QUANTUM THEORY OF INTERSTITIAL ATOMIC DIFFUSION OF LIGHT IMPURITIES IN SEMICONDUCTORS

This research was prepared for Ph.Lic thesis in Spring 1979. It was approved at the University of Helsinki in 27.9.1979. The work was done under the supervision of professor Stig Stenholm.

A private study in the same subject but with completely different methods was made before this, "Quantum Theory of Interstitial Diffusion", done between June 1978 and April 1979.

Henrik Stenlund
26.8.2022

This is a scanned copy of the original work done during 1978 - 1979 at the University of Helsinki

27.9.79

Matemaattis-luonnontieteelliselle osastolle

Matemaattis-luonnontieteellisen osaston määrääminä olemme tarkastaneet filosofian kandidaatti Henrik Stenlundin lisensiaattitutkimuksen "Quantum theory of interstitial atomic diffusion of light impurities in semiconductors" ja esitämme siitä kunnioittavasti seuraavan lausunnon.

Lisensiaattitutkimuksen aiheena on keveän atomin (esimerkkitapauksena litium) diffuusioteoria pii- ja germaniumpuolijohteissa. Työssä kuvaillaan aluksi aikaisempia kyseessäolevaan ongelmaan kehitettyjä tai sovellettuja teorioita, jotka jakaantuvat klassisiin ja kvanttimekaanisiin. Tämän jälkeen työ jatkuu tarkastelemalla kvanttimekaanista mallia, jossa lähtökohtana ovat epäpuhtausatomin energiavyöt puolijohteessa ja jossa vyötilojen ja isäntähilan fononien väliset vuorovaikutukset aiheuttavat epäpuhtausatomin transitioita eri vyötilojen välillä. Diffuusion kannalta tärkeitä ovat transitiot niissä vöissä, joiden energia on hilan eri välisijojen välisen kynnyspotentiaalienergian suuruutta. Näissä vöissä tapahtuviin transitioihin liittyvää relaksaatioaikaa on käytetty relaksaatioaika-approksimaatiossa diffuusiovakion määrittelemiseen.

Teorian soveltaminen edellyttää energiavöiden eksplisiittistä tuntemista, jota varten tekijä kehittää ensin omaperäisen potentiaalimallin epäpuhtausatomin ja hilan atomien vuorovaikutuksille. Malli sisältää kaksi empiiristä parametriä, joista vain toinen on olennaisesti vaikuttava. Parametrin arvo on sovitettu siten, että toteutetaan diffuusiovakion kokeellisesti tunnettu eksponentiaalinen lämpötilariippuvuuden osa, millä on yhteys välisijojen välisen potentiaalikynnyksen korkeuteen. Koska ei ole olemassa tarkkoja menetelmiä energiavöiden laskemiseksi tällaiselle systeemille, on tekijä arvioinut tehtävän kannalta oleellisten vöiden leveydet ja väliset etäisyydet yksiulotteisen mallin avulla. Näin saatuja tuloksia on käytetty diffuusiovakion arvon ja lämpötilariippuvuuden laskemiseksi, ja tuloksia on työssä vertailtu sekä kokeellisiin että toisiin teoreettisiin arvoihin.

Lisensiaattityössä käsitelty ongelma on eräs kiinteän olomuodon fysiikan vaikeimpia. Näyttää sitä, että klassiseen mekaniikkaan perustuviin kvalitatiivisiin tuloksiin verrattuna kvanttimekaaniset raffinoidummat teoriat eivät juurikaan onnistu parantamaan tulosta. Niinpä teoreettisten ennusteiden yhtäpitävyys kokeellisten tulosten kanssa on vain suuntaa antava, vieläpä niin että eri koetuloksetkin ovat keskenään ristiriitaisia. Tässä tilanteessa on hankala arvioida tässä työssä saavutettujen tulosten tarkuutta; niiden suuruusluokka on järkevä mutta näyttää siltä että työ ei saavuta parhaitten teoreettisten laskujen yhtäpitävyyttä koemateriaalin kanssa. Työn arvokkain puoli on käsittääksemme teorian vaatimien perustietojen ja olettamusten seikkaperäinen analyysi, ja ilmiön fysikaalisen luonteen selvittäminen. Työn tekijä on varsin hyvin ymmärtänyt erilaisten teorioiden fysikaalisen sisällön, mutta toisaalta myös niiden heikkoudet, joista esitetään kriittisiä huomautuksia.

Lisensiaattityö on kirjoitettu englannin kielellä ja sisältää jonkin verran kielivirheitä. Esitetyn materiaalin valinta ja esitystapa ovat onnistuneita.

Mielestämme FK Stenlundin tutkielma täyttää hyvin lisensiaattityölle asetetut vaatimukset ja esitämme sen hyväksymistä tarkoitukseensa.

Helsinki 15.8.1979

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QUANTUM THEORY OF INTERSTITIAL ATOMIC DIFFUSION OF LIGHT IMPURITIES IN SEMICONDUCTORS

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ABSTRACT

A quantum theory of atomic diffusion in solids is presented and applied to a particular problem of interstitial diffusion, Li in Ge and Si. The theory is based on transport in narrow bands using the relaxation time approximation. The bands are evaluated by a one-dimensional method and the interaction potential between the impurity atom and lattice atoms is examined through numerical calculations, where the lattice potential difference between the equilibrium site and saddle-point, the potential barrier height, is fitted with experimental values.

The relaxation time is taken from the theory of Kagan and Klinger [21] and the diffusion coefficients are calculated. For comparison the result of the theory of Kagan and Klinger for the diffusion coefficient is also put in numerical form and it shows a relatively good agreement with experimental values (see table 1.). The result of the transport theory was smaller by an order of magnitude. The isotopic effect was also studied and D_0 and E_0 were found to have dependences $m^{-\frac{3}{2}}$ and m^{-1} respectively.

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Abstract

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1. INTRODUCTION

a. Introductory theory

An excess atom brought into solvent lattice finds itself located in an equilibrium site between the lattice atoms and vibrates about the site as the others do. At high temperatures it may randomly jump to the neighbouring free equilibrium site (see figure 1.), from which it can again move to another site. The interstitial atom may jump in one of 10^3 to 10^5 vibrations when it has received energy enough from the lattice in form of thermal excitations, phonons, to exceed the potential barrier separating the equilibrium sites.

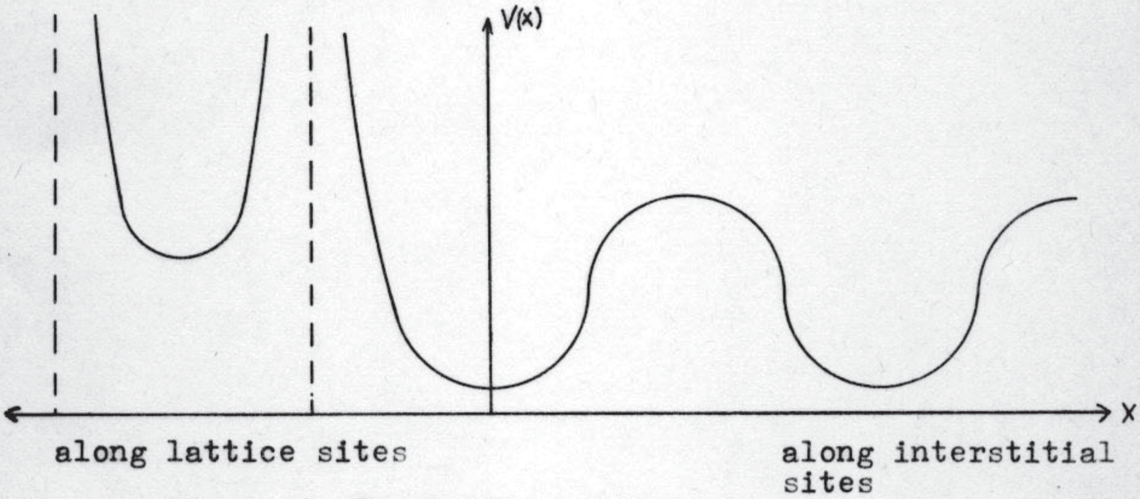


Figure 1. The lattice potential

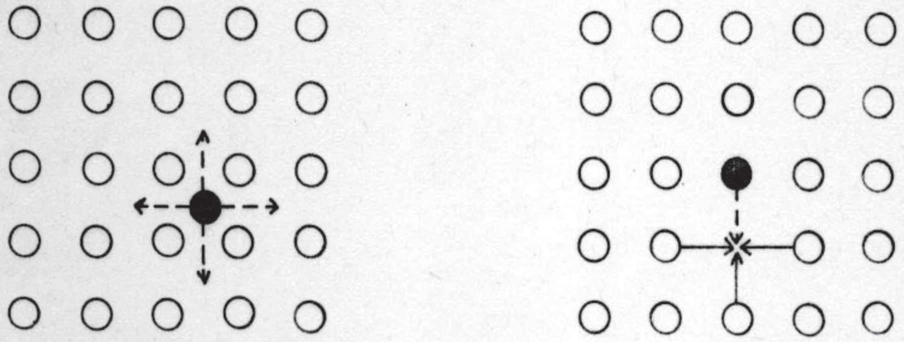
The transitions between vibrational energy levels are usually connected with single-phonon processes. Sometimes the gaps may be so large that single-phonon processes are not possible and then the transitions are produced by successive single-phonon processes (thus becoming a multi-phonon process).

The equilibrium distribution for interstitial atoms among their allowed energies is Boltzmann's classical distribution giving strong dominance to the lowest level and only a small fraction occupies the overbarrier levels. There is another phenomenon assisting the jump and it is due to the fluctuations of the surrounding atoms opening the barrier and making it easier for the atom to move. This is significant only for large interstitial atoms, whose ion cores are of so large radius that they are even from a geometrical standpoint prevented from moving.

From these random jumps it follows that the excess atom diffuses in the lattice by an interstitial mechanism. There are several other mechanisms causing mass transport in lattice and of these we can mention one of the most noteworthy, the vacancy mechanism. By it we mean a solute atom-solvent lattice vacancy pair moving together. The solute atom has substituted one lattice atom and the vacancy moves around the solute. This motion is, of course, due to the jumping of solvent atoms to the vacancy thus leaving vacancies behind them (see figure 2. below). Only as the solute atom jumps to the vacancy is diffusion brought about and thus the pair is strongly correlated in its motion. Vacancies are very common at high temperatures being formed by thermal excitations. The vacancy mechanism is dominating in self-diffusion and for some elements in solute diffusion in semiconductors. In this work diffusion by interstitial mechanism only is studied but the theory can usually be directly applied to other mechanisms.

Experimentally one has observed an interesting behaviour for the diffusion coefficient as a function of temperature, mostly

Figure 2. The two main diffusion mechanisms



interstitial mechanism

vacancy mechanism

at high temperatures

$$D = D_o e^{-U_o/kT} , \qquad (1)$$

where U_o is the potential barrier height and D_o is independent of T. This is called Arrhenius´ equation and D obeys it very well in almost all mass transport through solids. It is clear that the nature of the dependence derives its origin from the factor of Boltzmann for occupation as we shall later see.

In classical theories D_o is usually expressed in the form

$$D_o = n\bar{\nu} , \qquad (2)$$

where n is the number of directions for the particle to move from one equilibrium site to another and $\bar{\nu}$ is the vibrational frequency of the particle in the initial state. Often this frequency is set equal to the Debye frequency. By the random walk theory D_0 becomes

$$D = \frac{1}{6}\lambda^2\Gamma, \tag{3}$$

where λ is the jump distance and Γ is the jump frequency, with which the atom changes its equilibrium positions.

In the following two sections we will shortly rewiev some existing approaches in calculating D for particles in crystals considering both classical and quantum theories.

1.b. Classical theories

The first theory explaining the Arrhenius-type behaviour of $D(\beta)$ was the Absolute Reaction Rate Theory due to Glasstone et al. [1] using the concept of transition state in one dimension. They considered the activated state, which is produced at the moment the particle is in the region of the saddle point, to consist of similar energy levels as the normal state around the equilibrium point (see figure 3.). From this they concluded by statistical arguments that the jump rate Γ had to be a product of the concentration (fraction c_*) of the particles in the activated state (activated complexes) and the mean velocity $\bar{v}$ of the same particles moving in the direction of the irreversible jump divided by the width of the activated state (δ)

$$\Gamma = C'_{\ddagger} \frac{\bar{v}}{\delta} = C_{\ddagger} \frac{kT}{h} . \qquad (4)$$

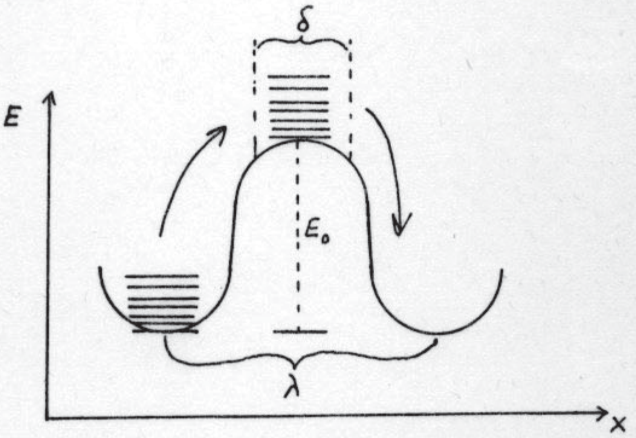


Figure 3. The activated state

Here h and k are the familiar constants of Planck and Boltzmann respectively. They obtained for the concentration the ratio between the partition functions of the activated state and the normal state and as a result of renormalization of energy zeros the factor $e^{-\beta E_0}$ appeared

$$D = \frac{\lambda^2 kT F_{\ddagger} e^{-\beta E_0}}{h F} , \qquad (5)$$

where $F_{\ddagger}$ is the partition function belonging to the activated state (energy normalized) and F is the one in the normal state and λ is the jump distance.

The principal assumption is that the particle is moving isothermally and reversibly from one equilibrium site to another along the reaction coordinate. The moving particle is considered to be in thermal equilibrium with the lattice at all times.

Wert and Zener [2] and Zener [3] developed the rate theory further to accomodate to the requirements of solid state diffusion and they obtained for the jump frequency Γ

$$\Gamma = n\bar{\nu}\, e^{-\Delta G^*/kT} = n\bar{\nu}\, e^{-\Delta H^*/kT}\, e^{\Delta S^*/k} . \qquad (6)$$

Here n is the number of ways available for the particle to move from site to site and $\bar{\nu}$ is the vibrational frequency of the particle in the initial state. ΔG^*, ΔS^* and ΔH^* represent the isothermal work associated with the motion of the particle to the activated state and changes of entropy and enthalpy respectively. When this expression is substituted into the basic equation of D in the random walk theory, we have (see Chandrasekhar [8])

$$D = \frac{\lambda^2 n\bar{\nu}}{6}\, e^{\Delta S^*/k}\, e^{-\Delta H^*/kT} . \qquad (7)$$

The basic assumptions of this theory have not been proved to be valid and it is difficult to believe that the motion of the particle would be reversible and the lifetime of the activated state could be long enough to allow the use of equilibrium statistical mechanics. The value of $\bar{\nu}$ is not clearly defined in this theory and is usually put equal to the Debye or Einstein frequency without giving any reason for its applicability. One of the main justifications of this analysis is that it often works (see Shewmon [4]).

An attempt to improve the definition of $\bar{\nu}$ was made by Wert [5], who used classical statistical methods to evaluate the jump rate and calculated Γ using the assumption of small harmonic vibrations around the equilibrium point. Wert calculated the jump rate by starting from the ratio of two partition functions (x' is the reaction coordinate)

$$\Gamma = \frac{C_{\ddagger}\bar{\nu}}{\lambda} = \frac{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\prod_i dq_i\, dy\, dz\, e^{-\phi(x',y,z,q_i)/kT}}{\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}\prod_i dq_i\, dx\, dy\, dz\, e^{-\phi(x,y,z,q_i)/kT}} \otimes$$

$$\otimes \frac{\int_{0}^{\infty}\frac{P_x}{M}\, e^{-P_x^2/2MkT}\, dP_x}{\int_{-\infty}^{\infty}\frac{P_x}{M}\, e^{-P_x^2/2MkT}\, dP_x} \,. \tag{8}$$

ϕ represents the potential energy of the system (the diffusing atom and the adjacent solute atoms with coordinates q_i) and M is the mass of the diffusing atom. By approximating this potential around the equilibrium site x_0 by an expression

$$\phi(x_0, y, z, q_i) + \tfrac{1}{2}Kx^2 \tag{9}$$

with K the force constant for a small region around x_o Wert evaluated the integrals with the aid of thermodynamical functions ΔG, ΔH and ΔS. Here ΔG is the work done when a mole of solute atoms is moved isothermally from x_o to x' at constant pressure. Wert gives

$$D = \gamma a_o^2 n \nu e^{\Delta S/R} e^{-\Delta H/RT} . \tag{10}$$

Here ν is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{K}{M}} , \tag{11}$$

R is the gas constant and γ is a numerical constant depending on the lattice structure with a lattice constant a_o. ΔS and ΔH must be evaluated experimentally since there is no simple way to calculate them.

Vineyard [6] derived a more general approach to calculate Γ avoiding thermodynamics. His theory gave the jump rate as a ratio of probabilities of all points on the saddle surface (in configuration space), which have positive velocities towards the diffusion direction to the sum of all points in configuration space around the initial equilibrium site. Thus Vineyard obtains

$$\Gamma = n \sqrt{\frac{kT}{2\pi}} \frac{\int_S e^{-\phi/kT} dS}{\int_V e^{-\phi/kT} dV} , \tag{12}$$

where ϕ is the potential energy. This is essentially a ratio of two configurational partition functions. Employing the theory of small vibrations Vineyard expanded the potential around the extremal points and neglected terms of higher order than harmonic. His result for Γ was

$$\Gamma \simeq \frac{n \prod_{i=1}^{3N} \nu_i \, e^{-\Delta G'/kT}}{\prod_{i=1}^{3N-1} \nu_i'} \quad , \qquad (13)$$

where ν_i are the 3N normal frequencies of atoms in their equilibrium states and ν_i' are the 3N-1 normal frequencies associated with the activated complex . $\Delta G'$ is the free energy difference between the initial site and the saddle point.

It is readily realized that this theory contains many crucial hypotheses, which limit the validity of the theory. Vineyard's Γ is based on the assumption that an activated state exists and that when an atom passes over the potential barrier the probability of reversing the direction is vanishingly small.

The advantages of Vineyard's theory over Absolute Reaction Rate Theory are that the frequencies are defined in terms of the solvent lattice normal frequencies in the normal state and in saddlepoint configuration but finally the calculation of $\bar{\nu}$ is still not well defined (in fact it is almost incalculable in Vineyard's theory).

Rice [7] has avoided the use of equilibrium statistical mechanics in his dynamical theory by using a normal mode analysis in the harmonic approximation. Rice calculated the frequency of occurrence $P(\{\delta\})$ of the appropriate configuration, in which the diffusing atom has a large enough vibration amplitude to diffuse in the right direction and the surrounding atoms are appropriately in an out-of-phase motion giving

$$\Gamma = n \sum \frac{[V]}{S} P(\{\delta\}) , \qquad (14)$$

where

$$P(\{\delta\}) = \bar{\nu}\, e^{-U_0/kT} \prod_j e^{-U_j/kT} \prod_{k>l} g^{(2)}_{kl} . \qquad (15)$$

Here $\bar{\nu}$ is some weighted mean frequency and U_o is the critical energy needed for the atoms to reach the proper amplitude. U_j is the energy required to shift the barrier atoms in the lattice from their equilibrium positions and $g^{(2)}_{kl}$ is the pair correlation function for atoms k and l. [V] and S stand for the concentrations of vacancies and solvent lattice atoms respectively.

Although this theory has been derived for diffusion by the vacancy mechanism, it is directly applicable to other mechanisms, e.g. to interstitial mechanism. The equation for Γ is very general and in order to obtain calculable expressions simplifying assumptions are to be made. Clearly the critical amplitude must be at least one-half the jump distance (small frequency oscillation) and the oscillators must be harmonic. The number of normal modes associated with the process of achieving a critical amplitude is essentially smaller than the total number of modes of the crystal. Finally the frequency of thermal fluctuations around the diffusing atom is much greater than the jump rate.

Rice obtained for the pair correlation function in terms of the potential W_{kl} between atoms k and l

$$g^{(2)}_{kl} = e^{-W_{kl}/kT}, \qquad W_{kl} = \Delta H_{kl} - T\Delta S_{kl} \tag{16}$$

and Γ becomes

$$\Gamma = n\bar{\nu}\, e^{\sum_{k>l} \Delta S_{kl}/k}\; e^{-(U_0 + \sum_j U_j + \sum_{k>l} \Delta H_{kl})/kT} . \tag{17}$$

In this equation we can identify the term

$$\Delta H^k = U_0 + \sum_j U_j + \sum_{k>l} H_{kl} \tag{18}$$

as the activation enthalpy of the rate theory.

The main weakness of the theory of Rice is the assumption of harmonicity and to obtain better correlation with experimental data, anharmonic terms must be included. The theory of Rice gives a many-body approach to the problem and it is in this respect closer to real processes than rate theories although it contains too many incalculable frequencies.

Glyde [9] calculated the jump rate by using first a dynamical method and then a purely statistical one making a kind of synthesis of Vineyard´s and Rice´s theories showing their equivalence. The dynamical part uses classical mechanics in normal coordinates and Glyde calculated correlation functions with the aid of normal frequencies. Through calculation of fluctuations Glyde arrived at the jump frequency. By a statistical mechanical derivation he calculated the same fluctuations and similar expressions for Γ but by using different random variable theorems than

Rice to obtain the probability of a fluctuation. The results of Glyde are applicable when the force constants are known, although the frequencies must be in some way approximated to obtain numerical results from the expressions. The approach of Glyde is without any doubt one of the best classical treatments of the diffusion coefficient.

Nardelli and Reatto [10] studied interstitial diffusion by Kubo's formalism starting from the Liouville equation for the total system and derived the evolution equation for a particle in a periodic potential. They coupled the equation to lattice vibrations in thermal equilibrium and obtained the expression for the diffusion coefficient of ionized impurities in silicon and germanium in good agreement with the experimental data

$$D = D_o e^{-U_o/kT} \tag{19}$$

$$D_o = c_L Z^{-2} kT \sqrt{U_o/2m} \tag{20}$$

$$c_L = 2 \mathcal{J} 4^4 3^{-10/3} \pi^{-2/3} \frac{r_o^6 \epsilon_o^2 \delta c_L^2}{Z_L^2 e^4 (1 + 2(\frac{c_L}{c_t})^2)} ,$$

where the Z's are effective valences and $\mathcal{J}$ is a numerical factor equal to 0.525. r_o is the nearest neighbour distance, δ is the mass density and the c's are the familiar sound velocities.

In all of these classical theories the isotopic mass dependence of D_o is $m^{-\frac{1}{2}}$, which is typical for all classical theories. Usually they do not show any mass dependence in activation energy.

LeClaire [11] has given thought to this subject and he has calculated the ratio of jump frequencies w belonging to two different isotopes α and β

$$\frac{w^\alpha}{w^\beta} = 1 + \Delta K\left(\sqrt{\frac{m^\beta}{m^\alpha}} - 1\right). \tag{21}$$

Here m^α is the mass of isotope α and ΔK is the fraction of the kinetic energy, which is possessed by the solute atom as it passes the saddle point. His calculations are based on normal frequencies and the theory of Vineyard [6] mentioned earlier. LeClaire also gives expressions for ΔK in terms of the displacements of adjacent atoms. He calculated the ratio w_α/w_β by using quantum partition functions obtaining essentially a very similar result as the classical one with some correction factor. However, quantum diffusion is of different nature and this calculation is not justified as will be seen later from the quite different isotopic dependences in quantum theories. Based on this quantum analog he evaluated the relation between the ratio of diffusion coefficients and activation energies Q

$$\begin{aligned}\frac{D_\alpha}{D_\beta} &= \sqrt{\frac{m^\beta}{m^\alpha}}\left(1 - \frac{Q^\alpha - Q^\beta}{2kT}\right) \\ &= \sqrt{\frac{m^\beta}{m^\alpha}}\left(2 - \sqrt{\frac{m^\alpha}{m^\beta}}\,\frac{w_0^\alpha}{w_0^\beta}\right).\end{aligned} \tag{22}$$

Here the w_0's are prefactors of the jump frequencies (independent of temperature)

$$w^\alpha = w_0^\alpha\, e^{-\beta Q^\alpha}. \tag{23}$$

1.c Quantum Theories

One of the first papers devoted to the quantum mechanical diffusion of massive particles in solids was by Gosar [12]. He studied the interstitial diffusion using a temperature dependent Green´s function method taking into account the interaction between phonons and impurity atoms. However, Gosar´s model for the ion-lattice interaction was perhaps too simple to correspond to real solids because he used a one-dimensional model with harmonic wells and his quantum states were those of a harmonical oscillator. Gosar recognized the existence of allowed energy bands, whose widths he evaluated employing the WKB-method obtaining for the band s

$$\Delta \epsilon(s) \simeq \frac{\pi}{2\,l(s)} \sqrt{\frac{\varepsilon(s) - U_0}{2m}}\,, \tag{24}$$

where $\varepsilon(s)$ is the energy of the bottom of the band and U_0 is the height of the potential barrier. $l(s)$ is approximately equal to the width of the potential barrier between the two interstitial cavities at the height of the band s.

Andreev and Lifshitz [13] studied the motion of crystal defects, impurities and vacancies, quantum mechanically in a periodic lattice at low temperature showing that they move practically freely through the crystal in narrow energy bands. Their approximate evaluation of the diffusion coefficient was based on the assumption of tight-binding-like bands

$$\varepsilon(\bar{k}) = \varepsilon_1 + \varepsilon_2 \left(\cos \bar{k}\cdot\bar{a}_1 + \cos \bar{k}\cdot\bar{a}_2 + \cos \bar{k}\cdot\bar{a}_3 \right), \qquad (25)$$

where the $\bar{a}_i$ are the primitive vectors of the lattice. Andreev and Lifshitz approximated this near $\bar{k} = 0$ as

$$\varepsilon = \varepsilon_0 + \frac{\hbar^2 k^2}{2M} \qquad (26)$$

M being some effective mass. They exhibited the temperature dependence of the diffusion coefficient from low temperatures, where the band motion is predominating, to intermediate temperatures, where D suffers a minimum because of interactions with phonons, up to high temperatures, where the activation type exponential is prevalent (classical diffusion).

At the time of publication of their study several papers appeared, where the motion of impurities or vacancies (defectons) were examined quantum mechanically (e.g. Hetherington [14], Klinger [15], Guyer and Zane [16] and Klinger [17]) from different points of view. To these papers belongs one by Flynn and Stoneham [18]. They considered the motion as hopping between localized eigenstates ϕ_p of the particle using perturbation theory. In their approach the saddlepoint itself played no important role, only the localized initial and final state wave functions were relevant. Naturally the overlap between these states in the saddlepoint region is principal factor in determining the hopping probability.

They calculated the hopping probabilities in terms of the matrix elements $J_{pp'}$ of the interaction potential between the ion and the lattice

$$W_{pp'} = \left\langle \sum_{n_{\bar{q}'}} w_{pp'}(n_q, n_{q'}) \right\rangle . \tag{27}$$

Here $w_{pp'}$ is the partial transition rate from the state $|p, \{n_q\}\rangle$, with the interstitial at site p and phonon occupation numbers n_q, to the state $|p', \{n_q^{\prime}\}\rangle$. It can be expressed as follows (a standard result from perturbation theory)

$$w_{pp'}(n_q, n_{q'}) = \frac{2\pi}{\hbar^2} \left| \langle \bar{p}, \{n_{\bar{q}}\} | \mathcal{H}_{int} | p' \{n_q^{\prime}\} \rangle \right|^2 D(\tilde{\omega}, t) . \tag{28}$$

The function $D(\tilde{\omega},t)$ represents a delta-function in the limit of long time t to ensure that the energy is conserved

$$D(\tilde{\omega}, t) = \frac{1}{2\pi} \int_{-t}^{t} d\xi \, e^{i\tilde{\omega}\xi} . \tag{29}$$

$\tilde{\omega} \cdot \hbar$ is equal to the change in the phonon system energy

$$\hbar\tilde{\omega} = \sum_q \hbar\omega_q (n_q' - n_q) . \tag{30}$$

By separating the phonon and particle variables and taking the thermal average they obtained after some calculations

$$W_{pp'} = \frac{|J_{pp'}|^2}{\hbar^2} \int_{-t}^{t} d\xi \, \exp\left\{ \sum_{\bar{q}} \frac{\omega_q^2 |\Delta Q_{\bar{q}}|^2}{2\hbar\omega_{\bar{q}}} \Big[(2n_{\bar{q}}+1)(\cos\omega_q\xi - 1) + \right.$$
$$\left. + i \sin\omega_q\xi \Big] \right\} . \tag{31}$$

Here $J_{pp'} = \langle \phi_p | \mathcal{H}int | \phi_{p'} \rangle$ and the $\Delta Q_q = Q_q^p - Q_q^{p'}$ are equal to the changes of the mean values of the normal-mode (mass-weighted) coordinates of the lattice during the transition.

Flynn and Stoneham approximated this integral to obtain different expressions for the high and low temperature regions. The preceding result was derived under the assumption that $J_{pp'}$ is independent of the lattice configuration and therefore they also calculated, in the latter part of their work, the role of lattice-activated processes. In lattice-activated diffusion the interstitial atom moves unhindered as the surrounding atoms fluctuate to "open" the barrier. In this case the potential barrier and the activation energy, respectively, can be very low. The theory of Flynn and Stoneham still leaves open the nature of localized states, which is difficult to determine and is strongly dependent on ion-lattice interaction.

Mineev [19] studied vacancies in crystals quantum mechanically in tight-binding bands. He evaluated approximately the bandwidths and -gaps and compared them with experimental values for the case of ^{3}He and ^{4}He crystals. This was done by solving approximately the system of Schrödinger equations for the vacancy and the surrounding atoms using as a pair interaction the Lennard-Jones potential model.

After the investigations of Flynn and Stoneham and Mineev a series of papers appeared devoted to studying the motion of defects in crystals, mainly vacancies and interstitial impurities. Of these we can mention Kagan and Maximov [20], Kagan and Klinger [21] and Klinger [22].

Kagan and Maximov [20] explored quantum diffusion in extremely narrow bands, whose widths $\Delta\epsilon$ are small compared with typical phonon frequencies. They derived an equation of motion for the density matrix including the interaction with phonons. Starting from the standard equation for the density matrix ρ

$$i \frac{\partial}{\partial t} \rho = \frac{1}{\hbar} [H, \rho] , \tag{32}$$

where $H = H_1^\circ + H_2 + H'$ and H_1° is the Hamiltonian of the particle in the periodic potential, H_2 is the Hamiltonian of the phonon subsystem and H' is the Hamiltonian of the particle phonon interaction. Using the particle density matrix $\rho_1 = \mathrm{Tr}_2\, \rho$ and $V = H' - \langle H \rangle$ they transformed the differential equation to an integral equation and finally obtained in the site representation ($\bar{m}$ is the site vector of the interstitial) a differential equation

$$\frac{\partial}{\partial t} \rho_{1\bar{m},\bar{n}} + \frac{i}{\hbar} [H_1 , \rho_1]_{\bar{m},\bar{n}} = - I_{\bar{m},\bar{n}} , \tag{33}$$

where

$$I_{\bar{m},\bar{n}} = \frac{\pi}{\hbar^2} \sum \rho_{2\alpha}^{(0)} \delta_\gamma (E_\alpha - E_\beta) \left\{ V_{\bar{m}\bar{s}}^{\alpha\beta} V_{\bar{s}\bar{l}}^{\beta\alpha} \rho_{1\bar{l}\bar{n}} + V_{\bar{l}\bar{s}}^{\alpha\beta} V_{\bar{s}\bar{n}}^{\beta\alpha} \rho_{1\bar{m}\bar{l}} - 2 V_{\bar{m}\bar{s}}^{\alpha\beta} V_{\bar{l}\bar{n}}^{\beta\alpha} \rho_{1\bar{s}\bar{l}} \right\} . \tag{34}$$

Here $V_{\bar{m},\bar{s}}^{\alpha\beta}$ means a double matrix element with respect to phonon states α and β and localized states centered around sites $\bar{m}$ and $\bar{s}$ respectively. The function $\delta_\gamma(x)$ (a Lorentzian approaching δ - function in the limit of small γ) is defined as

$$\delta_\gamma(x) = \frac{1}{\pi}\left(\frac{\gamma}{x^2+\gamma^2}\right). \tag{35}$$

γ equals

$$2\pi \sum_{p',\beta} \langle |V_{pp'}^{\beta\alpha}|^2 \, \delta(E_\alpha - E_\beta) \rangle \tag{36}$$

and E_α is a phonon energy.

One of the basic assumptions in deriving this equation was that the characteristic time within which the density matrix ρ_1 changes ($10^{-7}\ldots10^{-12}$ s) is large compared with all the characteristic interaction times ($\ll 10^{-15}$ s). Recognizing that the off-diagonal matrix elements of V in the site representation are very small they obtained

$$I_{\bar{m}\bar{n}}^{(0)} = \Omega_{\bar{m}\bar{n}} \, \rho_{1\,\bar{m}\bar{n}} \tag{37}$$

$$\Omega_{\bar{m}\bar{n}} = \frac{\pi}{\hbar^2} \sum \rho_{2\alpha}^{(0)} \, \delta_\gamma(E_\alpha - E_\beta) \left\{ V_{\bar{m}\bar{m}}^{\alpha\beta} V_{\bar{m}\bar{m}}^{\beta\alpha} + V_{\bar{n}\bar{n}}^{\alpha\beta} V_{\bar{n}\bar{n}}^{\beta\alpha} - 2 V_{\bar{m}\bar{m}}^{\alpha\beta} V_{\bar{n}\bar{n}}^{\beta\alpha} \right\}, \tag{38}$$

where $\rho_{2\alpha}^{(0)}$ is the phonon equilibrium density matrix, because we can clearly assume that the phonons are in equilibrium with the impurity atom. $I_{\bar{m}\bar{n}}$ describes a kind of a collision integral and determines the attenuation of the off-diagonal elements. Clearly $\Omega_{\bar{m}\bar{n}}$ determined by the intrasite scattering has nothing to do with the overlap between the states of the neighbouring sites. Because $\Omega_{\bar{m}\bar{m}} = 0$, $I_{\bar{m}\bar{m}}$ has to be calculated more accurately to second order as was done in [17]

$$I^{(2)}_{\bar{m}\bar{m}} = \frac{2\pi}{\hbar^2}\sum \rho^{(0)}_{2\alpha}\,\delta_\gamma(E_\alpha - E_\beta)\,|V_{\bar{m}\bar{s}}|^2\,(\rho_{1\bar{m}\bar{m}} - \rho_{1ss}). \qquad (39)$$

This gives the attenuation factor for the diagonal elements of the density matrix corresponding to intersite scattering ($\bar{m} \to \bar{s}$) in noncoherent tunneling. Approximating further these expressions Kagan and Maximov obtained finally for D

$$D = D_{coh} + D_{incoh}, \qquad (40)$$

where

$$D_{coh} = \frac{h^2 a^2 z}{3\hbar^2 \Omega_1} \qquad (41)$$

$$D_{incoh} = \frac{\pi z a^2}{3\hbar}\sum \rho^{(0)}_{2\alpha}\,|V^{\alpha\beta}_{\bar{m},\bar{m}+\bar{g}}|^2\,\delta(E_\alpha - E_\beta)\,. \qquad (42)$$

h means here the matrix element of H′ between the states of the nearest sites, z the number of nearest sites and a the interatomic distance $a_0\sqrt{3}/4$. The frequency Ω_1 equals $\Omega_{\bar{m}\bar{n}} = \Omega_{\bar{m}-\bar{n}} = \Omega_{\bar{g}}$, where $\bar{g}$ is the difference between neighbouring sites, $\bar{m} - \bar{n} = \bar{g}$. D_{coh} derives from the coherent tunneling of the particles and is limited by the correlation-breaking frequency or attenuation frequency Ω_1 of the nondiagonal elements of the density matrix. The correlation breaking is due to intrasite scattering by phonons and the tunneling happens without the assistance of phonons. In contrast to this is the incoherent diffusion, in which tunneling into the neighbouring site takes place through excitation by the phonon system and so D_{incoh} is determined by intersite scattering. Taking into account that the particle distribution in the intra-well levels is of the Boltzmann type, the diffusion coefficient can be written

$$D = \sum_s (D^s_{coh} + D^s_{incoh}) e^{-\epsilon_s/kT} Z^{-1} \qquad (43)$$

$$Z = \sum_s e^{-\epsilon_s/kT} \qquad (44)$$

and this gives the familiar activation type exponent at high temperatures, where the overbarrier diffusion is strongest.

Kagan and Klinger [21] developed further the previous method by more detailed calculations and by using a two-phonon coupling as an interaction between the particle and the phonons. Klinger [22] revised the theory making it more general and using as interaction a multi-phonon coupling. In the following both of these theories shall be reviewed parallel and we shall present a few results, some of which will later be used in this study.

Kagan and Klinger showed that the basic scattering mechanism limiting the coherent diffusion is due to dynamical destruction of the bands, which is caused by fluctuations of the relative shifts of energy levels between neighbouring wells. The fluctuations arise from the interaction between the ion and the phonons. They showed too that at high temperatures and at practical concentrations of impurities the overbarrier diffusion is dominating.

Kagan and Klinger [21] started from the same equation of motion for the density matrix as Kagan and Maximov, where their

Hamiltonian was $H = H_0 + H'$. Here H_0 is diagonal in the phonon states and H' is off-diagonal corresponding to the interaction with phonons. They obtained, after similar calculations, the same result for Ω_1, which corresponds to two-phonon intraband scattering. Kagan and Klinger evaluated Ω_1 (after this called Ω_{ib}) approximately at high temperatures within the Debye model

$$\Omega_{ib} \cong \left(\frac{kT}{\hbar\omega_D}\right)^2 \omega_D \left(\frac{\omega_D}{\omega_p}\right)^4, \qquad (45)$$

where $\hbar\omega_p$ is the characteristic gap for the bands. This result will later be used in connection with the relaxation of the particle distribution in the bands (in fact the distribution within a single band).

The expressions for the coherent and noncoherent (hopping) diffusion coefficients become of the following forms

$$D^s_{coh} = \frac{z a^2 \Delta_s^2}{3\hbar^2 \Omega_{ib}^2} \approx \frac{z a^2 J_s}{3\hbar^2 \Omega_{ib}} \qquad (46)$$

being the approximate coherent part and

$$D^s_{incoh} = \frac{z a^2}{3\hbar^2} J_s^2 \, e^{-2\phi^s(T)} \int_0^\infty dt \left(e^{\psi^s(t)} - 1 \right). \qquad (47)$$

Here J_s equals the coherent bandwidth and

$$\psi_s(t) = \sum_\lambda \frac{2|W_\lambda(s)|^2 (1-\cos(\bar{f}\cdot\bar{g}))\cos(\omega_\lambda t)}{\hbar^2 \sinh\left(\frac{\omega_\lambda}{2kT}\right)} \qquad (48)$$

and

$$\phi^{s}(T) = \sum_{\lambda} |W_{\lambda}(s)|^{2} (1 - \cos(\bar{f} \cdot \bar{g}))(2\bar{n}_{\lambda} + 1) . \qquad (49)$$

The dimensionless component of the distortion field near the interstitial for the λth normal mode is

$$W_{\lambda}(s) = \sqrt{2M\omega_{\lambda}^{3}N} \sum_{j} \left(\left(\frac{\partial V(\bar{r},\bar{R})}{\partial \bar{R}_{j}} \right)_{\bar{R}_0^0} \right)_{ss} \hat{e}_{\lambda} \left(e^{i\bar{f}\cdot\bar{R}_j} - 1 \right) . \qquad (50)$$

Here ω_{λ} is a normal mode frequency with wavevector $\bar{f}$ and polarization $\hat{e}_{\lambda}$ having the equilibrium occupation $\bar{n}_{\lambda}$.

Kagan and Klinger approximated these equations in order to obtain numerical results for real systems and after summing the contributions from all overbarrier bands at high temperatures they gave the result

$$D_{0} \simeq \frac{z a^{2}}{\hbar^{2}} \sqrt{\frac{\hbar^{3} k T^{*} \omega_{p}}{2 m l_{0}^{2} \Delta E_{gap}}} . \qquad (51)$$

l_o is the width of the barrier ($\approx \alpha$, the jump distance) and $\hbar\omega_p$ describes the typical underbarrier band gap; ΔE_{gap} is the same for overbarrier bands. With this result in mind we shall estimate D_o numerically in section 3.c.

Kagan and Klinger have also treated lattice-activated processes [23] caused by fluctuational barrier "preparation". They showed that in this mechanism the coherent diffusion coefficient may increase with increasing temperature contrary to its normal behaviour. For the noncoherent part they showed that in general the lattice activated process is of importance at high temperatures.

Weiner [24] studied interstitial diffusion applying his theory to hydrogen diffusion in metals with fcc structure. He approximated the lowest region of the potential well with a harmonic potential and examined the motion of a time dependent Gaussian wave packet in it

$$\psi(x,t) = (\pi\sigma)^{-1/4}\, e^{\frac{i\bar{p}x}{\hbar} - \frac{(x-\bar{x})^2}{2\sigma^2}}. \tag{52}$$

Here the bar denotes a quantum mean value and the width σ is equal to

$$\sigma = \sqrt{\frac{\hbar}{m\omega}}\,. \tag{53}$$

m represents the mass of the interstitial and ω is the frequency of the oscillator in the harmonic region. With the aid of this packet Weiner calculated the rate at which the impurity atoms leave the well

$$f_Q = \frac{1}{m}\int_0^\infty d\bar{p}\;\bar{p}\,\rho_Q(0,\bar{p})\,K_Q(\bar{p})\,. \tag{54}$$

Where $K_Q(\bar{p})$ is the quantum transmission function and it has the form in the case of piecewise quadratic potential

$$K_Q(E_k) = \frac{1}{2}\,\mathrm{erfc}\left\{\sqrt{\frac{2E_b}{\hbar\omega}}\left(1-\sqrt{\frac{E_b}{E_k}}\right)\right\}. \tag{55}$$

$f_Q(x,p)$ is the distribution function and E_b is the barrier height and $E_k = \bar{p}^2/2m$. He obtained for the actual activation energy

$$U_0 = E_b + \tfrac{1}{4}\hbar\omega . \tag{56}$$

From this rate it is easy to calculate D in various cases.

Finally we can mention the recent quantum approach of Gorham-Bergeron [25]. He applied the Kubo expression for D to the problem of motion of hydrogen atoms in metals. He used as an interstitial atomic wave functions harmonic states obtaining for D

$$D = \frac{1}{m}\sqrt{\frac{\pi\hbar^2 kT}{2(E_b + \frac{1}{2}\hbar\omega\bar{b}^2)}}\ \exp\left\{-\frac{1}{2kT}\left(E_b + \tfrac{1}{2}\hbar\omega\bar{b}^2\right) - \frac{\hbar\omega}{2kT\left(2b^2 + \frac{E_b}{\hbar\omega}\right)}\right\}, \tag{57}$$

where

$$\bar{b}^2 = b^2\left(\frac{m\omega}{2\hbar}\right) \tag{58}$$

b being the jump distance and E_b is the binding energy of the lattice deformation caused by the interstitial. $\frac{1}{4}\hbar\omega\bar{b}^2$ describes the height of the barrier U_0 approximatively.

In the following chapters we will represent, in more detail, an application of some of the preceding quantum theories to an existing and experimentally important diffusion problem; lithium atom (which exists as a singly ionized impurity in most crystals) in germanium and silicon.

Section a. in chapter 2. deals with the band structure of an interstitial in the lattice and shows how to calculate it. In section b. the diffusion coefficient is calculated using Boltzmann's transport equation and the respective relaxation time is taken from the theory of Kagan and Klinger just reviewed. Chapter 3. section a. is devoted to study the suitable potential model conforming to experimental activation energies. In the next section b. the band structures are evaluated and in section c. are the final expressions for D. Chapter 4. discusses the results obtained and compares them with experimental values shown in table 1. in section 3.c.

2. DIFFUSION IN NARROW BANDS

a. Band model for interstitials

When an interstitial atom or ion moves in a perfect periodic lattice it experiences the lattice periodic even in the case when it distorts the lattice around it over a large volume (the adiabatic approximation). By Bloch´s theorem the particle behaves in a periodic lattice according to

$$\psi_{\bar{k}}(\bar{r}) = e^{i\bar{k}\cdot\bar{r}}\, u_{\bar{k}}(\bar{r}), \tag{59}$$

where $u_{\bar{k}}(\bar{r})$ is periodic in the lattice. Fluctuations in lattice atoms owing to thermal excitations can be handled in this model as perturbations although larger than in the case of electrons moving in the lattice.

Using the Born-von Karman boundary conditions we obtain the allowed $\bar{k}$-values in reciprocal lattice

$$\bar{k} = \sum_{i=1}^{3} \frac{n_i}{N} \bar{b}_i, \tag{60}$$

where the $\bar{b}_i$ are the reciprocal lattice primitive vectors and N is the number of lattice sites n_i being some integer. For the density of $\bar{k}$-values we have the familiar result $\frac{V}{(2\pi)^3}$.

The strongly repulsive potential between interstitial and lattice atoms causes the bands to separate and they become extremely narrow. The narrowing is mostly due to the large masses of solute atoms compared with electrons ($m \sim 10^3 \ldots 10^5 m_e$) and the potential causes further the effective masses to be very large, especially for bands below the barrier. The widths of the bands can easily be evaluated to be of order

$$\Delta \epsilon_n \simeq \frac{2\pi^2 \hbar^2}{m_n^* \, a_0^2} \qquad (61)$$

by supposing the bands to have a simple free-particle-like dispersion

$$\varepsilon_n(\bar{k}) = \varepsilon_n^0 + \frac{\hbar^2 k^2}{2 m_n^*}, \qquad (62)$$

n is the band index and m_n^* is the effective mass in band n.

The width of a band tells us the size of the overlap of the interstitial wavefunctions between neighbouring interstitial sites. Since the velocity of a Bloch particle in a band is determined by the relation

$$\bar{v}_n(\bar{k}) = \frac{1}{\hbar} \nabla_{\bar{k}} \, \varepsilon_n(\bar{k}) \qquad (63)$$

we can infer that in these bands the velocities are small, of the order $2\pi\hbar/m^* a_0$. As long as there exists any overlap between the states of the neighbouring sites the particles will have finite velocities to move freely through the crystal. At high temperatures large fluctuations scatter the particles and their average free path becomes shorter than the lattice constant a_0.

We can use as the Bloch wave function a wave packet composed of all Bloch states in a given band

$$\psi_{\bar{k}}(\bar{r}) = \sum_{\bar{k}'} u_{\bar{k}'}(\bar{r})\, e^{i\bar{k}'\cdot\bar{r}} \qquad (64)$$

provided that $u_{\bar{k}}(\bar{r}) \approx 0$ when $|\bar{k}-\bar{k}'| > \Delta\bar{k}$. This wave packet is localized in $\bar{k}$-space around the value $\bar{k}$ and in spatial space we can use the uncertainty relation with the uncertainty in $\bar{k}$ of order of the size of the Brillouin zone $2\pi/a_0$ (see Garćia-Moliner [26])

$$\Delta x \Delta k \simeq \frac{1}{2} \quad \Rightarrow \quad \Delta x \simeq \frac{a_0}{4\pi}. \qquad (65)$$

This certainly localizes the particle within one primitive cell.

At the moment we are lacking methods to calculate band structures for massive particles in repulsive potentials. In this work we have used a simple one-dimensional method to approximatively find out the band structures (se appendix B). In general the band spectrum falls into the relevant energy interval as shown in figure 4. below.

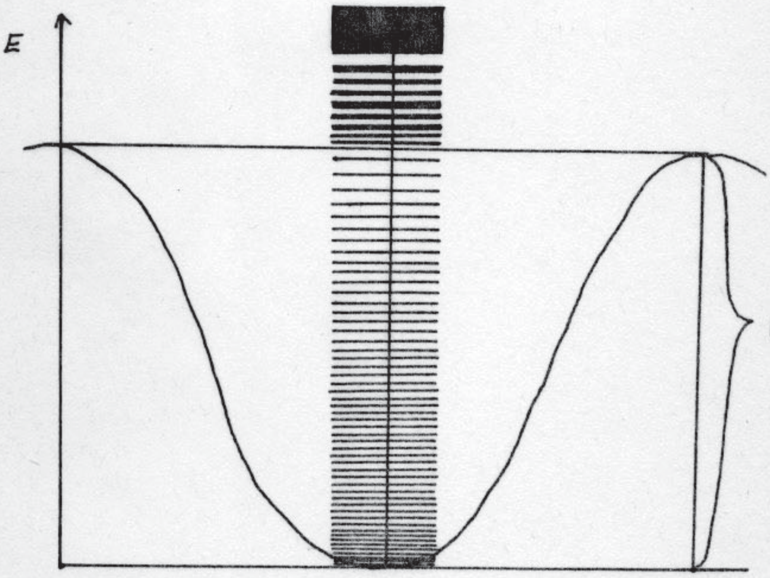


Figure 4. Typical energy bands

The bands are extremely narrow below the barrier and the gaps are also relatively small. Around the top of the barrier the bands are much broader and the gaps are smaller than below the barrier. The widths and gaps grow steadily as the energy is increased and at some specific energy the spectrum turns into a continuum (see [22]).

2.b. Calculation of the diffusion coefficient

The narrow bands of allowed particle energies are occupied by interstitial atoms and due to the high temperature they obey classical Boltzmann statistics. The degeneracy temperature is very low for massive particles (compared with electrons); e.g. for Li atoms $T_{deg} \sim 10°K$ and even for H-atom it is less than 70°K. The equilibrium occupation is the Boltzmann factor

$$f(\varepsilon) = \frac{e^{-\beta\varepsilon}}{Z(\beta)} . \tag{66}$$

The mechanism that brings the system to equilibrium after perturbations is particle-phonon intra-band scattering and to some extent the inter-band scattering causes relaxation. The roles of these processes depend critically upon the band structure, especially the bandgaps.

Klinger has calculated the relaxation time due to the inter-band scattering and he gives (see Klinger [22])

$$\tau_{IB} = \Omega_{IB}^{-1} \tag{67}$$

$$\Omega_{IB} \simeq \omega_p \left(\frac{kT}{\hbar\omega_p}\right)^{\nu} , \tag{68}$$

where $\hbar\omega_p$ is a typical bandgap and ν tells how many phonons are needed in the process

$$\nu = \left(\frac{\omega_p}{\omega_{phonon}}\right) . \tag{69}$$

In the Debye model ($\omega_{phonon} \approx \omega_D$ for most phonons) we can evaluate this and we have e.g. for Li in Ge at T~1000°K

$$\Omega_{1B} \simeq 1,3 \cdot 10^{14} \frac{1}{s} \quad (\nu = 1\ ,\ \hbar\omega_{phonon} \leq \hbar\omega_D). \qquad (70)$$

This compared with the intra-band two-phonon inverse relaxation time (see section 1.c.)

$$\Omega_{ib} \approx 5 \cdot 10^{17} \frac{1}{s} \ldots\ 2 \cdot 10^{15} \frac{1}{s} \quad (\hbar\omega_p \simeq 0.005\,eV \ldots\ 0.02\,eV) \qquad (71)$$

is a factor of approximately same order and we can use both of them in the calculation of the relaxation time

$$\frac{1}{\tau_{rel}} = \frac{1}{\tau_{1B}} + \frac{1}{\tau_{ib}} = \Omega = \Omega_{1B} + \Omega_{ib}. \qquad (72)$$

Kagan and Klinger [21] and Klinger [22] have stated that at high temperatures the overbarrier noncoherent diffusion (excitation of phonons) is dominating and we can neglect the underbarrier contribution. With this in mind we can calculate the mobility μ for interstitials in the relaxation time approximation assuming that the dominating mechanism for relaxation is a two-phonon intra-band intra-site scattering with the single-phonon inter-band scattering mechanism assisting.

We have, in appendix C, calculated the mobility by means of the Boltzmann transport equation under the action of a small external field on the charged interstitial ions. The Nernst-Einstein relation

$$\mu = M \beta Z e D \tag{73}$$

has been used to connect μ and D. Here M is an empirical coefficient, which depends on solute-solvent pairs. In the case of Li in Ge and Si, M has been observed experimentally to be equal to 1.0 (see Shaw [27]). We obtain

$$D = \frac{\int_{B.Z.}^{\epsilon \geq \epsilon_0} d\bar{k}\, \bar{v}_{\bar{k}}^2 \cos^2\theta\, \tau(\bar{k}) f^0(\bar{k})}{\int_{B.Z.}^{\epsilon \geq 0} d\bar{k}\, f^0(\bar{k})} \; . \tag{74}$$

The denominator acts here as a partition function and normalizes the numerator.

To transform D to form suitable for numerical calculations we need to do some approximations. First we must take $f^0(k)$ outside the integral sign because the variation of $f^0(k)$ in extremely narrow bands is vanishingly small and we get

$$D \simeq \frac{\sum_{j=n}^{\infty} e^{-\beta E_j} \int_{B.Z.}^{band\, j} d\bar{k}\, \bar{v}_{j\bar{k}}^2 \cos^2\theta\, \tau_j(\bar{k})}{\sum_{j=1}^{\infty} e^{-\beta E_j} \int_{B.Z.}^{band\, j} d\bar{k}} \, , \tag{75}$$

where E_j means the lower edge of band j. The index n means naturally the first band, which exceeds the barrier. Next we shall approximate the Brillouin zone (the first one) with a sphere of the same volume v_B without making any crucial error. As can easily be seen the terms $j \geq n + 1$ in the numerator are small compared with the dominating $j = n$ term due, of course, to the exponential functions in front of the integrals. This allows us to neglect all other terms provided that the difference between E_{n+1} and E_n is more than kT.

With these approximations D becomes

$$D \simeq \frac{\sum_{n}^{m} e^{-\beta E_j} \int_{v_B}^{\text{band } j} d\bar{k}\, v_{j\bar{k}}^{2} \cos^2\theta\, \tau_j(\bar{k})}{v_B \sum_{1}^{\infty} e^{-\beta E_j}}, \qquad E_m - E_n \leq kT \tag{76}$$

Now we can use the relaxation time calculated in the preceding section

$$\frac{1}{\tau_{rel.}} = \Omega_{IB} + \Omega_{ib} \tag{77}$$

$$\begin{aligned} \Omega_{IB} &\approx \Delta E_{gap} \left(\frac{kT}{\Delta E_{gap}}\right)^{\nu} \\ \Omega_{ib} &\approx \left(\frac{kT}{\hbar\omega_D}\right)^2 \omega_D \left(\frac{\omega_D}{\Delta E_{gap}}\right)^4, \end{aligned} \tag{78}$$

where ΔE_{gap} represents the typical (dominating) bandgap. Because Ω is nearly band independent and does not have any $\bar{k}$-dependence we can take it in front of the summation

$$D \simeq \frac{\sum_{m}^{n} e^{-\beta E_j} \int_{v_B} d\bar{k}\, v_{j\bar{k}}^{2} \cos^2\theta}{\Omega\, v_B \sum_{j=1}^{\infty} e^{-\beta E_j}}. \tag{79}$$

This expression for D we can use in numerical calculations in the next chapter after we have obtained the band structures.

The temperature dependence of D is primarily due to the exponential functions from two sources as can easily be seen;

the term $e^{-\beta E_n}$ in the numerator and $e^{-\beta E_1}$ in the denominator giving

$$D \propto e^{-\beta(E_n - E_1)} \tag{80}$$

and we can in most cases neglect the other terms. This is valid, of course, when assuming that the bandgaps are relatively large ($\Delta E_{gap} >$ kT and kT$\gg$0). If two or more bands were very near each other, we can handle them as a single band (energy-averaged in some suitable way). The other bands act only at very high temperatures often above T_m, the melting temperature) causing the otherwise straight-line behaviour in an Arrhenius-plot (logD vs. β) to bend. Clearly $E_n - E_1$ gives the classical activation energy, which in many cases may be larger than the height of the potential barrier.

The β-dependence of Ω will be omitted in this study because the value given by Klinger et al. is only an estimation at high temperatures and it must be calculated at one single temperature T^* in the middle of the temperature range at hand. The same applies to D_o, which Kagan and Klinger gave and where we have the dependence $D_o \propto \beta^{-1/2}$. This fact also strains other theories; we remember the theory of Nardelli and Reatto and the theory of Gorham-Bergeron, where T has to be fixed (see also Flynn and Stoneham [18]).

3. APPLICATION OF THE THEORY

a. The potential model

The preceding theory is in this chapter used to calculate explicit numerical expressions for the diffusion coefficients of a singly ionized lithium atom in germanium and silicon by first determining the interaction potential and then calculating the energy band structures. The unknown potential parameters are fitted to achieve experimental activation energies after which D is available through application of the previous equations.

The lattice potential seen by the interstitial has the form

$$U(\bar{r}) = \sum_{\bar{R}_j, i} \mathcal{V}(\bar{r} - \bar{R}_j - \bar{d}_j). \qquad (81)$$

$\mathcal{V}(r)$ is the direct ion-lattice potential, which consists mainly of two parts; the dominating repulsive part coming from the overlap of tightly bound inner shell electrons and the screened Coulomb interaction between nuclei and the small attractive part coming from the polarization of host atoms surrounding the interstitial and possibly from other effects, e.g. van der Waals interaction. The distortion in the lattice structure caused by the interstitial around itself will in general bring a contribution to the migration energy but in the case of lithium we shall neglect this term because lithium has a small ionic radius (~ 0,60 Å) and is generally considered to have only a very small distorsive effect (see [33]). All attractive terms will also be neglected in the following due to their smallness and because their behaviour as a function of r is relatively flat (see [31]).

The lattice potential U(r) was calculated with a computer using several models for the repulsive potential taking into account the contribution of several million surrounding atoms. This was necessary due to the long ranges of the potential models used and it was observed that the lattice sum converged in the case of screened Coulombic potentials rather slowly. The points in the primitive cell, where the potentials were calculated in double precision, are shown in appendix A. The tetragonal site T is located in the center of the conventional cell and has four nearest neighbours and the hexagonal site H is located in the center of the six member ring commposed of the lattice atoms. These sites are possibly the only points, where the lattice potential could reach its minimum (in case of repulsive potential) the other of them working as a saddlepoint, through which the diffusion occurs. In all of the calculations it was revealed that the tetragonal site had a lower lattice potential, thus being the equilibrium point and the hexagonal point was the saddlepoint. Thus an atom residing at the T-site has four nearest equivalent T-sites available to go through the respective H-sites ($z = 4$).

The repulsive potential has acquired several forms in the theory of migration of atoms in semiconductors. A model called the Born-Mayer potential (see Weiser [29]) was earlier used in studying the atomic migration. It corresponds mainly to the repulsive action of core electrons and has no diverging (r^{-1}) behaviour

$$V_{BM}(r) = A e^{-r/r_0}. \qquad (82)$$

In this work calculations were made with V_{BM} but it had to be rejected due to its weakness, that is the potential barrier height was far too low compared with experimental values.

The second model employed in the calculations was the ordinary screened Coulomb potential (Hu [31] and Nardelli and Reatto [10])

$$V_c(r) = \frac{A e^{-\lambda r}}{r} \qquad (83)$$

Here λ is the screening length defined by the solute concentration and varies from 2 Å to 40 Å. It has been evaluated by Dingle [32] and Kennedy [35]. Dingle´s suggestions varied from 40 Å in dilute solutions (calculated with his equations) at about 1000 °K temperature, to 7 Å (Ge) and 4 Å (Si) at large concentrations (near the limit of solid solubility of Li). Kennedy proposed values between a_0 and 10 Å both for Ge and Si at practical concentrations.

The prefactor A has the form

$$A = \frac{Z_1 Z_2 e^2}{4\pi \epsilon_0 \epsilon} \qquad (84)$$

ϵ being the dielectric constant Z_1 and Z_2 being determined by Pauling [34] and Swalin [33] from an empirical standpoint. Pauling introduced the concept of imperfect screening and a value of the screening coefficient 0.4 was found for electrons in valence orbitals and for deeper lying core electrons a value equal to 1.0. Because Ge and Si have four valence electrons forming the tetrahedral bonds this rule gives effective valence $Z_2 = 2.4$ for both atoms. Lithium exists in a singly ionized state and its value for Z_1 will be 1.0 (if Li could be neutral in the lattice, Z_1 would be 0.6). The values of ϵ used in A are 16.0 for Ge and 11.8 for Si. The resulting behaviour of the potential barrier for Li in Ge is shown in figure 5. as a function of λ calculated with the aid of lattice sums as described earlier. But the experimental value for U_o, the activation energy, is about 0.53 eV (for Li in Si it is about 0.66 eV, see table 1.) so this model can not correspond to reality and it must be likewise rejected.

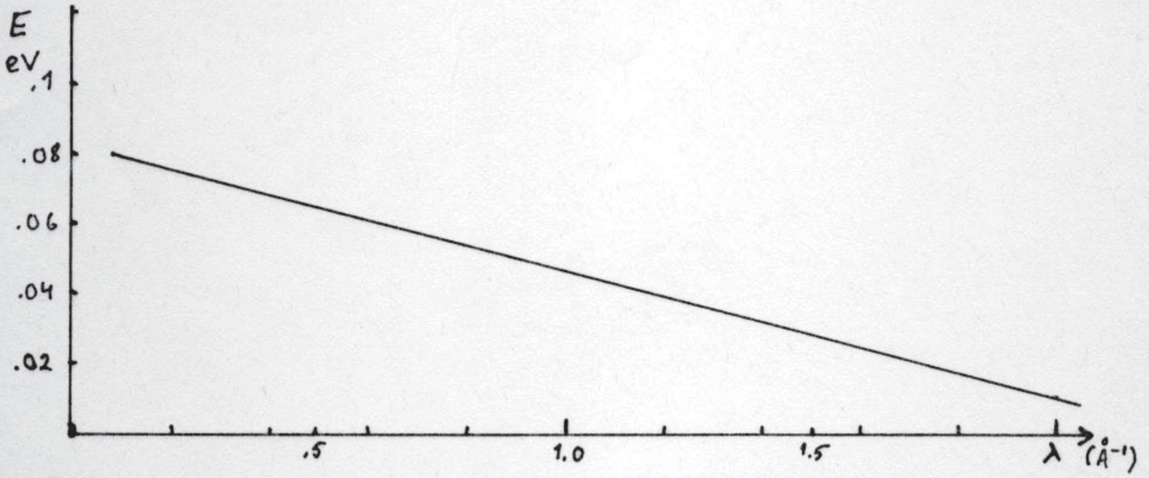


Figure 5. The potential barrier height $U_o(\lambda)$ using V_C (Ge)

In fact we can modify this potential to achieve satisfying results. The screened Coulomb potential corresponds mainly to the screened electrostatic interaction between positively charged nuclei without taking into account the repulsivity of ion cores and weakening of screening at short distances ($r < r_I + r_L$, where r_I = ion core radius of Li $\approx$ 0.60 Å and $r_L = r(\mathrm{Ge}) \approx$ 1.22 Å and for Si $r(\mathrm{Si}) \approx$ 1.17 Å, see Weiser [29]). We can understand that the macroscopic dielectric constant ϵ must diminish as the interaction distance r becomes of microscopical order of length and it must approach its vacuum value 1.0 due to weakening of the screening. This transition from ϵ to 1 can be made in the spirit of screened interaction and we assume the following exponentially damping form for $\epsilon(r)^{-1}$

$$\frac{1}{\epsilon(r)} = \frac{1}{\epsilon}\left(1 + (\epsilon - 1)e^{-\alpha r}\right). \tag{85}$$

This gives $\epsilon(r)^{-1} \approx 1/\epsilon$ at large distances and unity at very short r and this function can be substituted for $1/\epsilon$ in the expression for A

$$\mathcal{V}(r) = \frac{Z_1 Z_2 e^2 e^{-\lambda r}\left(1 + (\epsilon - 1)e^{-\alpha r}\right)}{4\pi\epsilon_0 \epsilon r}. \tag{86}$$

This modification strengthens the potential at very short distances ($r \lesssim 1/\alpha$) taking better into account the contribution from the repulsive cores. It also gives us two adjustable parameters, λ and α . As can be seen from figure 5. the potential barrier height does not much change as a function of λ and this applies to the corrected model as well. The main variable is α and the behaviour of $U(\lambda,\alpha)$ in this new model can be seen in figures 6.

and 7. as a function of α for Li in Ge and Si respectively.

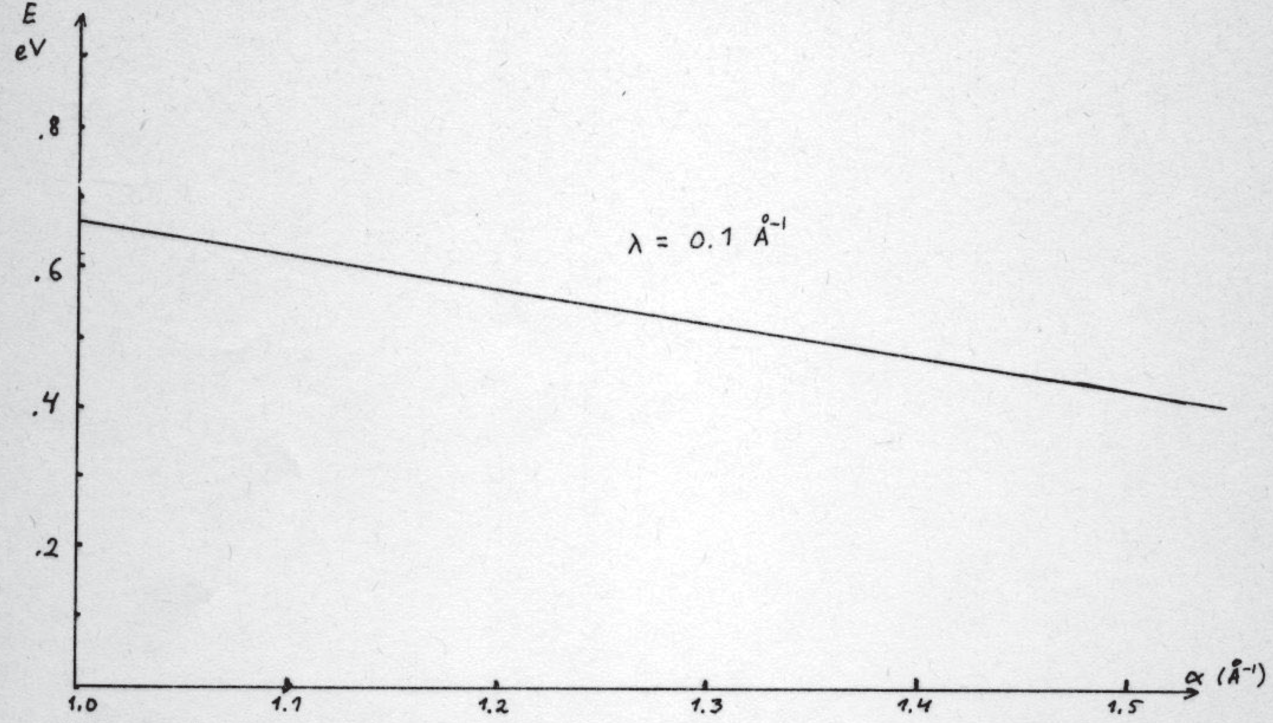


Figure 6. The potential barrier height $U(\lambda,\alpha)$ as a function of α in the corrected Coulomb potential model (Ge)

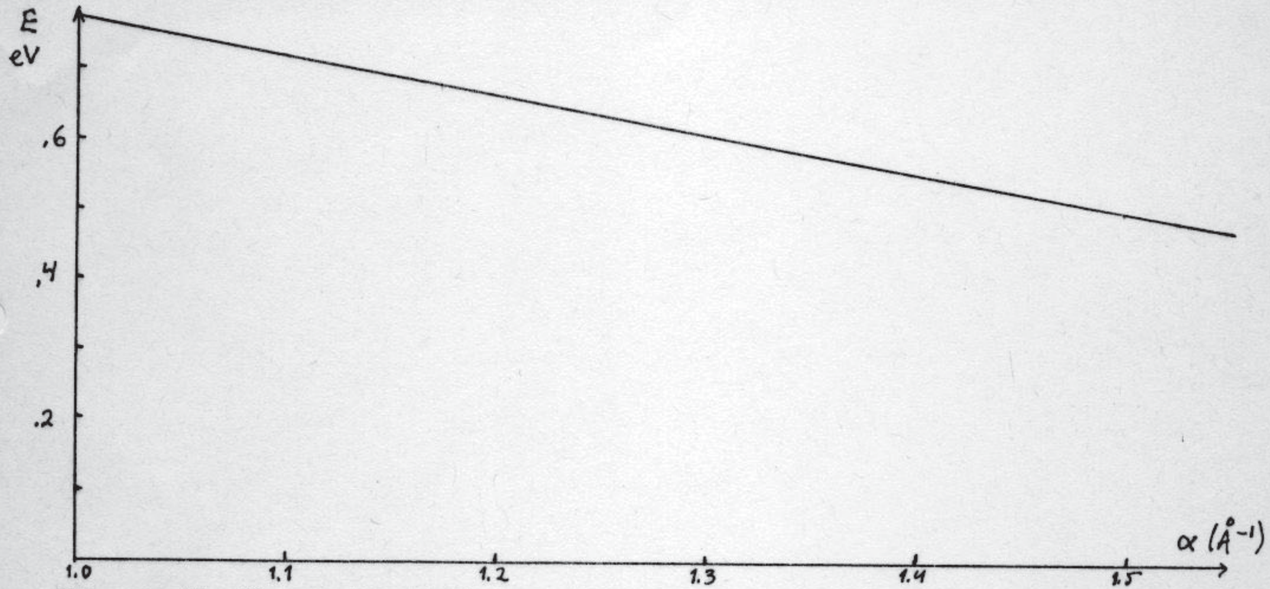


Figure 7. The potential barrier height $U(\lambda,\alpha)$ as a function of α in the corrected Coulomb potential model (Si)

Clearly this model gives realistic activation energies and we can now pick the proper values of λ and α. λ can be fixed by the previous arguments to have the value 0.1 $Å^{-1}$ for both Ge and Si corresponding to a screening length 10 Å being far from critical, thus the principal problem lies in choosing α. It can be done by comparing the resulting activation energies with the experimental values. This method gives values of α for Ge and Si 1.275 $Å^{-1}$ and 1.210 $Å^{-1}$ respectively.

3.b. Calculation of band structures

The band structures for Li in Ge and Si were calculated approximatively with a one-dimensional method having as the lattice potential a model similar to that used by Gosar [12], see figure 8. below. The assumption of a one-dimensional motion is not far-fetched in interstitial diffusion in diamond structure although it is not exactly correct (see appendix A)

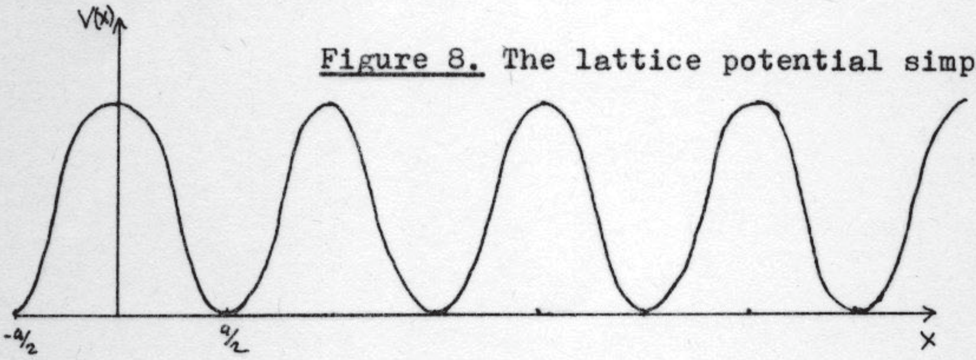


Figure 8. The lattice potential simplified

The bandwidths and -gaps were evaluated in this model after a relation between the transmission coefficient $|t|$ (penetration through the single potential barrier) and the particle energy parameter q was established (see appendix B for details)

$$\frac{\cos(qa+\delta)}{|t|} = \cos ka \, . \qquad (87)$$

Here k is the particle wave vector and a is the period of the potential and δ is the phase shift, which the barrier causes to the transmitted particle wave function. The energy dispersion relations $E = E(\bar{k})$ were not calculated explicitly in the bands. It is a good approximation to assume that the dispersion relations for underbarrier bands (and for the lowest bands over the barrier) are of the form (see [13]) typical in tight-binding states

$$E(\bar{k}) = E_1 + E_2 \left(\cos \bar{k}\cdot\bar{a}_1 + \cos \bar{k}\cdot\bar{a}_2 + \cos \bar{k}\cdot\bar{a}_3\right) \qquad (88)$$

The overbarrier bands are more or less of this form with various effective masses. As a result of the calculations done in appendix B we have the bandwidths and -gaps near the barrier top ($|t| \approx 1$)

$$\Delta E_{gap} \approx \frac{\hbar^2 4\pi n}{2ma^2}\sqrt{1-|t|} \qquad (89)$$

$$\Delta E_{band} \approx \frac{\hbar^2 \pi^2 (2n+1)}{2ma^2} \qquad (90)$$

and below the barrier ($|t| \approx 0$)

$$\Delta E_{gap} \approx \frac{\hbar^2 2\pi^2 (n+1)}{2ma^2} \qquad (91)$$

$$\Delta E_{band} \approx \frac{\hbar^2 4\pi (n+1)|t|}{2ma^2} . \qquad (92)$$

Here a is the period of the potential, which is equal to the jump distance $a_0\sqrt{3}/4$. These equations give us simple means to calculate numerically the band structures at least approximatively. The transmission coefficient $|t|$ can be calculated with the aid of the standard expression from the WKB-theory (see [49]) below the barrier

$$|t| = \frac{4}{\left(2\theta + \frac{1}{2\theta}\right)^2} \tag{93}$$

$$\theta = e^{\int_a^b dx \sqrt{\frac{2m}{\hbar^2}(V(x)-E)}} . \tag{94}$$

a and b are the classical turning points and the potential can be approximated with a sinusoidal or quadratic function near the top of the barrier if needed.

3.c. Results for D

The numerical values for the diffusion coefficient will be calculated in this section by means of the transport theory, equation (79), and the result of Kagan and Klinger, equation (51). This will take place after we have obtained the approximate band structures of Li in Ge and Si in those bands, which participate in diffusion.

The inverse transport time Ω, from the theory of Kagan and Klinger, shall be used as the relaxation time. In its definition, equation (78), the typical bandgap ΔE_{gap} will be obtained from the calculated band models. Since the transitions between bands near the barrier top are the most important for the transport process we can use the corresponding expression for the underbarrier gaps

$$\Delta E_{gap} \approx \frac{\hbar^2 2\pi^2 (n+1)}{2 m a^2} . \tag{95}$$

For the temperature T^* we will use values in the middle of the experimental high temperature range ($T^* = 900\,^\circ K$ for Ge and $T^* = 1100\,^\circ K$ for Si). This applies as well to the result for D_0 of Kagan and Klinger.

Taking in the result of transport theory only the first overbarrier band into account and neglecting all others except the lowest in energy (E_1) we obtain

$$D = D_o \, e^{-\beta (E_n - E_1)} , \tag{96}$$

where

$$D_o \approx \frac{\int_{v_B}^{band\,n} d\bar{k}\; v_{\bar{k}}^2 \cos^2\theta}{\Omega\; v_B} \qquad (97)$$

To simplify the calculations we make the assumption of spherical symmetrical bands of tight-binding type

$$E_n(k) = E_n^{o} + \Delta E_{band} \cos ka, \qquad a = \frac{\pi}{2k_s} = \frac{a_o}{4} \qquad (98)$$

This gives for the velocity

$$v_{\bar{k}} = \frac{-\Delta E_{band}\; a_o\; \sin\left(\frac{a_o k}{4}\right)}{4\hbar} \qquad (99)$$

and after a simple integration we obtain

$$D_o = \frac{\Delta E_{band}^2\; a_o^2}{\Omega\; \hbar^2} \left\{ \frac{3}{2\pi^2}\left(1 - \frac{2}{\pi}\right) \right\}$$

$$= \frac{\Delta E_{band}^2\; a_o^2\, \gamma}{\Omega\; \hbar^2} \qquad (100)$$

The number of underbarrier bands can be evaluated approximately by using the equation for the gap and taking into account that the bandwidths are extremely small. We can use the equation

$$\sum_{n=1}^{N} n = \tfrac{1}{2}\left(N^2 + N\right) \qquad (101)$$

to sum all gaps. Calculating in this way with various values of N we can fit N to obtain the experimental activation energies ($\approx$ 0.53 eV for Ge and $\approx$0.66 eV for Si) and we have $N \approx 32$ and $N \approx 34$ for Ge and Si respectively.

The bandgap below the barrier can be evaluated approximately by the previous equation

$$\Delta E_{gap} \approx \frac{\hbar^2 2\pi^2 (n+1)}{2m\, a^2}\ , \qquad E < U_0 \qquad n+1 \simeq N\ . \tag{102}$$

For the overbarrier gap we must find some other estimation instead of equation (89) to avoid the complicated calculation of $|t|$. In this purpose we shall use the estimation given by Kagan and Klinger [21] calculated by the WKB-method for the overbarrier bands near the top of the barrier

$$\Delta E_{gap} \approx \pi \sqrt{\frac{U_0 \hbar^2}{2m\, \beta^2}}\ , \qquad E > U_0\ . \tag{103}$$

U_0 is the barrier height and β is the typical linear dimension of the potential well near the barrier top. Thus β is approximately the jump distance minus the 90% limits of the barrier top assuming e.g. a sinusoidal barrier. This gives

$$\beta(\mathrm{Ge}) \approx 2.0\,\mathring{A} \tag{104}$$

$$\beta(\mathrm{Si}) \approx 1.9\,\mathring{A}\ . \tag{105}$$

Now we can modify the D_0 of Kagan and Klinger, equation (51), according to the present band model. The ratio between the underbarrier and overbarrier gaps needed to calculate D_o is now at our hands and so

$$D_o \simeq \frac{Z\alpha^2}{\hbar}\sqrt{\frac{\hbar^3 kT^* \Delta E_{gap}(E<U_o)}{2m\,\Delta E_{gap}(E>U_o)\,l_o^2}} \,. \tag{106}$$

l_o can be approximated by α , the jump distance, which equals $a_o\sqrt{3}/4$ in the case of diamond structure.

$$D_o \approx Z\alpha\sqrt{\frac{kT^* \Delta E_{gap}(E<U_o)}{2m\,\Delta E_{gap}(E>U_o)}} \tag{107}$$

becomes now

$$D_o \approx Z\sqrt{\frac{kT^*\hbar\,(n+1)\sqrt{2m\beta^2}}{2m^2\,\sqrt{U_o}}} \,. \tag{108}$$

Now we are in the position to give numerical estimates for D_o and table 1. below represents these values calculated by means of the data given in appendix D and in this section. In table 1. there are also some experimental values and results given by other theories.

The isotopic dependences of the bandwidth ΔE_{band} and the activation energy E_o can also be studied by employing the previous equations for the bandwidths and -gaps. For the bandwidth we get immediately

$$\Delta E_{band} \propto \frac{A}{m} \,. \tag{109}$$

Table 1. Results for $D = D_0 e^{-\beta E_0}$

	D_0(Ge)cm^2/s	D_0(Si)cm^2/s		E_0(Ge) eV	E_0(Si) eV
this work eq.(100)	$0.79\ 10^{-3}$	$0.30\ 10^{-3}$	values selected to represent the experimental average	0.53	0.66
Kagan & Klinger eq.(108)	$5.0\ 10^{-3}$	$5.2\ 10^{-3}$		-	-
exp. results	$1.3\ 10^{-3}$ [40]	$2.7\ 10^{-3}$ [42]	exp. results	0.46 [40]	0.62 [42]
	$2.5\ 10^{-3}$ [41]	$2.5\ 10^{-3}$ [44], [45]		0.51 [41]	0.66 [44],[45]
	$9.1\ 10^{-3}$ [42]	$2.2\ 10^{-3}$ [43]		0.56 [42]	0.70 [43]
	-	$3.3\ 10^{-3}$ [41]		-	0.65 [41]
	-	$4.4\ 10^{-3}$ [40]		-	0.78 [40]
other theories	$1.7\ 10^{-3}$ [29]	$1.6\ 10^{-3}$ [29]	other theories	0.57 [29]	0.52 [29]
	$3.6\ 10^{-3}$ [10]	$2.6\ 10^{-3}$ [10]		-	-
	$0.44\ 10^{-3}$ [12]	$0.94\ 10^{-3}$ [12]		-	-

The activation energy obeys the law

$$E_o \propto \frac{B}{m} \qquad (110)$$

as can easily be calculated. To study the isotopic dependence of D_0 in the transport theory, equation (100), we must take into account the mass dependence of Ω (see [22])

$$\Omega \propto m^{-1/2} \qquad (111)$$

giving for D_0

$$D_o \propto m^{-3/2} . \qquad (112)$$

The mass dependence of the result of Kagan and Klinger, equation (108), has clearly the form

$$D_o \propto m^{-1/2} , \qquad (113)$$

4. DISCUSSION

Now we are able to compare the results of our calculations with the experimental results and other theoretical calculations.

As we can see in table 1. the calculated results for D_o in the theory of Kagan and Klinger are of the same order of magnitude as the experimental values, which are rather diffuse and lack precise measurements over large temperature intervals. Other theoretical results are just as diffuse and scattered as can be seen in table 1. D_o's from transport theory are smaller than experimental values and besides rather critical in ΔE_{gap}. A small shift in ΔE_{gap} can change D_o by an order of magnitude.

The temperature dependence of Ω is quite strong giving D_o a dependence β^2, which has a too large impact on the total behaviour of D as a function of temperature (see appendix E). This anomaly was referred to in section 2.b. This in addition to the smallness of D_o shows clearly that the relaxation time must be calculated more precisely taking into account corrections from all phonon processes in addition to the two-phonon one.

The D_o's of Kagan and Klinger agree well with the experimental values showing that their theory is valid at high temperatures although the weak dependence $D_o \propto \beta^{-\frac{1}{2}}$ is not exactly in accord with the experimental behaviour, which to a high degree of accuracy is a straight line in an Arrhenius-plot (see appendix E).

The isotopic behaviour of D_o and E_o are in the transport theory

$$D_o \propto m^{-3/2} \qquad (114)$$

$$E_o \propto \frac{A}{m} . \qquad (115)$$

Let us for the sake of comparison recall some other theories: Flynn and Stoneham [18] have obtained in their theory the same behaviour for E_o in their oscillator model and for D_o the dependence $m^{\frac{1}{2}}e^{-\xi\sqrt{m}}$. Gorham-Bergeron [25] has achieved the same dependence for E_o also and for D_o he has the same result as Gosar [12] does

$$D_o \propto \frac{A}{m} . \qquad (116)$$

Weiner [24] obtained

$$E_o \propto \frac{A}{\sqrt{m}} + B . \qquad (117)$$

Klinger's theory gives the following (see ref. [22])

$$D_o \propto \frac{A}{m} \qquad (118)$$

$$E_o \propto \frac{B}{m} + C \qquad (119)$$

and finally the more general results of Kagan and Klinger [21]

$$D_o \propto m^{-\frac{1}{2}} \text{ to } m^{-1} \qquad (120)$$

It seems evident that quantum theories in general give dependences $D_0 \propto m^{\alpha}$ and $E_0 \propto m^{\beta} + \mathcal{H}$, where $\alpha = -\frac{1}{2} \cdots -1$ or stronger and $\beta = -1$. This differs from the classical theories, where D_0 is always exactly proportional to $m^{-\frac{1}{2}}$, E_0 having no mass dependence.

Experimentally the mass dependence is not solved because we are lacking precise measurements and large fluctuations in this respect have been observed (see LeClaire [11], Mundy [46], Pegel [47] and Matthews [48]). It is evident that there are many factors influencing the final mass dependence of D_0, e.g. the fraction, with which the lattice-activated process participates the diffusion.

The calculated bandwidths and -gaps are of the same order of magnitude as calculated by the WKB-theory in the article of Kagan and Klinger [21]. The results from the WKB-method are

$$\Delta E^{n}_{band}\,(E > U_0) \simeq \pi \sqrt{(E_n - U_0)\frac{\hbar^2}{2m\alpha^2}} \gtrsim 10^{-3}\ \mathrm{eV} \qquad (Li) \qquad (121)$$

$$\Delta E_{gap} \approx \pi \sqrt{\frac{U_0 \hbar^2}{2m\beta^2}} \gtrapprox 10^{-3} - 10^{-2}\ \mathrm{eV} \qquad (Li) \qquad (122)$$

Here α is the jump distance and β represents the typical linear dimension of the potential well near the barrier top.

The one-dimensional method employed in calculating the band structures in terms of the transmission coefficient is very simple and thus can not give very reliable results and for future calculations some tight-binding method converging fast enough should be developed to achieve more accurate results.

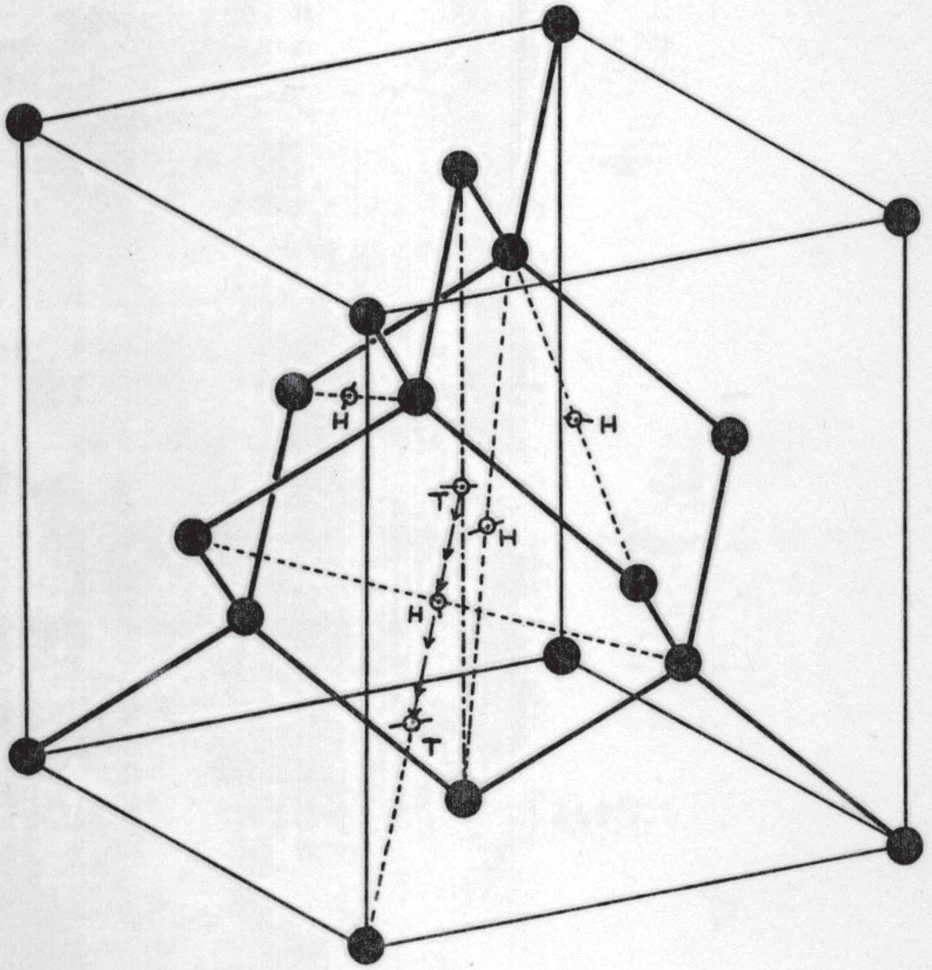
The potential model obtained in section 3.a. represents in some way the actual interaction between the Li-ion and lattice atoms. Of course it neglects the four bonds giving only a spherically symmetric pair potential (the bonds are implicitly contained in the effective valence).

It seems that quantum theories are able to tell us more about the physics of diffusion in solids than classical ones but at the cost of more complicated calculations. There are, however, many questions for the quantum methods to answer, which classical theories can not treat, e.g. the concentration dependence of D_0 and the motion of an interstitial atom in lattice dislocations and grain boundaries.

5. APPENDICES

Appendix A

Diamond structure and equilibrium sites



T = tetragonal site

H = hexagonal site

Appendix B

Solution of band structure

The band structure of an interstitial atom in diamond structure can be evaluated as a first approximation through the following, very simple, method (see [50]) without having any recourse to complex numerical methods. The actual three-dimensional potential may be approximated by a one-dimensional periodic potential (period a) of the same height as the potential barrier (see figure 9.)

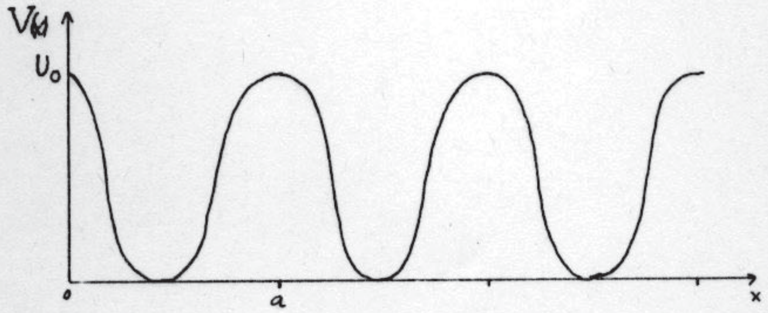


Figure 9. The lattice potential

This model can be composed of separate barriers of the type shown in figure 10. below

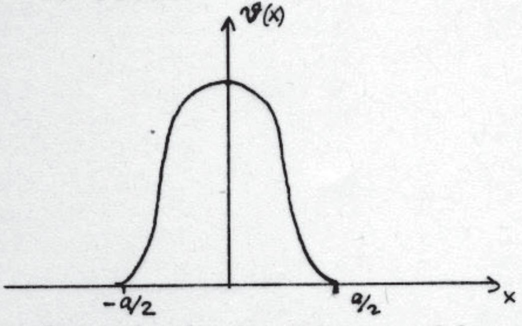


Figure 10. The single barrier problem

We may assume that v(x) is symmetrical about its mid-point leaving other properties of the barrier open. The band structure can be revealed by investigating the transmission and reflection coefficients of the interstitial in the presence of a single barrier v(x).

An atom coming from the left has the energy $\hbar^2 q^2/2m$. For the regions, where the potential is zero, the wave function will be of form

$$\psi_1(x) = e^{iqx} + r\,e^{-iqx} \qquad x \leq -a/2 \qquad (B\,1)$$

$$= t\,e^{iqx} \qquad x \geq a/2\,. \qquad (B\,2)$$

r and t represent the complex reflection and transmission probability amplitudes for the barrier being at the same time functions of the energy parameter q. As the potential was assumed even we have another solution for the particle coming from the right with the same energy

$$\psi_2(x) = t\,e^{-iqx} \qquad x \leq -a/2 \qquad (B\,3)$$

$$= e^{-iqx} + r\,e^{iqx} \qquad x \geq a/2\,. \qquad (B\,4)$$

The general solution with the same energy ($E = \hbar^2 q^2/2m$) in the interval $|x| \leq a/2$ will be a linear combination of ψ_1 and ψ_2.

$$\psi(x) = C_1\,\psi_1 + C_2\,\psi_2 \qquad |x| \leq \frac{a}{2}\,. \qquad (B5)$$

Using Bloch's theorem for the wave function we have

$$\psi(x+a) = e^{ika}\psi(x) \tag{B 6}$$

and this applies to the derivative as well. Using these conditions at the points x = -a/2 and calculating the determinant of the coefficients of C_1 and C_2 we obtain

$$\cos ka = \frac{t^2-r^2}{2t}e^{iqa} + \frac{1}{2t}e^{-iqa}. \tag{B 7}$$

We can easily show that the Wronskian determinant of any two solutions to the single-barrier Schrödinger equation with the same energy is constant in the spatial variable. By calculating the Wronskian determinant

$$W(\psi_1, \psi_2^*) = \psi_1'\psi_2^* - \psi_1\psi_2^{*\prime} \tag{B 8}$$

at the points x = - a/2 and x = a/2 we can show that

$$W(\psi_1, \psi_2^*)_{x=-a/2} = -2iqrt^* \tag{B 9}$$

and

$$W(\psi_1, \psi_2^*)_{x=a/2} = 2iqr^*t. \tag{B 10}$$

It therefore follows

$$rt^* = -r^*t = -(rt^*)^* \Rightarrow \qquad rt^* = \text{pure imaginary} \tag{B11}$$

and that

$$r = \pm i\,|r|\,e^{i\delta} \tag{B12}$$

when

$$t = |t|\,e^{i\delta}. \tag{B13}$$

This gives us easily the final relation

$$\cos ka = \frac{\cos(qa+\delta)}{|t|}. \tag{B14}$$

Here q is just the energy parameter ($E = \hbar^2 q^2/2m$) and not any reciprocal lattice vector. This equation gives us the means to evaluate the bandwidths and -gaps with relative ease.

Since cos(ka) and $|t|$ are always less than or equal to one we can evaluate the allowed and forbidden energy bands by observing the points, where $\cos(qa + \delta)$ is equal to one. In this way we obtain the approximate bandwidths and -gaps (around the points $qa = n\pi$) when the particle has energy near the barrier top ($|t| \simeq 1$, $|r| \approx 0$)

$$\Delta E_{band} \approx \frac{\hbar^2 \pi^2 (2n+1)}{2ma^2} \tag{B15}$$

and

$$\Delta E_{gap} \simeq \frac{\hbar^2 \, 4\pi n \sqrt{1-|t|}}{2ma^2} . \qquad (B16)$$

When the particle has a small energy compared with the barrier ($|t| \approx 0$, $|r| \approx 1$), we have

$$\Delta E_{band} \approx \frac{\hbar^2 \, 4\pi^2 (n+1)|t|}{2ma^2} \qquad (B17)$$

and

$$\Delta E_{gap} \approx \frac{\hbar^2 \, 2\pi^2 (n+1)}{2ma^2} . \qquad (B18)$$

Appendix C

Steady state solution of transport equation

We shall examine the influence of a weak external electric field on the distribution function of the interstitial ions and on the current, from which we will calculate the mobility μ. The basic assumption is the band model described earlier and knowledge of the band dispersion relations $\varepsilon_n = \varepsilon_n(\bar{k})$.

Boltzmann's equation for the distribution function is

$$\frac{d}{dt} f(\bar{k}) = \left.\frac{\partial f}{\partial t}\right|_{coll} + \left.\frac{\partial f}{\partial t}\right|_{field} . \qquad (C1)$$

The collision term becomes in the relaxation-time approximation

$$\left.\frac{\partial f}{\partial t}\right|_{coll.} = - \frac{f - f^o}{\tau} , \qquad (C\ 2)$$

where τ is the time of relaxation of $f(\bar{k})$ and $f^o(\bar{k})$ is the equilibrium distribution

$$f^o(\bar{k}) = \frac{e^{-\beta \varepsilon(k)}}{Z(\beta)} \qquad (C\,3)$$

$\varepsilon(\bar{k})$ referring to all bands. The field term is

$$\left.\frac{\partial f}{\partial t}\right|_{field} = \dot{\bar{k}} \cdot \nabla_{\bar{k}} f = \frac{Ze\bar{E}}{\hbar} \cdot \nabla_{\bar{k}} f = \frac{Ze\bar{E}}{\hbar} \cdot \nabla_{\bar{k}} \varepsilon(\bar{k}) \left(\frac{\partial f}{\partial \varepsilon}\right) . \qquad (C\,4)$$

Steady state solution of the transport equation is easily achieved

$$\frac{f - f^o}{\tau} = Ze\left(\bar{E} \cdot \frac{1}{\hbar} \nabla_{\bar{k}} \varepsilon(\bar{k})\right)\left(\frac{\partial f}{\partial \varepsilon}\right) = Ze\left(\bar{E} \cdot \bar{v}_{\bar{k}}\right)\left(\frac{\partial f}{\partial \varepsilon}\right) . \qquad (C\,5)$$

This has an approximate solution in the limit of a small external field

$$f \simeq f^{\circ} + \tau Z e (\bar{E}\cdot\bar{v}_{\bar{k}}) \frac{\partial f^{\circ}}{\partial \varepsilon} \, , \qquad (C\,6)$$

which becomes

$$f \simeq (1 - \tau \beta Z e (\bar{E}\cdot\bar{v}_{\bar{k}}))\, f^{\circ}(\bar{k}) \, . \qquad (C\,7)$$

The current density can be expressed in terms of f as follows

$$\bar{j} = - Z e \int_{B.Z.}^{\epsilon \geq \epsilon_0} d\bar{k}\, \bar{v}_{\bar{k}} \, \frac{f(\bar{k})}{(2\pi)^3} \, . \qquad (C\,8)$$

Here the integration over the first Brillouin zone takes place only over those bands which participate in the current; that is bands exceeding the barrier, which will be denoted as $\epsilon \geq \epsilon_0$. So we have

$$\bar{j} = \beta Z^2 e^2 \int_{B.Z.}^{\epsilon \geq \epsilon_0} \frac{d\bar{k}}{(2\pi)^3}\, \bar{v}_{\bar{k}} \left(\bar{v}_{\bar{k}} \cdot \bar{E} \right) \tau \, f^{\circ}(\bar{k}) \qquad (C\,9)$$

because the symmetric f°-term vanishes in the integration and the relaxation time has been considered to have some possible $\bar{k}$- or band-dependence.

On the other hand the density of particles (normalized as the current) can be determined by

$$n = \int_{B.Z.}^{\epsilon \geq 0} \frac{d\bar{k}}{(2\pi)^3} f(\bar{k}) = \int_{B.Z.}^{\epsilon \geq 0} \frac{d\bar{k}}{(2\pi)^3} f^{\circ}(\bar{k}) \, . \qquad (C\,10)$$

The integration is here naturally over all bands and the small antisymmetric correction term vanishes in turn during the integration. Now we can define the mobility in the following manner

$$\bar{j} = \mu n Z e \bar{E} \, . \qquad (C\ 11)$$

We have assumed μ to be a scalar as always in cubic crystals (just as D is too). The preceding relation becomes

$$\beta Z e \int_{B.Z.}^{\epsilon \geq \epsilon_0} d\bar{k}\, \bar{v}_{\bar{k}} (\bar{v}_{\bar{k}} \cdot \bar{E}) \tau f^{\circ}(\bar{k}) = \mu \bar{E} \int_{B.Z.}^{\epsilon \geq 0} d\bar{k}\, f^{\circ}(\bar{k}) \, . \qquad (C\ 12)$$

Let us take the scalar product with $\bar{E}$ on both sides of the equation and choose the direction of the field in the $\bar{k}$-space along $\hat{k}_z$-axis

$$\beta Z e \int^{\epsilon \geq \epsilon_0} d\bar{k}\, E^2 v_k^2 \cos^2\theta\, \tau f^{\circ}(k) = E^2 \mu \int^{\epsilon \geq 0} d\bar{k}\, f^{\circ}(\bar{k}) \, . \qquad (C\ 13)$$

This gives

$$\mu = \frac{\beta Z e \int^{\epsilon \geq \epsilon_0} d\bar{k}\, v_k^2 \cos^2\theta\, \tau f^{\circ}(\bar{k})}{\int^{\epsilon \geq 0} d\bar{k}\, f^{\circ}(\bar{k})} \, . \qquad (C\ 14)$$

Now we can assume the validity of the Nernst-Einstein relation

$$\mu = M \beta Z e D \qquad (C\ 15)$$

and we have for D

$$D = \frac{\int^{\epsilon \geq \epsilon_0} d\bar{k}\, v_k^2 \cos^2\theta\, \tau(\bar{k}) f^{\circ}(\bar{k})}{M \int^{\epsilon \geq 0} d\bar{k}\, f^{\circ}(\bar{k})} \, . \qquad (C\ 16)$$

Appendix D

Table of important numerical values and results

entity	Ge	Si	ref. or eq.
a_o	5.66 Å	5.43 Å	[36]
v_c	45.33 Å^3	40.03 Å^3	$a_o^3/4$
ϵ	16.0	11.8	[10]
ϵ_o	8.85416 10^{-12} F/m		[37]
A	2.160 eVÅ	2.929 eVÅ	$Z_1 Z_2 e^2/(4\pi\epsilon_o\epsilon)$
Z_1	2.4	2.4	[10], [38]
Z_2	1.0	1.0	[10], [38]
m(Li)	1.1526 10^{-26} kg		[39]
λ	0.1 Å^{-1}	0.1 Å^{-1}	fitted potential parameters
α	1.275 Å^{-1}	1.210 Å^{-1}	
R_L	40 a_o	40 a_o	range of the lattice sum
z	4	4	number of nearest equivalent sites
T^*	900 °K	1100 °K	midpoint of high temp. range
N	32	34	appr. number of bands $E < U_o$
$\Delta E_{gap}/\hbar$	4.55 10^{13} 1/s	5.3 10^{13} 1/s	eq. (91) $(E < U_o)$
ΔE_{band}	3.0 10^{-2} eV	3.5 10^{-2} eV	eq. (90) $(E > U_o)$
Ω_{ib}	3.4 10^{14} 1/s	1.4 10^{15} 1/s	$\omega_D \left(\frac{kT^*}{\hbar\omega_D}\right)^2 \left(\frac{\hbar\omega_D}{\Delta E_{gap}(E < U_o)}\right)^4$
Ω_D	4.7132 10^{13} 1/s	8.1827 10^{13} s^{-1}	[36]
Ω_{IB}	1.2 10^{14} 1/s	1.4 10^{14} 1/s	$\frac{kT^*}{\hbar}$

Appendix E

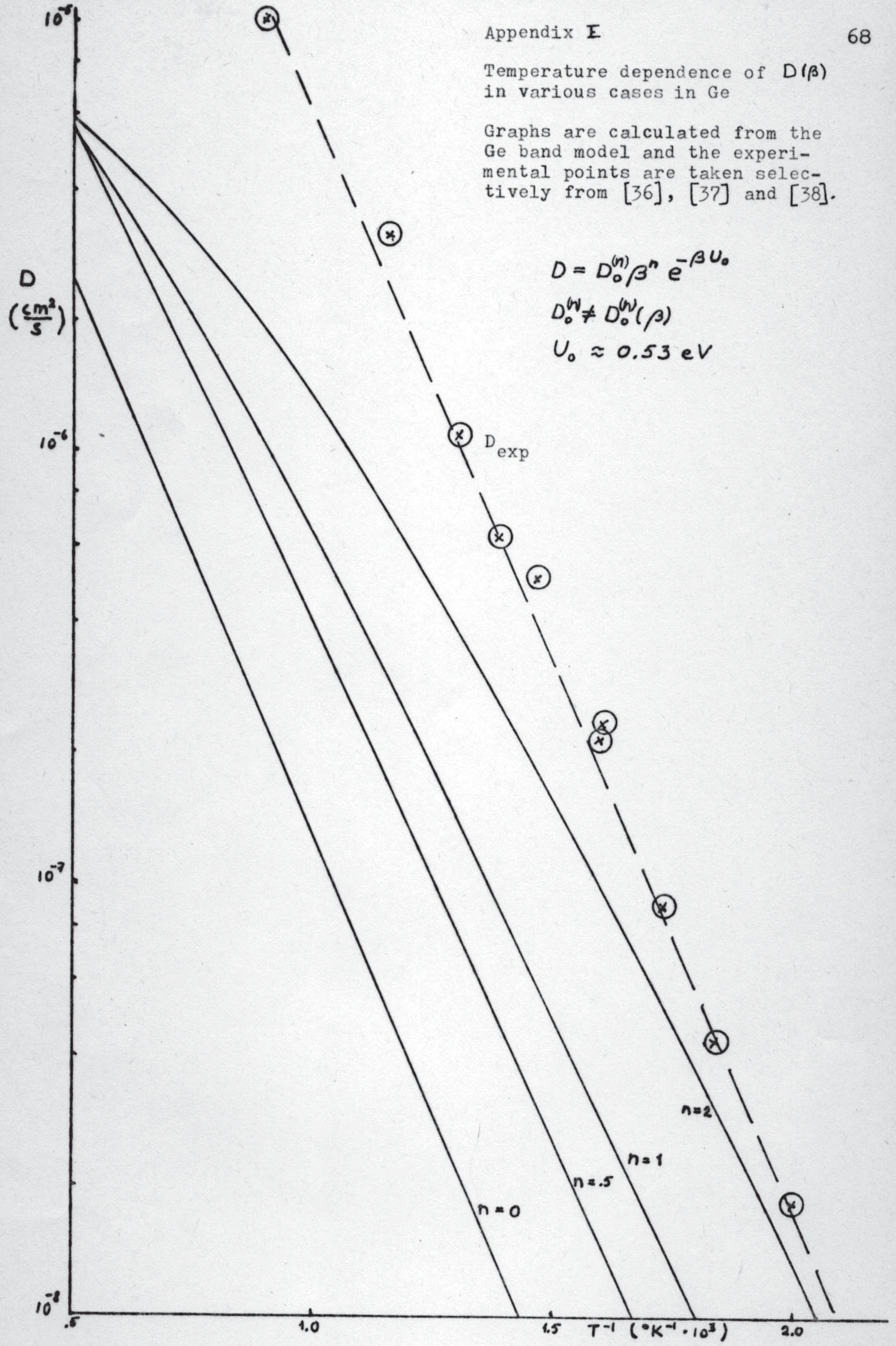
Temperature dependence of $D(\beta)$ in various cases in Ge

Graphs are calculated from the Ge band model and the experimental points are taken selectively from [36], [37] and [38].

$$D = D_0^{(n)} \beta^n e^{-\beta U_0}$$

$$D_0^{(n)} \neq D_0^{(n)}(\beta)$$

$$U_0 \approx 0.53\ eV$$



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