into a drift technique. Both techniques required correction factors in the evaluation of the magnitude of the diffusion constant. The diffusion constant of lithium in germanium, at temperatures in the neighborhood of 50°C. showed about 15% smaller slope than at higher temperatures. In the classical picture this means that the activation energy has decreased by 15% with temperature. This suggests the possibility of a tunneling effect's becoming important at the low-drift temperatures. Such a tunneling effect would further increase the mobility of ⁶Li compared to that of ⁷Li. The diffusion constant of ⁷Li has already been measured in the low-temperature range¹¹ so that only a ratio of diffusion constants needed to be measured.

Extensive use has been made of the Einstein relationship between diffusion constant and mobility, applicable to the "dilute semiconductor solutions'" it is given by μ = eD/kT.

7.1 Reasons for Measuring the Mobility Ratio

Since an absolute magnitude of the diffusion constant was not required, the measurement was simplified for several reasons: First, a measurement of the diffusion constant would have required a determination of the internal enhancement field across the junction at the diffusion front. This effect tends to increase the diffusion rate by a factor of $\begin{bmatrix} -1/2 \\ [1+ [2n_i(T)/N)^2+1] \end{bmatrix}$, where n_i(T) is the density of intrinsic carriers. 49 Thus an accurate knowledge of the donor concentration N would be required. This, in turn, would require an accurate determination of the diffusion temperature and some means of assuring its stability. Secondly, silicon and germanium are difficult to obtain in ultrapure form; there are typically 10^{13} to 10^{14} traps/cm³ (usually oxygen) remaining in the best crystals. * Consequently, during the drift or diffusion process the lithium tends to form pairs, thereby effectively reducing the diffusion rate. This effect can be neglected if the lithium concentration is large compared with the concentration of trapping sites, as is the case for diffusion temperatures above 150°C. Finally, a measurement based on a drift technique would require an additional correction factor to account for that component of mobility due to diffusion. In the determination of the ratio of mobilities of 6 Li to 7 Li, all

It has recently become possible to produce germanium crystals with less than 10^{10} traps/cm³; such material does not require a lithium drift to compensate trap sites in the production of nuclear detectors.⁵⁰

of the effects mentioned above are equal for both isotopes and therefore cancel. It is only necessary to insure that both samples are drifted or diffused at the same temperature.

In an effort to assure equal drift temperatures, a drift experiment was done with both ⁶Li and ⁷Li deposited on the surface of the same crystal. All germanium was detector-grade, doped with typically 5×10^{13} gallium/cm³. Half of one surface was coated with ⁶Li and the other half with 7 Li, followed by a 10-minute diffusion at 400°C. The sample was then drifted at about 25°C. The results showed nearly equal drift depths for 6 Li and 7 Li regions. A closer study showed two mechanisms which tended to equalize the drift depths: First, the field across the junction depended upon the drift depth. If ⁶Li had drifted further than 7 Li, the resulting decreased E field would reduce the ⁶Li drift rate. Also, the I^2R heating would be larger in the region of shortest drift depth, tending to thermally increase the drift rate. Differences in drift depth were, therefore, quickly reduced. Further drift measurements were tried based on the technique of Fuller and Severins; $\frac{14}{3}$ however, the CuSO_{μ} stain test used to define the junction region did not give sufficient accuracy. All drift measurements were further complicated by variations in contact resistance. This effect was minimized by coating the sample contacts with a liquid mixture of indium and gallium.

7.2 The Ratio Measurement

Most of our ratio measurements were done with a diffusion process. Two samples of 12 ohm-cm gallium-doped detector-grade germanium were lapped and cleaned. One sample was evaporated with 6 Li, then placed in mineral oil while the next sample was evaporated with 7 Li. $\overset{*}{}$ The two samples were then placed side-by-side in the preheated diffusion oven. An argon flow of 10,000-15,000 cm³/min. was maintained throughout the diffusion. After completing the diffusion, the samples were quenched to room temperature. Temperature gradients in the oven were the most likely source of error, since the two samples could consequently be at slightly different temperatures. Efforts were therefore made to eliminate or determine any such temperature gradients. For example, one diffusion was done on a single crystal, one surface of which was half ^bLi and half ⁷Li. Another diffusion was done with four pairs of samples, each pair consisting of one 6 Li and one 7 Li specimen. Each sample was typically 4x12 mm of surface area and about 2mm thick. Thermal variations were found to be small, but a possible temperature gradient may have existed along the direction of argon flow. Several measurements on single pairs of samples were done at 200°C and at 400°C. Diffusion times at 200°C were typically on the order of two hours or more.

The lithium isotopes were 99.99% pure and obtained from ORTEC.

This gave diffusion depths on the order of 8 mils or more. Two measurements at 200°C for six hours were tried in order to improve the accuracy by diffusing to a greater depth, i.e. about 14 mils. At 400°C the diffusion time was generally 20 minutes, and diffusion depths of typically 25 mils were measured. The results of these measurements are given in Table II. The ratio of diffusion constants was taken as the square of the ratio of diffusion depths, i.e. the diffusion depth x was approximated as $x = 2\sqrt{Dt}$ so that D is proportional to x^2 . The correction factors belonging to this expression then cancelled in the ratio.

An accurate measurement of x required that the surface of the sample, upon which lithium was to be evaporated, be parallel to its opposite surface. After some practice, we found that two surfaces could be made parallel to within 1 mil by successive grinding and checking for variations with calipers. Better accuracy was then obtained by using a sensitive pressure gauge.^{*} This gauge had a full-scale variation of ± 2.0 mils; each mil was divided into 10 parts, so 0.1 mil accuracy was possible. Variations in the sample thickness were measured with this gauge; if the two surfaces were not parallel, one of them would be lapped with more pressure on the thickest area. The sample was then cleaned and the uniformity of thickness checked again with the pressure gauge. In this manner we were able to obtain surfaces parallel to within 0.1 mil. More typical variations,

The pressure gauge was a style 1000 gauge made by the Sheffield Corporation with serial number 2201RS.

Table II - Experimental Results of Isotopic Studies

Diffusion Temperature 673°K

Notes	Diffusion De	pth (mils)	Ratio D ₆ /D ₇	Time (min)
	6 _{Li}	7 _{Li}		
	31.51 <u>+</u> .3	30.31 <u>+</u> .15	1.084 <u>+</u> .012	23
	36.40 <u>+</u> .15	34.85 <u>+</u> .15	1.091 <u>+</u> .008	29
	26.00 <u>+</u> .3	24.70 + .20	1.126 <u>+</u> .015	20
	Average	Ratio	1.091 <u>+</u> .02	

Diffusion Temperature 473°K

Diff. exp	7.84 <u>+</u> .1	7.49 + .2	1.096 + .09	120
	7.84 <u>+</u> .1	7.41 <u>+</u> .2	1.120 <u>+</u> .09 [*]	120
	9.71 <u>+</u> .1	8.83 <u>+</u> .06	1.210 <u>+</u> .02	120
	8.48 <u>+</u> .1	8.09 + 0.1	1.102 + .04	120
	8.48 <u>+</u> .1	7.89 <u>+</u> .1	1.158 <u>+</u> .05 ["]	120
	14.34 <u>+</u> .2	13.64 <u>+</u> .1	1.105 <u>+</u> .05	360
2 pairs	8.61 <u>+</u> .2	8.35 + .2	1.07 + .10	
diffused together	9.18 <u>+</u> .2	8.91 <u>+</u> .2	1.06 <u>+</u> .10	120
4 pairs	8.01 <u>+</u> .15	7.60 + .15	1.11 <u>+</u> .08	
diffused	7.69 <u>+</u> .15	7.38 + .15	1.08 <u>+</u> .08	
simultaneously	7.37 <u>+</u> .15	6.68 + .15	1.22 <u>+</u> .08	120
	6.85 <u>+</u> .15	7.00 + .15	.96 <u>+</u> .08	
average	7.16	7.48	1.09 <u>+</u> .08	
	Average	Ratio	1.096+ .06	

Drift Temperature 318°K

	1		1									-
Drift exp.	84.20	<u>+</u>	.3	80.00	+	.3	1.110	+	.02	23	hrs.	
			Construction of the local division of the lo	and the second se	_	and the second se	and the second se	_		the second se		

* This is a repeat of the data on the above line with a correction factor to account for room temperature drift and diffusion.

however, were 0.2 or 0.3 mils (0.1 mil = 2.54 μ). At this point the thickness of the sample was measured. This measurement was made with the pressure gauge and a set of reference blocks which varied in thickness by one-mil steps. The pressure gauge was first adjusted to read zero on some combination of reference blocks whose thickness was near that of the sample. The reference blocks were then removed and the sample was inserted under the pressure gauge. The gauge then measured the difference in thickness between the reference blocks and the sample. For samples which were not flat within 0.2 mil, the thickness was recorded at the center and four corners of the sample. The sample was then beveled at one edge to assure its orientation. This procedure was followed for both samples in the experiment. The samples were then ready for the lithium deposition without further surface treatment.

Following the diffusion, we generally observed a surface layer of black material one mil thick or less. Measurements indicated 0.5 mil increase over the original thickness before diffusion. This thin black layer was probably a Ge-Li alloy with some residue from the mineral oil burned off during diffusion; it could be easily rubbed off with CH₃OH and a Q-tip. Measurements were taken from a zero diffusion depth at the cleaned surface. The cleaned surface often had small pits which were avoided in the measurement.

Mineral oil was used to coat the lithium surface following the evaporation. Also, the sample evaporated first was

stored in mineral oil for the nearly one hour needed to perform the second evaporation. The amount of mineral oil on the sample surfaces was reduced to a minimum immediately prior to placing the samples in the oven, in order to minimize the time needed for it to be burned off. One possible source of error may be due to the mineral oil's burning off one sample sooner than the other, hence allowing that sample to become slightly hotter than the other. In retrospect, it appears that xylene should have been used instead of mineral oil for this reason.

The measurement technique was similar to that used by Pratt and Friedmann⁵¹ and consisted of measuring the sample thickness and the conductivity of the lithium surface between successive lappings of the lithium surface. Each lapping removed 0.3 to 0.5 mil of material; the sample was cleaned before each measurement with trichloroethylene. The conductivity was measured with the hot-point probe, which was found to give readings that were strongly dependent on the applied pressure. Consequently, a mechanical support was arranged to apply equal pressure on each measurement. The hot-point probe, as described earlier, was connected to a voltmeter to indicate the thermallyinduced voltage. The location of the junction at the diffusion front required only monitoring variations in the thermal voltage, hence the actual conductivity was not determined. The thermal voltage was found to be constant away from the junction; it began to decrease at about 1 to 2 mils from

the junction. At that point, the amount of material ground off after each measurement was reduced to 0.1 to 0.3 mil. Grinding and measuring were continued until the thermal voltage changed polarity. In this manner we were generally able to measure the diffusion depth to 0.1 mil. The measurement process generally took one-to-two hours. If work was done on one sample until the measurement was complete, the sample with the other isotope would be left standing. During this time, lithium continued to drift through the crystal due to the built-in field of the junction. Measurement of the diffusion depth in one crystal obviously does not stop this drift effect in the other crystal. An estimate of the largest effect to be expected can be made by assuming a step junction. The internal junction voltage is then about V = 0.4 volt and the resulting drift depth is given by W = $(2\mu V_{,t})^{1/2}$. At room temperature the mobility μ is $3 \times 10^{-10} \text{ cm}^2/\text{volt-sec}^{11}$, and a drift depth of 0.4 mil results in one hour. The actual junction is graded so that drift depths of 0.2 mil or less may be expected in one hour. Similarly, the diffusion would continue at room temperature and produce an additional .13 mil in the diffusion depth in one hour. Most of our measurements, with the exception of a few of the earlier ones, were done on the 6 Li and 7 Li samples simultaneously. That is, a thin layer was ground off the ⁶Li sample, and the thickness and thermal voltage were recorded. The same was then done for the 7 Li sample, and the measurements alternated back and forth until the
junction depth of both samples was recorded. The difference in time between the location of the two junction depths was consequently reduced to five minutes or less.

Measurements were also performed on crystals diffused at 100°C; however, the solubility of lithium in germanium at 100°C is only about 2×10^{14} /cm³. This is not significantly different from the original acceptor concentration. The hotpoint-probe measurements therefore showed large variations in thermal voltage, and the junction could not be located within 1 mil.

7.3 Comparison of Experiment with Tunneling Calculations

The 200°C and 400°C measurements did show variations from the classical prediction in the ratio of diffusion constants. This led us to try and fit the tunneling theory (eq. 2.5) to the existing data on 7 Li diffusion constant simultaneously with our own data on the ratio. To do this we first needed the distance (a) between adjacent lithium interstitial sites in germanium. The value finally arrived at was scaled from existing data on lithium local-modes in silicon.^{3b} This left us with the barrier height Q and the local-mode frequency as parameters to be scanned. The best fit of the diffusion constant was obtained for 0 in the range 0.515 to 0.530 electron volt, and any value of localmode frequency in the neighborhood of 10¹³ Hz. The classical activation energy (Q) given by Fuller and Sevriens¹⁴ was 0.465 ev; Q determined by the tunneling expression, (eq. 2.5) is expected to be larger because it includes the energy between

the bottom of the potential well and the ground state of the ion. The fit of the tunneling expression to 7 Li diffusion data is shown in Figure 7.1. Error bars indicate the range of variation in the calculated values as Q varies from 0.515 to 0.530 ev. The local-mode frequency (v) was scanned for a constant ratio of v_6 to v_7 equal to 1.08. The range of frequencies scanned was determined from the coefficient D_{o} in the classical expression for the diffusion constant (see eq. 2.2). We found that any frequency in this range would give agreement with the experimental data on diffusion constants but only a discrete set of frequencies would fit both the magnitude and ratio of diffusion constants. These results are shown as a plot of ratio vs. local-mode frequency (v) in Figure 7.2. The shaded area represents the error in our measurements of the ratio. The best fit of the calculations to all the data indicates a ratio $(D_6/D_7) = 1.12$ at room temperature. This effect is considerably smaller than hoped for, and represents a savings of only 14 hours in a ten-day detector drift.



FIGURE 7.1 Tunneling calculations compared with experimental high and low temperature data.



CHAPTER 8

SUMMARY AND CONCLUSIONS

The purpose of our isotopic-diffusion studies has been to determine whether a significant time saving could result in nuclear-detector fabrication if 6 Li is used instead of ⁷Li. A review of existing data showed that the apparent activation energy Q for 7 Li in germanium increased with increasing temperatures. Such an effect might be caused by barrier tunneling at the lower temperatures; such a tunneling mechanism would tend to increase the ratio of diffusion constants D_6/D_7 at the lower temperatures. We have measured this ratio and found it to be 1.091 at 400°C and 1.096 at 200°C. These ratios are greater than the 1.080 value obtained from classical calculations and therefore indicate the possibility of tunneling. Calculations based on a diffusion theory which incorporated tunneling effects were performed. Good agreement was found to exist between the calculations and existing 7 Li diffusion data with our measured ratios. These calculations and experimental data indicate a ratio of about 1.12 at room temperature. This effect is smaller than had been hoped for and translates into a saving of only 14 hours in a ten-day detector drift. These calculations did not evaluate the ⁷Li local-mode frequency or any of the effects of the lattice on the local mode. Consequently, the infrared-absorption studies were undertaken.

The study of local modes in germanium proved to be too difficult because of sample-preparation problems; we therefore studied local modes in silicon. These local modes are similar in many important respects to the local modes in germanium. For this work it was necessary to compensate the lithium with boron in order to reduce the free-carrierabsorption background. We then set out to evaluate the effects of anharmonic terms in atomic displacements on the local modes through application of a uniaxial stress. The uniaxial-stress experiments, however, did not show any splitting of the local modes. In fact, the stress necessary to split the two-fold degeneracies appears to be considerably larger than the stress necessary to fracture the sample.

The thermal experiments determined the line width and centroid shifts of the local modes as a function of temperature. A linear temperature dependence in line width and centroid shift was observed at temperatures above 300° K. A theory describing these anharmonic effects on local modes in a C_{3v} symmetry has not yet been developed. We modified the theory of Elliott *et al.* in an effort to account for the actual C_{3v} symmetry of the lithium-boron system. We then compared calculations based on these ideas with the observed temperature dependences.

Data and calculations for centroid shift were found to agree reasonably well. On the basis of the modified theory of Elliott *et al.*, this agreement indicated that the centroid shifts were the result of anharmonic effects due to fourth-order terms in atomic displacement.

Two processes were considered in calculating the localmode line widths; two-phonon decay and elastic-scattering of band phonons. The elastic-scattering mechanism was rejected on the basis of its T^2 dependence at high temperature. The two-phonon-decay process was then fit to the experimental data at 300°K and above. The agreement between calculations and experiments at temperatures above 300°K was fair; however, below 300°K there was no agreement. It will therefore be necessary for a rigorous theory, based on the actual C_{3v} symmetry of the local mode, to be developed in order to fully explain both the line width and centroid shift processes.

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APPENDICES

APPENDIX A

Because of the small local-mode absorption coefficients in germanium, an optimization technique was used to determine the best sample thickness. This technique was carried out for the split-beam system described in section 4.2. We have considered the system in which a difference measurement is formed with a compensated ⁷Li sample in the upper beam, and either a pure silicon sample or a compensated ⁶Li sample in the lower beam. The intensity of the upper beam (S_u) and (S_L) of the lower beam, upon entering the monochromator, can be expressed as

 $S_{u} = S_{O}^{u} e^{-\alpha_{u}X_{\mu}}$ $S_{L} = S_{O}^{L} e^{-\alpha_{L} X_{L}}$,

where x is the sample thickness and S_0^u and S_0^L are the initial upper and lower beam intensities; α_{μ} and α_{L} refer to absorption coefficients due to sample attenuation. Background effects are tuned to a zero on a spectral region of no local-modes, i.e. we adjust S_0^L by means of a variable wedge so that

$$S_{O}^{u} E = S_{O}^{L} e^{-(\alpha_{FC} X_{u} + \alpha_{L}, X_{u})} = S_{O}^{L} e^{-(\alpha_{FC} X_{L} + \alpha_{L}, X_{L})}$$

The absorption coefficient α_{FC} and α_L , refer to the freecarrier-background absorption and lattice absorption respectively. We then have

$$S_o^L = S_o^u e^{-\Delta A}$$

,

where

$$\Delta A = (\alpha_{FC} X_u - \alpha_{FC} X_L + \alpha_L, X_u - \alpha_L, X_L)$$

The detected signal S is then the difference between S_u and S_L . For a compensated sample in the upper beam and pure germanium, of the same thickness, in the lower beam

$$S = S_{o}^{u} e^{-\alpha_{B}X} [e^{-\alpha_{LM}X} - 1]$$
,

where α_{LM} is the local-mode absorption coefficient and α_B is the background absorption, i.e. $\alpha_{FC} + \alpha_L$. For

α_{LM}X<<1

we have

$$S = S_o^u e^{-\alpha_B X} \alpha_{LM}^X$$
.

The optimum signal with respect to sample thickness is then given by

$$\frac{dS}{dx} = \left(-\alpha_B S + \frac{S}{x}\right) = S\left(-\alpha_B + \frac{1}{x}\right) = 0$$



The optimum sample thickness is X_{O} given by

•

$$X_{o} \approx \frac{1}{\alpha_{B}} = \frac{1}{\alpha_{FC}^{+}\alpha_{L}}$$
.

The typical values of $\alpha_{FC} + \alpha_L$, in a reasonably compensated sample are 20-40 cm⁻¹ so that $X_o \approx 330 \ \mu$. However, the function $(-\alpha_B + \frac{1}{x})$ is slowly varying near the maximum so that 600-700 μ thicknesses are also adequate. These thicker samples are much easier to prepare.

APPENDIX B

In order to evaluate the thermal breaking of Li-B complexes, eq. 2.19 is first expressed in terms of θ = P/N and $\Omega(T)$ in the form

$$Ω(T) = 4 \pi \left(\frac{e^2}{\epsilon kT}\right)^3 Q(\alpha)$$

The integral Q(α) is then defined by eq. 2.18 where $\alpha = e^2/\epsilon kTa$. The form

$$\log Q(\alpha) = \log \left\{ \frac{1}{4\pi} \left(\frac{\epsilon kT}{e^2} \right)^2 \frac{\theta}{N(1-\theta)^2} \right\}$$

then results, where, for our samples, $N = 10^{19}/cm^3$. Tables of log Q(α) vs. α then allow θ to be evaluated for any temperature. This has been done for several temperatures using as a distance of closest ion-to-ion approach 2.6 Å. The results are plotted in Figure B.1. The observed thermal breaking of complexes would be much more rapid for larger values of N.



APPENDIX C

Use of bakelite contacts between the sample and the pressure clamp, raised the question of friction at the sample contacts and the resulting possibility of large components of stress perpendicular to the direction of application. When uniaxialstress is applied to silicon, it expands in directions perpendicular to the applied force. But, friction at the pressure applicator contacts opposes this expansion. The result may be local stress components considerably larger than the applied stress. The amount of lateral expansion is indicated by Poisson's ratio, defined as the change in sample width perpendicular to the applied force, divided by the change in length along the directions of applied force. For stress applied to the [110] direction of silicon, Poisson's ratio is 0.33.45 It is also possible that stress variations may exist in the sample around regions of lithium precipitation discussed earlier. It was therefore decided to evaluate the stress variations across the loaded sample by birefringence techniques.46

The test set-up for the birefringence work is shown in Figure C.1. In this system circularly polarized and nearly monochromatic light is incident upon the sample such that the two components of the light are in the plane of the







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sample. The silicon crystal under applied stress is optically anisotropic, <u>i.e</u>., it has different values of refractive index is different directions, or in other words, the two components of light will propagate through the sample at slightly different velocities.^{*} When these two components are remixed to produce a plane polarized wave, an interference pattern results. The pattern of a loaded sample (one which has uniaxial stress applied) indicates the amount of applied stress when compared to the pattern of an unloaded sample.

The components of the birefringence system are standard, and their function is easily explained. The incandescent source has approximately a black-body radiation characteristic. The filter is used to block most of the unwanted visible radiation which would not pass through the silicon sample. The first polarizer, ^{**} set at zero degrees, is used to establish a polarization reference; it produces planepolarized light which can be represented by P_x . The x axis has been arbitrarily chosen as vertical, and the z axis is in the direction of propagation. The first quarter-wave plate ^{***} then produces a sum of left (P_) and right (P_) circularly polarized light. Each circularly polarized wave can be represented by components P_x and P_y , of plane polarization as $P_{\pm} = (1/2)^{1/2} (P_{x-}^{+} i P_y)$. The sample then retards

If the crystal is viewed as a continum of refractive index n, the velocity of propagation is given by c/n. **Ahren's-type polarizers made of calcite crystals are used. They have typically 40% transmittance out to 2.3 microns. ***The necessary retardation material is available from Polaroid Corporation.

the propagation of P_x with respect to P_y as determined by the corresponding anisotropy in refractive index. The second quarter-wave plate combines the resultant field into a plane-polarized wave. The second polarizer can be rotated to determine the angle of maximum intensity or to determine variations in intensity vs. polarization angle. Since silicon doesn't transmit in the visible, infrared radiation had been used throughout. The photo-converter tube is necessary to convert the infrared light to visible light for the measurements.

The intensity maxima or minima are referred to as fringes. They arise as the x and y components of P_{+} and P_{-} are recombined following passage through the sample. If loading produces a uniform stress across the sample, the whole sample surface would appear to change uniformly from light to dark as the second polarizer angle is varied. A nonuniform variation in applied stress gives rise to light and dark regions or fringes as the different polarization COmponents are delayed by different amounts. To evaluate the total stress variation across a loaded sample, a fringe line is located at one edge of the sample by rotation of the second polarizer. The polarizer angle θ_1 is then recorded. The second polarizer is then rotated slowly so that the fringe line appears to move across the sample. When the fringe line appears to reach the opposite edge $\circ f$ the sample, the polarizer angle θ_2 is again recorded. While the polarizer is being rotated, the number of times n

that the original fringe line position changes from light to dark to light again is also noted. This is usually observed to be less than one cycle; hence it doesn't enter the calculations. The total stress variation across the loaded sample is then simply

 $\frac{\Delta\sigma}{\sigma} = (n + \frac{\theta}{130}) 100\%$

This technique was applied to pure silicon and to borondoped lithium-compensated silicon samples. No significant differences were observed. In particular, we did not observe any local stresses which could be attributed to lithium precipitation sites. We found that the stress variations were determined primarily by how uniformly the ends of the sample made contact with the bakelite. The sample ends were ground with aluminum oxide on a glass plate until they appeared to be parallel to the bakelite contacts in the pressure clamp. In order to ascertain an upper limit on the possible stress variations, a compensated sample was made up for the birefringence testing which had a more non-uniform contact with the bakelite than did any of the actual experimental samples. These results showed that the stress variations decrease with applied pressure. At 7.6 kg/mm^2 the stress variations were ± 100 %, while at 18 kg/mm² the variations were +50% and at 23 kg/mm² the variations were +41%. When some care was taken to fit the sample into the pressure clamp, the typical stress variation

at 23 kg/mm² was ±10%. The decrease in stress variations with pressure is likely to be due to compression of the bakelite causing more uniform contacts to the sample. Friction between the sample and the bakelite was found to be a relatively small effect, possibly as a result of expansion of the bakelite.

APPENDIX D

In their analysis of lithium-boron pairs in silicon, Elliott and Pfeuty⁷ have considered a basic six-atom model described in the text (see Figure D.1). The pair symmetry in C_{3v} which has a mechanical representation for displacement vectors given by $5\Gamma_1 + \Gamma_2 + 6\Gamma_3$ for the six-atom model chosen. The $\Gamma_{i,s}$ are irreducible representations of the C_{3v} symmetry with Γ_1 and Γ_2 being one dimensional and Γ_3 two dimensional. Both Γ_1 and Γ_3 are infrared active. The symmetry coordinates given by Elliott and Pfeuty for Γ_1 are

$$\zeta_{1} = \frac{1}{\sqrt{3}} (X_{1} + Y_{1} + Z_{1}) ,$$

$$\zeta_{2} = \frac{1}{\sqrt{3}} (X_{5} + Y_{5} + Z_{5}) ,$$

$$\zeta_{3} = \frac{1}{\sqrt{3}} (X_{2} + Y_{3} + Z_{4}) ,$$

$$\zeta_{4} = \frac{1}{\sqrt{6}} (Y_{2} + Z_{2} + Z_{3} + X_{3} + X_{4} + Y_{4})$$

and

$$\zeta_5 = \frac{1}{\sqrt{3}} (X_y + Y_6 + Z_6)$$
.

for Γ_3 they are



FIGURE D.1 The 6-atom model used as basis for Lithium-boron local-mode calculations.

 $n_{1} = \frac{1}{\sqrt{3}} (X_{1} + jY_{1} + j^{2}Z_{1} ,$ $n_{2} = \frac{1}{\sqrt{3}} (X_{5} + jY_{5} + j^{2}Z_{5}) ,$ $n_{3} = \frac{1}{\sqrt{3}} (X_{2} + jY_{3} + j^{2}Z_{4}) ,$ $n_{4} = \frac{1}{\sqrt{3}} (Y_{2} + jZ_{3} + j^{2}X_{4}) ,$ $n_{5} = \frac{1}{\sqrt{3}} (Z_{2} + jX_{3} + j^{2}Y_{4}) ,$

and

$$n_6 = \frac{1}{\sqrt{3}} (X_6 + jY_6 + j^2 Z_6)$$
,

with a second coordinate for Γ_3 of $\zeta_i = \eta_i^*$, where i = 1,2,3,4,5,6. The coordinates X,Y,Z are cartesian coordinates Of the atoms, where each atom is represented by a subscript, $\underline{i} \cdot \underline{e}$. the subscript 1 refers to the lithium ion and 5 refers to the boron ion: j represents the complex cube root of unity, and 2,3,4 and 6 refer to the surrounding silicon The two-fold-degenerate boron local mode is then atoms. represented by one of the two dimensional $\Gamma_{3's}$ while the One-fold degenerate boron local mode is represented by one Of the r_{1's}. The two-fold-degenerate lithium local mode is similarly represented by one of the remaining five $r_{3's}$. It is observed that the above symmetry coordinates do not involve a mixing of the silicon, lithium, and boron coordinates. Therefore, in a first-order approximation to the actual dynamics of the lithium-boron system, each local

mode may be considered independently of the other local modes. An analysis of anharmonic effects similar to that of Elliott *et al.*²⁵ can be done for each local mode, taking care to note the appropriate representations as Γ_1 or Γ_3 . Whereas, Elliott *et al.* find a Green's function which transforms like the irreducible representation Γ_5 of Td symmetry, we would have a Green's function which would transform like the irreducible representation Γ_1 or Γ_3 of the C_{3v} symmetry. After performing symmetric products on these representations and by use of symmetry arguments to determine which terms are zero, a third-and fourth-order Hamiltonian of the same form found by Elliott *et al.* is expected. However, the local-mode operators and expansion coefficients should be labeled according to which representation and which ion they represent. Equations 2.9 and 2.10 would then appear as

$$H_{3} = \sum_{\vec{k}} \left(\frac{\hbar_{w}(\vec{k})}{2MN} \right) \left(\mathcal{B}_{\Gamma_{3}}^{2} \left(\frac{\hbar}{2M_{2}\Omega_{\Gamma_{3}}^{2}\omega_{M}} \right) \left[\sum_{x,y} (b_{x\Gamma_{3}}^{2} + b_{x\Gamma_{3}}^{+} 2)^{2} \right] \right) \\ + \mathcal{B}_{\Gamma_{1}}^{2} \left(\frac{\hbar}{2M_{2}\Omega_{\Gamma_{3}}^{2}\omega_{M}} \right) \left(b_{z\Gamma_{3}}^{1} + b_{z\Gamma_{1}}^{+} 2)^{2} \right) \\ + \mathcal{B}_{\Gamma_{3}}^{1} \left(\frac{\hbar}{2M_{1}\Omega_{\Gamma_{3}}^{2}\omega_{M}} \right) \left[\sum_{x,y} (b_{x\Gamma_{3}}^{1} + b_{x\Gamma_{3}}^{+} 1)^{2} \right] \right) \\ \left(a(\vec{k}) + a^{\dagger}(\vec{k}) \right)$$

$$H_{\mu} = \sum_{\vec{k},\vec{k}} \frac{\pi (\omega(\vec{k})\omega(\vec{k}^{*}))^{1/2}}{4\omega_{M}^{2}MN} \{ \frac{\zeta_{\Gamma_{3}}^{2}}{M_{2}^{\Omega}r_{3}^{2}} \sum_{\vec{k},\vec{y}} (b_{\vec{x}\Gamma_{3}}^{2} + b_{\vec{x}\Gamma_{3}}^{+} 2)^{2} + \frac{\zeta_{\Gamma_{1}}^{2}}{M_{2}^{\Omega}r_{1}^{2}} (b_{\vec{x}\Gamma_{1}}^{2} + b_{\vec{x}\Gamma_{1}}^{+} 2)^{2} + \frac{\zeta_{\Gamma_{3}}^{2}}{M_{1}^{\Omega}r_{3}^{1}} \sum_{\vec{k},\vec{y}} (b_{\vec{x}\Gamma_{3}}^{1} + b_{\vec{x}\Gamma_{3}}^{+} 1)^{2} \} (a(\vec{k}) + a(\vec{k})) (a(\vec{k}^{*}) + a^{*}(\vec{k}^{*}))$$

where M_1 is the lithium mass and M_2 is the boron mass. The notation of Elliott and Pfeuty has been changed slightly so that the boron ion is designated by a 2 instead of a 5. The labeling of each of the observed local modes is summarized in Table 3.

Table III - Labeling of Local Modes

local -l.					
mode (cm ⁻)	label				
522	r ₃ l				
564.5	r _l ²				
654	۲ ₃ 2				

The temperature dependence of the centroid shift and line width then takes on the form of Eq. 6.1 and 6.5 for each individual local mode in this approximation.

The presence of two boron local modes at the same coordinate location makes it seem likely that their interaction is comparable with the above effects. By analogy with the development of Elliott *et al.*, a line-width temperature dependence is expected to be given by

$$\sum_{\vec{k}} \omega(\vec{k})(\eta(\vec{k})+1)(\eta(\Omega')+1)\delta(\omega(\vec{k})-\Omega_{\Gamma_3} 2 +\Omega_{\Gamma_1} 2),$$

where Ω^{\star} is the boron local-mode frequency which is not decaying.

APPENDIX E

The programs for centroid shifts and line widths incorporated a silicon phonon density of states taken from a paper by Dawber and Elliott.^{19a} The values are given below for $\Delta \omega = 8 \ 1/3 \ cm^{-1}$.

i	g(i∆w)	i	g(iAw)	l i	g(iAw)
1	0.0	21	0.20	41	1.40
2	0.0	22	0.05	42	1.80
3	0.10	23	0.25	43	0.80
4	0.10	24	0.25	44	0.90
5	0.0	25	0.45	45	0.35
6	0.10	26	0.30	46	0.55
7	0.40	27	0.60	47	1.80
8	0.40	28	0.45	48	1.55
9	1.00	29	0.60	49	2.30
10	1.35	30	0.70	50	2.80
11	2.40	31	0.85	51	2.85
12	3.50	32	0.95	52	3.00
13	7.80	33	1.10	53	3.05
14	9.50	34	1.45	54	3.20
15	10.60	35	2.00	55	2.30
16	12.15	36	2.55	56	1.95
17	9.55	37	2.85	57	1.40
18	0.25	38	2.40	58	1.20
19	0.0	39	2.15	59	18.60
20	0.25	40	2.40	60	31.00
				61	9.80

Table IV - Phonon Spectrum

For normalization purposes, it can be noted that

The equation to be programmed for centroid shift is

$$\frac{\Delta\Omega}{\Omega_{O}} = \text{constant.} \qquad \frac{\int_{0}^{\omega_{M}} g(\omega) \hbar \omega [n(\omega) + 1/2] d\omega}{\int_{0}^{\omega_{M}} g(\omega) d\omega} e.1$$

To program this equation it was first necessary to convert the integrals to sums; then d ω becomes $\Delta\omega$, ω becomes i $\Delta\omega$ for integer values of i, and ω_{M} becomes $61\Delta\omega$. Equation el then becomes

constant
$$\cdot \frac{\int_{1}^{61} g(i\Delta\omega) \hbar i\Delta\omega [\eta(i\Delta\omega+1/2]\Delta\omega)}{\int_{1}^{61} g(i\Delta\omega)\Delta\omega}$$

which simplifies to

$$\frac{\Delta\omega\hbar}{173.55} \sum_{i=1}^{61} i g(i\Delta\omega)[\eta(i\Delta\omega+1/2)]$$

The term $\zeta/M_1 \Omega_0^2 M \omega_M^2$ determines the leading constant and has been denoted as GAMMA in this program. It is evaluated in terms of the local-mode frequency OMEGA on line 5 of the program for centroid shift which follows. As a first try ζ was taken as 10^{21} ergs/cm⁴. GAMMA is multiplied by 6 on line 8, to account for the six branches in the phonondispersion relation. The loop over temperature, in 20°K steps, begins on line 11; the sum over the lattice spectrum begins on line 13. The term AA represents the temperaturedependent factor. On line 17 the coefficients GAMMA and $\hbar\Delta\omega/\sum_{1}^{\circ} g(i\Delta\omega)$ are multiplied in to form $\Delta\Omega/\Omega_{0}$. The program was then run with lines 7 and 18 deleted. The results of this calculation were then expressed as $\Delta\Omega/\Omega_{0} = Cf(T)$ and compared with the experiments. The constants C and Ω_{0} were adjusted to fit our high-temperature data in magnitude and slope. The constant C then represented the variation of ζ from the value of $10^{21} \text{ ergs/cm}^{4}$. For the purpose of calculating Ω , the zero temperature shift in $\Delta\Omega/\Omega_{0}$ was subtracted out by adding $\Omega_{0}C$ f(T=0) to Ω_{0} . This sum is denoted OMEGO in the following program where line 18 calculates

$$\Omega = \Omega_{+}\Omega_{0}Cf(T=0) - \Omega_{0}Cf(T) - \Omega_{0}C^{2}f(T=0) f(T)$$

$$\simeq \Omega_{+}\Omega_{0}Cf(T=0) - \Omega_{0}Cf(T)$$

The second-order term $-\Omega_0 C^2 f(T=0) f(T)$ represents an error of typically less than 1% in calculations of the hightemperature slope. The scale factor C can be conveniently multiplied into GAMMA on line 8. The program for centroid shift of the 654 cm⁻¹ local mode is

1		DIMENSION G(62),ANS(40),GG(62)
2		READ 100, (G(I),I=1,61)
3		CENTROID SHIFT - 654 - SILICON PHONON SPECTRUM
4		OMEGA = 654
5		GAMMA = (1.0/(10.81*1.6*28.09*1.6*((6*3.1416*5.18
6		C*6*3.1416*OMEGA)**2)))*(10**25)
7		OMEGO = 663.0
8		GAMMA = 6*GAMMA
9		GG(1) = 0.0
10		$DP = (6.625 \pm 2.5/1.38)$
11		DO 40 N=1,36
12		T=20*O*N
13		DO 30 I=1,60
14		AA= (1.0/(EXP(I*DP/T)-1.0))+0.5
15		GG(I+1)=GG(I)+I*G(I)*AA
16	30	CONTINUE
17		ANS(N)=GG(61)*GAMMA*50*3.1416*1.054/((10**173.55)
18		ANS(N)=OMEGO*(1.0-ANS(N))
19		PRINT 200,(T,ANS(N))
20	40	CONTINUE
21	100	FORMAT (6F10.3)
22	200	FORMAT (8X,I3,10X,E10.5)
23		END

DATA

The data is right justified in each of six fields per data card. There are three decimal places to the right of the decimal point, and each field is 10 characters wide. The calculations for the 564.5 cm⁻¹ local mode can be done by simply replacing line 4 with OMEGA = 564.5 once the appropriate factors C and Ω_0 have been determined as above. Calculations for the 522 cm⁻¹ local mode are similar, except that GAMMA must be multiplied by 10.81/6.94 to account for the change to a lithium atomic mass.

The equations to be programmed for the two-phonon-decay line width is

$$\frac{1}{\tau} = \frac{\text{GAMMA } \Delta \omega}{\left[\sum_{\alpha} g(i\Delta \omega)\right]^2} 36 \sum_{i=M-6l}^{6l} g(i\Delta \omega) g(M\Delta \omega - i\Delta \omega)i(M-i)\{(n(i\Delta \omega)+1)\}$$

$$X(n(M\Delta\omega - i\Delta\omega) + 1) - n(i\Delta\omega)n((M - i)\Delta\omega)$$

where

$$GAMMA = \frac{\beta^{-2} \pi h \nu}{4 M \Omega M^{2} \omega_{M}^{4}}$$

and

M is an integer such that MAw = Ω_{Γ_j} i .

In this program the total temperature dependence is calculated to be the variable AC. The sum over the phonon spectrum is done in the variable X(J). In line 21 the sum over the phonon spectrum is multiplied by GAMMA and $\Delta \omega$ in CM⁻¹ and divided by the phonon-spectrum normalization factor squared. The coefficient β ' was varied until a best fit in magnitude and slope was obtained. The resulting program is
l		DIMENSION X(61),G(61),ANS(40)
2		READ 50, (G(I),I=1,61)
3	С	LINEWIDTH-2 PHONON DECAY - SILICON SPECTRUM
ц		OMEGA = 654
5		M = OMEGA/8.333
6		GAMMA=((4*3.1416*1.054)/(4*10.81*1.6*OMEGA*6*3.1416* ((2.809*1.6)
7		C**2)*((5.18*2*3.1416*3)**4)))*(10**9)
8		GAMMA = 36*GAMMA
9		DP=12.01
10		L=(M-61)
11		DO 30 K=1,36
12		T=20.0*K
13		DO 20 J=L,61
14		AA= 1.0/(EXP(DP*J/T)-1.0)
15		AB= 1.0/EXP(DP*(M-J)/T)-1.0)
16		AC= (AA+1.0)*(AB+1.0)-AA(AB
17		X(L-1)=0.0
18		X(J)=X(J-1)+G(J)*G(M-J)*J*(M-J)*AC
19	20	CONTINUE
20		ANS(K)=(X(61)*GAMMA)/((173.55)**2)*8.33
21		PRINT 40,(T,ANS(K)
22	30	CONTINUE
23	40	FORMAT (8X,I3,10X,E10.3)
24	50	FORMAT (6F10.3)
25		END
		D ATA

The equation to be programmed for the elastic-scattering line width is

$$\frac{1}{\tau} = 2\pi \left[\left(\zeta - \frac{2B^2}{M^2 \Omega^2} \right) \left(\frac{\pi (2\nu + 3)}{4M^2 \Omega M \omega_M^2} \right)^2 \right] \frac{36 \Delta \omega}{\left(\sum g (i\Delta \omega) \right)^2}$$
$$\int_{i=1}^{61} g^2 (i\Delta \omega) i^2 n (i\Delta \omega) (n (i\Delta \omega) + 1) \quad .$$

The coefficient in square brackets is equal to $(89.0/0MEGA) \times 10^{-2}$ for $(\zeta - 2\beta^2/M^2 \alpha^2) = 10^{21} \text{ ergs/cm}^4$ and OMEGA in cm⁻¹. The sum $\sum g(j\Delta\omega)$ is done with the variable S(J) with the result stored in S(61). The temperature dependence is given by the variable AA and the sum over the phonon spectrum is done in the variable GA(J). In line 19, GA(61) is multiplied by $\Delta\omega$ and GAMMA, and divided by (S(61))². The program is

l			DIMENSION S(62),G(62),GAS(40),GA(62)
2			READ 50,(G(I),I=1,61)
3	С		LINEWIDTH, ELASTIC SCATTERING-SILICON PHONON SPECTRUM
4			DO 10 J=1,60
5			S(1)=0.0
6			S(J+1)=S(J)+G(J+1)
7		10	CONTINUE
8			OMEGA = 654
9			GAMMA = 2*3.1416*(89.0/(OMEGA*10**2))*36
10			GAMMA=GAMMA/OMEGA
11			DP=12.01
12			GA(1)=0.0
13			DO 40 K=1,36
14			T=20.0*k
15			DO 30 J=1,60
16			AA= 1.0/(EXP(DP*(J+1)/T)-1.0)
17			GA(J+1)=GA(J)+((G(J+1))**2)*(J+1)*(J+1*AA*(AA+1.0)
18		30	CONTINUE
19			GAS(K)=GAMMA*GA(61)*8.3333/((S(61))**2)
20			PRINT 60, (T,GAS(K))
21		40	CONTINUE
22		50	FORMAT (6F10.3)
23		60	FORMAT (8X,I3,10X,E10.3)
24			END
			DATA

