Transitions of electrons and holes drive diffusion in crystals, glasses and melts

Übergänge von Elektronen und Löchern als Antrieb der Diffusion in Kristallen, Gläsern und Schmelzen

H.-J. Hoffmann

Diffusion of atoms or molecules (generally: particles) is driven by differences and gradients of the chemical potential of the particles in their accessible space. If the difference of the chemical potential is due to differences of concentrations alone, one arrives at the diffusion equations of Fick. The diffusion coefficients are described in known models by vibrations of atoms in condensed matter which cause the exchange of preferentially neutral particles with neighbouring particles, impurities, interstitial places and vacancies near or on surfaces, grain boundaries, dislocation lines and in the homogeneous bulk. The rates of electronic transitions, however, increase also in melts and solids of chemically bonded particles with increasing temperature. Such transitions cause large fluctuating deviations of the local energy, the charge distribution and the local chemical and electrical potentials. The fluctuating deviations interact with the core ions and drive particles to interchange. This mechanism that supplements the known mechanisms of diffusion has not yet found adequate attention in the literature until now. Foundations, experimental results, evidence and consequences for diffusion are discussed.

Keywords: Diffusion in solids / mechanism of diffusion / diffusion coefficient / self-diffusion / diffusion and transitions of electrons and holes

Die Diffusion von Atomen oder Molekülen (allgemein: Teilchen) hat ihre Triebkraft infolge von Unterschieden und Gradienten des chemischen Potenzials der Teilchen in ihrem zugänglichen Raum. Wenn der Potenzialunterschied allein von Konzentrationsunterschieden herrührt, gelangt man zu den bekannten Diffusionsgleichungen nach Fick. Um die Diffusionskoeffizienten auf atomare Bewegungen in kondensierter Materie zurückzuführen, wurden in bisher bekannten Modellen Platzwechselvorgänge zumeist neutraler Teilchen mit Nachbarteilchen, Verunreinigungen, Zwischengitterplätzen, Leerstellen an Oberflächen, Korngrenzen, Verzerrungen und im homogenen Volumen betrachtet. Es ist bekannt, dass in Schmelzen und Festkörpern mit chemischen Bindungen mit zunehmender Temperatur elektronische Übergänge auftreten, wodurch fluktuiierende Abweichungen in der Ladungsverteilung und den lokalen chemischen und elektrischen Potenzialen entstehen. Diese Abweichungen üben Kräfte auf die Position der Rumpf-Ionen aus und machen daher ebenfalls Platzwechsel von Teilchen möglich. Dieser er-
gänzende Mechanismus für die Diffusion wurde bisher in der Literatur nicht hinrei-
chend beachtet. Grundlagen, experimentelle Ergebnisse, Hinweise und Folgerun-
gen für den Diffusionsvorgang werden aufgezeigt und diskutiert.

Schlüsselwörter: Diffusion in Festkörpern / Diffusionsmechanismus /
Diffusionskoeffizient / Selbstdiffusion / Diffusion und Übergänge von Elektronen und
Löchern

1 Introduction

Mixing and reacting particles are basically trans-
ported by convection and diffusion. The macro-
scopic flowing and stirring are examples to trans-
port masses convectively or by external forces in
reaction chambers. Diffusion of particles without
convection is a widespread phenomenon in materi-
als science and technology which is driven by gra-
dients of their chemical potential with or without
other additional potential gradients and forces. It
plays a decisive role in preparation, processing and
application of materials in materials science and en-
gineering. Some examples are
– chemical reactions of condensed matter,
– sintering (glass, ceramics or metals),
– classical doping of semiconductors by diffusion,
– surface hardening by diffusion,
– colouring glasses by diffusion and striking,
– precipitating silver halides in doped glass and its
effect of photochromism (both rendering the
glass photochromic by striking in production and
darkening the glass by UV-photons in applica-
tion),
– pre-stressing the surface of glasses by ion ex-
change with salt baths,
– general phase separation and de-mixing,
– nucleation and crystal growth in producing glass
ceramics,
– refining glasses in melting tanks or
– relaxation of locally stressed glasses.

These are just a few examples of an uncounted
number of possible effects and applications of dif-
fusive processes in crystalline, vitreous and liquid
or molten materials. The present article refers to
such processes and materials. Abundant pub-
ications on diffusion are available from the liter-
ature, of which references are selected arbitrarily
[1–15].

The paper starts in sections 2 to 5 with a sum-
mary of the laws and notions of diffusion and some
examples of the classical interpretation based on
thermal atomic vibrations. The experimental data
lack very often reproducibility and consistency.
Comparing the discrepancies between the data of
different papers from the literature, the ex-
perimental conditions do not seem to be described
and recognized comprehensively. To avoid un-
certainty in the following considerations, we con-
sider essentially the limiting case of self-diffusion.
Even in this case, however, the diffusion mecha-
nisms based on thermal vibrations as the driving
force alone do not explain the values of the data on
an atomic scale adequately.

Sections 6 to 9 deal with a second influence on
the diffusion, namely transitions of electrons and
holes as an additional driving force for diffusion,
which is missing widely in the literature. The driv-
ing force due to such transitions is twofold: The
electronic transitions change the wave functions of
the charge carriers and the probability distribution
of their charge in space. The resulting electrical
forces can cause a rearrangement of the atoms and
the core ions (atoms without the bonding elec-
trons). Secondly, the recombination of the electrons
with holes releases energy and increases the local
temperature. These fluctuations can break bonds
and their relaxation causes rearrangements of the
atoms.

Data of the specific heat capacity already deliver
evidence that vibrations and electronic transitions
occur simultaneously in solids and melts. Section 7
gives clear evidence that transitions of electrons
can drive diffusion, since photons induce such elec-
tronic transitions and drive diffusion experiments
independently of vibrations. The new interpretation
does not replace but supplements the former de-
scription of diffusion by vibrational effects. Con-
sidering electronic transitions helps to explain in
section 9 several experimental observations that
have not yet been interpreted convincingly. The fi-
2 Basic laws and notions

Neutral constituents of matter, such as atoms, molecules and defects – or particles of kind \( A \) for short – are assumed to be driven by gradients of their chemical potential \( \mu_A \). If the constituents carry charge, they are driven by gradients of the electrical potential, in addition. In one dimension with the space variable, \( x \) the particle flow density reads for a given temperature \( T \)

\[
j_A(x, T) = -c_A \omega_A(T) \frac{d\mu_A(x, T)}{dx}.
\] (1)

Herein, \( c_A \) is the concentration of particles and \( \omega_A(T) \) is the mechanical mobility of the particles at location \( x \) in the system (see many textbooks on diffusion, e.g. pages 430+ in [12]). The minus sign in (1) takes into account that the particles move to ranges with lower chemical potential, i.e. against the gradient of \( \mu_A(x, T) \).

In the limit of non-interacting particles sufficiently diluted in a homogeneous medium, such as \( c_A(x) \ll 10^{-3} \text{mol/cm}^3 \), their chemical potential can be expressed as

\[
\mu_A(c_A(x), T) = \mu_{A,0}(c_{A,0}, T) + RT \ln \frac{c_A(x)}{c_{A,0}}.
\] (2)

In (2), \( \mu_{A,0}(c_{A,0}, T) \) is the chemical potential of particles \( A \) for its reference concentration \( c_{A,0} \) at the temperature \( T \) in the ambient medium. \( R \) is the universal molar gas constant. Equation 2 transforms by derivation into

\[
\frac{d\mu_A(c_A(x), T)}{dx} = \frac{RT}{c_A(x)} \frac{dc_A(x)}{dx}.
\] (3)

Inserting (3) into (1) yields the first law of Fick for the isothermal flow density of the particles

\[
j_A(x, T) = -RT \omega_A(T) \frac{dc_A(x)}{dx} = -D_A(T) \frac{dc_A(x)}{dx}.
\] (4)

Comparing the coefficients of the derivatives in Equation 4 defines the relation of Einstein or Nernst-Einstein between the diffusion coefficient / constant or diffusivity \( D_A \) and the mobility \( \omega_A \) of the particles [5] (see pages 84+)

\[
D_A(T) = RT \omega_A(T).
\] (5)

Sometimes Equation 5 is called Einstein-von Smoluchowski relation, [12] (page 435, e.g.).

In order to extend Equation 4 to three dimensions, it is assumed for simplicity that the diffusion coefficient is isotropic. If in addition \( \omega_A(T) \) and \( D_A(T) \) are independent of the concentration of the diffusing particles, Equation 4 yields the vector relation in three dimensions

\[
\vec{j}_A(x, y, z, T) = -RT \omega_A(T) \nabla(c_A(x, y, z)) = -D_A(T) \nabla(c_A(x, y, z)).
\] (6)

Accordingly, the flow of particles is proportional to the gradient of the concentration of particles. If the transport coefficients \( \omega_A(T) \) and \( D_A(T) \) are anisotropic, these coefficients are tensors and the direction of the concentration gradient differs from that of the flow vector. Anisotropy of \( \omega_A(T) \) and \( D_A(T) \) is excluded in the present article for simplicity to avoid distraction from the proper topic.

Usually one presumes that the diffusivity as a function of temperature can be written in the case of isotropy as

\[
D(T) = D_0 \exp \left( -\frac{Q_{diff}}{RT} \right).
\] (7)

Herein, \( D_0 \) is a pre-exponential factor and \( Q_{diff} \) is the activation energy of diffusion. A possible temperature dependence of \( D_0 \) is neglected if the exponential function in (7) is dominant. Since the diffusion coefficient obviously characterizes the diffusing particles in their environment, we omit its index \( A \) in (7) and the following sections.

The expected concentration of diffusing particles as a function of time and position, \( c_A(x, t) \), for a given diffusion coefficient, \( D(T) \), is calculated in the one-dimensional case via the partial differential equation
The diffusion coefficient, \( D(T) \), changes \emph{qualitatively} as a function of \( T_m/T \) (\( T_m \) is the melting temperature as a reference) with the structure of the system and the dominating diffusion path, Figure 1, redrawn from Figure 2 of [1], pages 1–3. Large values of \( D(T) \) occur if the diffusing particles move on the surface of the sample as they interact only partially with the system under consideration. Diffusion is also fast due to reduced interaction, if it occurs between the grain boundaries or along dislocation lines. Diffusion coefficients for the homogeneous bulk are comparatively small in most cas-

\[
\frac{\partial c_A(x, t)}{\partial t} = D(T) \frac{\partial^2 c_A(x, t)}{\partial x^2}.
\]  

(8)

It is derived in textbooks on diffusion, e.g. [11]. In the case of isotropic diffusion (8) is readily extended to three dimensions as

\[
\frac{\partial c_A(x, y, z, t)}{\partial t} = D(T) \left( \frac{\partial^2 c_A(x, y, z, t)}{\partial x^2} + \frac{\partial^2 c_A(x, y, z, t)}{\partial y^2} + \frac{\partial^2 c_A(x, y, z, t)}{\partial z^2} \right) \]  

(9)

\( \Delta c_A(x, y, z, t) \)

Equations 8, 9 are called second law of Fick. Numerous solutions of these partial differential equations for different initial and boundary conditions and coordinate systems are published in the literature, [13], e.g. The diffusion coefficient or diffusivity, \( D(T) \), is determined by fitting theoretical solutions of the second law of Fick for suitable boundary conditions to the profile \( c_A(x, y, z, t) \) determined experimentally.

\( D(T) \) is usually determined as a function of temperature with all other parameters, such as the composition of the initial basic material including impurities, the pressure and stress distribution, being constant. Intrinsic defects may also play a role, because their concentration can change, if the temperature varies and reactions with the diffusing particles have to be taken into account.

Since the experimental data of the diffusion coefficient are usually determined under constant external pressure, \( p \), as a function of temperature, \( Q_{\text{diff}} \) is also called “activation enthalpy”. However, it is not an enthalpy function in the proper sense of the thermodynamic Gibbs functions, even if \( Q_{\text{diff}} \) is determined in thermal equilibrium. \( Q_{\text{diff}} \) is not the thermal enthalpy of a given system or reaction but characterizes the activation energy for the probability of a sufficiently large fluctuation (of the local energy) to perform the steps of the diffusion under constant external pressure. This is clearly a kinetic property. Once such a step is performing, the local energy fluctuates mainly due to vibrations and electronic excitations of the diffusing atom and its neighbouring atoms. Finally, the activation energy dissipates in the sample.

**Figure 1.** Diffusion coefficients of different dominating paths on a logarithmic scale as a function of the reciprocal temperature normalized to a reference temperature \( T_m \) that characterizes roughly the bonding strength between the constituents of the bulk material. It is assumed that the melting temperature \( T_m \) can serve as such a reference temperature (schematically). Redrawn from ref. [1], Figure 2.

**Bild 1.** Diffusionskoeffizienten für unterschiedliche dominante Diffusionswege mit logarithmischer Skala in Abhängigkeit von der reziproken Temperatur \( T \) normiert auf eine Referenztemperatur \( T_m \), wodurch die Bindungsstärke zwischen den Bausteinen des Werkstoffs charakterisiert wird. Es wird angenommen, dass die Schmelztemperatur \( T_m \) als Referenztemperatur dienen kann (schematisch). Neu gezeichnet nach Ref. [1], Bild 2.
es, except for fast ionic conductors, e.g. Accordingly, $D(T)$ is not necessarily a unique function for a given diffusing species in a system, as it may depend on different diffusion paths and mechanisms.

3 Selection of atomic diffusion mechanisms from the literature

Different atomic diffusion mechanisms are selected from the literature and illustrated in a two-dimensional scheme, Figure 2, taken from [1], Figure 8 on pages 1–13. Most atomic diffusion mechanisms are connected with impurities and intrinsic defects in the lattice. Such defects are necessarily present in the lattice for thermodynamic reasons. However, possible charge states of the constituents participating in the diffusion are not considered in the mechanisms shown in Figure 2 (corresponding to Figure 8 of [1]). Therefore, the notion “atom” includes also core ions or even larger constituents such as electrically charged or uncharged groups of particles and different defect centres. If the diffusing particles are in different charge states, the local electric fields are affected and the fluctuations of the local electrical potential modify the local activation energies and correlation factors.

The charge of different particles is not necessarily balanced locally in small volumes but over large volumes as the samples are not charged. To interpret diffusion experiments quantitatively by a special mechanism, it is mandatory to consider the statistics of both the concentrations of the diffusing particles and their different charge states in practice.

Well-known is the diffusion of vacancies in the lattice, Figure 2. Vacancies can be created and annihilated in the sample or disappear, if they reach surfaces or interfaces or recombine with interstitials. The energy to create a vacancy is different from that to reach the next site in the lattice.Interstitials can be created simultaneously with vacancies, which results in the same energy of formation for both. The enthalpies for creation and transport are in general different. The path of an interstitial is limited if the interstitial recombines with a vacancy or reaches the surface, interface or dislocation line. In an “indirect interstitial mechanism”, an interstitial particle may replace a lattice atom and kick out or shift the predecessor to an interstitial site. If the interstitial particle recombines with a vacancy, we have an example for an inverse “dissociative mechanism”. To keep the concentration of recombining entities constant, new defects must be created thermally by dissociation with the same rate as they disappear. Then, a particle is transferred from a lattice site to an interstitial site and diffuses as an interstitial. Simultaneously, a vacancy appears and diffuses independently.

In the “kick-out mechanism” the direct interstitial diffusion ends by replacing a lattice atom which is kicked out to an interstitial position. Direct exchange of neighbouring atoms seems to be possible by rotating larger entities such as a “ring exchange” of four atoms, e.g.

In practice, it is difficult to control and determine all parameters relevant for the diffusion. Such problems are minimised if external driving forces are avoided at all and homogeneous systems are investigated in (or at least close to) thermodynamic equilibrium. Therefore, data of self-diffusion

Figure 2. Examples of different diffusion mechanisms of atomic particles in crystalline solids (projected on a plane). Redrawn from ref. [1], Figure 8. See text for explanation.

Bild 2. Beispiele für unterschiedliche Diffusionsmechanismen atomarer Teilchen in kristallinen Festkörpern (projiziert auf eine Ebene). Zur Erklärung siehe Text. Neu gezeichnet nach Ref. [1], Bild 8.
or close to self-diffusion (tracer diffusion) are kept in mind in the present article to serve as basis for interpretation and to focus on a new diffusion mechanism in subsequent chapters.

In the case of self-diffusion, the diffusing particles are not driven by a macroscopic gradient of the chemical potential or other gradients. Instead, their diffusion is driven by spontaneous transitions of charge carriers (electrons and holes) and unavoidable local fluctuations of the temperature, vibrations, the concentrations of the particles and – more generally – fluctuations of the chemical potential. This is basically due to the graininess of condensed (solid or molten) matter.

The chemical potential does not depend only on the chemical components, their concentration including their charge state and the structure of the respective system, but it is also modified by the presence of impurities, defects, illumination, space charge, stress of all kinds or gravitational, electrical and temperature potentials or their gradients and magnetic forces. Diffusion depends on parameters of these quantities and their effects. Thus, all effects creating local fluctuations of the chemical potential may modify diffusion and the transport properties of the material. This includes reactions of the diffusing particles within the system. Taking chemical reactions into account, the diffusion Equations 8 and 9 require additional terms as supplements. If the substance under investigation is not controlled carefully, it is difficult to obtain reliable and reproducible data on diffusion coefficients.

4 Qualitative explanation of the diffusion coefficient

In the following, diffusion is assumed to occur in isotropic media, which simplifies arguments. In most diffusion mechanisms, the moving particle is bound to a potential well formed by potential barriers shown in a 1-dimensional schematic, Figure 3. The minimum height of the energy barrier is \( Q_{\text{diff}} \) (corresponding to a possible saddle point in three dimensions). \( Q_{\text{diff}} \) is the activation energy or activation “enthalpy” as the diffusion experiments are performed under constant pressure. The energy required to overcome the barrier is released during the relaxation of the diffusing particle on its new location.

A simplistic explanation of the diffusion coefficient (7) is the following: The particle may escape from the potential well proportional to the rate of escape attempts (“escape frequency”), \( \nu_{\text{diff}} \), of which only a small fraction is successful. This successful fraction of attempts is quantified by Boltzmann’s factor \( \exp \left(- \frac{Q_{\text{diff}}}{RT} \right) \). (\( R \) is the universal molar gas constant and \( T \) is the absolute temperature.)

In a periodic lattice potential with simple cubic symmetry the diffusion particle can overcome diffusion barriers for six independent directions. Thus, only \( \frac{1}{6} \nu_{\text{diff}} \exp \left(- \frac{Q_{\text{diff}}}{RT} \right) \) successful jumps per time occur into a specified direction.

With the absolute value of the average jump width \( a \) the distance averaged over all positive and negative directions for many particles is zero. However, the averaged square of the jump width is \( a^2 > 0 \). Averaging over many single independent escape events and many independent particles of the same kind the projection into any specific direction of a simple cubic crystal is \( \frac{1}{6} a^2 \). Then, the diffusion coefficient or diffusivity (7) can be expressed basically by (see also textbooks on diffusion, such as references [5, 11]).
Prerequisite for this derivation is that successive jumps of the diffusing particles are independent of each other. Otherwise, Equations 10 and 11 must be supplemented by additional restrictions for the movement of the diffusing particles, such as a correlation factor which comes into play if sequential jumps depend on each other or are coupled to other diffusing particles (such as vacancies) or if a major part of possible sites is already occupied. Intrinsic defects, such as vacancies, may couple and interact with diffusing particles and enhance or at least modify their diffusion constant, $D(T)$. Then, $D(T)$ is not a true quantity characterizing the transport of one single kind of particles alone as it depends on the concentration of concomitant reacting intrinsic defects and their formation and reaction enthalpy and entropy. For examples of possible refinements see [5, 11], e.g.

5 Expectation and tests according to the classical interpretation of diffusion

Diffusion in glasses and glass melts consisting of few components has often been studied experimentally. Ample literature and data are available for comparison and interpretation. Grain boundaries and line defects can be neglected in glasses. Then, the diffusion constant is expected to depend essentially on the number and strength of bonds of the diffusing particles with the surrounding particles and local defects. Alkali ions are bonded to oxygen ions via a single bond. Therefore, their coefficient of self-diffusion is expected to show some systematic dependence on the kind of alkali. It may decrease with increasing diameter of the diffusing alkali ion due to steric hindrance. To test this expectation we compare data of the positive alkali ions as self-diffusing particles in binary alkali metal oxide-silicate glasses of the molar composition $75\text{SiO}_2\cdot25\text{Alkali}_2\text{O}$ from the literature [16–24]. Only data obtained for the temperature range below the glass transformation temperature $T_g$ are used. As the chemical reactivity and the bonding forces of different alkali ions in silicon dioxide (SiO$_2$) are expected to scale with their ionic radius, $r_i$, or diameter, $d_i = 2r_i$, one expects that the self-diffusion coefficient

$$D(T) = \frac{1}{6} v_{\text{diff}} a^2 \exp \left( -\frac{Q_{\text{diff}}}{RT} \right)$$

(10)

with the pre-exponential factor

$$D_0 = \frac{1}{6} v_{\text{diff}} a^2.$$  

(11)

varies systematically with $d_i$. The attempt rate $v_{\text{diff}}$ and, therefore, $D_0$ are expected to decrease with increasing mass of the ions, whereas the activation energy $Q_{\text{diff}}$ is expected to increase due to steric hindrance with the diameter of the ions. Experimental data of $D_0$ and $Q_{\text{diff}}$ are collected as a function of the diameter of the alkali ions, Figure 4. A systematic trend as a function of the diameter of the moving ions is not observed. Instead, the data of both the activation energy $Q_{\text{diff}}$ (upper section, left scale) and the pre-factor $D_0$ (lower section of Figure 4, right scale) from different authors show large scattering even if just one composition, such as $75\text{SiO}_2\cdot25\text{Na}_2\text{O}$, is considered.

To understand the discrepancy between expectation and experimental results, one can consider that the purities and the preparation techniques of the glasses may be different. This includes the selection of raw materials, deviations of the stoichiometry, redox potential, position of the Fermi-level, content of impurities, such as water or OH$^-$ groups, degree of fining, melting temperature, homogenization, cooling rate, stress relaxation and thermal history. In addition, phase separation seems to occur in lithium- and sodium-silicate glasses and play a role at least for temperatures sufficiently above $T_g$ [25]. Thus, the data of the diffusion coefficient – particularly at temperatures below $T_g$ – represent rather an extrinsic (i.e. depending on accidental effects, inhomogeneity and impurities) than an intrinsic property.

Comparing data on the diffusivities from a large collection of different materials and compositions such as in [1, 2], many pre-factors $D_0$ and activation energies $Q_{\text{diff}}$ are in the ranges

$$10^{-6} \text{ m}^2\text{s}^{-1} < D_0 < 10^{-3} \text{ m}^2\text{s}^{-1}$$

(12)
6 Basics of a new mechanism of diffusion

The diffusion mechanisms are characterized by oscillating and moving particles (atoms, ions, defects, impurities) and molecules or groups of such particles, Figure 2 (above). Their movement is driven by the momentum and energy transferred from the vibrating and fluctuating neighbouring atoms or core ions. The charge state of the diffusing particles is taken into account from their expected chemical valence. The number of defects and their charge state can shift if components react, such as by redox-reactions, valence alternation of polyvalent ions, irradiation and changing potentials. The chemical equilibrium of defects, such as vacancies and interstitials is generally adjusted according to the law of mass action, if reactions take place to adopt chemical equilibrium. On the other hand they may be fixed if they are frozen in [11].

The diffusing particles are usually considered to keep their state of charge according to the equilibrium value or at least to their adjusted values. The position of the Fermi-level can be taken into account for the diffusion doping of semiconductors to quantify the relative amounts of the diffusing particles in their different charge states. The continuous exchange of electrons and holes between different energy levels is often neglected. In practice, however, the charge state of a diffusing particle (in particular with energy levels near the Fermi-level) is not static but changes and fluctuates permanently depending on temperature. The average occupancy and probability distribution of elec-

\[ 0.5 \times 10^{-9} m < a < 2 \times 10^{-9} m. \]  

Accordingly, the range of \( D_0 \) is estimated at \( 4 \times 10^{-7} m^2 s^{-1} < D_0 < 6 \times 10^{-5} m^2 s^{-1} \). Therefore, values of \( D_0 \) outside this interval might be difficult to explain quantitatively by the basic model explaining Equation 10. In particular, it is not yet clear which frequency has to be inserted as the escape frequency: Phonons of which branch of vibrations or just local phonons in the vicinity of the moving particle or something else. It is also not clear which mechanism concentrates the energies of the phonons near the moving particles or core ions and which energies are needed further and are available to induce diffusion in solids and melts. Therefore, additional mechanisms seem necessary interpreting experimental data.

\[ 40 kJ \cdot mol^{-1} < Q_{\text{diff}} < 600 kJ \cdot mol^{-1}. \quad (13) \]

Replacing \( Q_{\text{diff}} \) by the activation energy per diffusing particle \( q_{\text{diff}} \) via the equivalence relation \( 96.485 \text{\,kJ/mol}=1 \text{\,eV/particle} \), the last inequality transforms to about

\[ 0.40 \text{\,eV/particle} < q_{\text{diff}} < 6 \text{\,eV/particle}. \quad (14) \]

To estimate the order of magnitude of \( D_0 = \frac{1}{2} \nu_{\text{diff}} a^2 \) we assume that the escape frequency \( \nu_{\text{diff}} \) is in the range \( 10^{13} \text{\,s}^{-1} < \nu_{\text{diff}} < 10^{14} \text{\,s}^{-1} \) and the distance \( a \) of a “jump” is in the order of few diameters of an atom or ion, i.e.
trons results from a dynamic equilibrium of capturing and reemitting charge carriers from local energy levels to valence and conduction bands or different states in the neighbourhood. Thus, changing the charge state of an atom (or equivalently changing the occupation probability of electronic energy levels) and breaking bonds in the system can be the reason for the elementary step of the diffusion, which seems having escaped in the literature. As thermal excitations of both vibrations and electronic transitions occur concomitantly, the changing charge state of a diffusing particle due to electronic transitions together with the excited phonons in the solid or liquid make the atoms and core ions diffuse. If electronic transitions induce the movement of core ions, one can interpret the formal escape rate or frequency $v_{\text{diff}}$ in Equations 10 and 11 as being proportional to the rate of capturing or emitting electrons or holes into or from the energy levels of the bonding states of the diffusing particle. This rate can be outside the rates presumed in section 5. Thus, one may consider electronic transitions and the changing charge states in the environment of the diffusing particle as the origin of the driving force. Consequently, the activation energy of diffusion $Q_{\text{diff}}$ relates to the energies of electronic transitions between the different electron or hole states of the bonding electrons. This basic possibility has been described already in [26]. Its foundations and some consequences are to be elaborated and discussed in the subsequent sections of the present paper in more detail.

Necessary for this interpretation is that sufficient electrons are captured or reemitted to possible excited states and over necessary barrier heights nearby to rearrange the position of the diffusing particles. The electrons and holes overcome the height of the energy barriers and the transition energies between ground and excited states with increasing temperature and reconfigure the arrangement of the core ions. Tunnelling is also possible. An estimate for the height of the energy barriers and their transition energies, which are overcome with reasonable rates at a given temperature in practice, can be obtained from glow curves of thermo-luminescence and thermally stimulated conductivity. For a detailed survey of many effects in this field see [27]. In such investigations, semiconducting or insulating solids are irradiated with photons of the band-gap energy or larger to fill or better recharge electrons and hole traps with energy levels in the bandgap of such solids. If this occurs at sufficiently low temperature the captured charge carriers are trapped without reemission and the charge population of the traps is stable as a function of time. In a second step, the charge carriers are reemitted from their traps by increasing the temperature of the sample with a constant heating rate. The charge carriers are released with a noticeable rate at a temperature $T_s$ for reasonable heating rates, if the energy difference for releasing (or the barrier height $\Delta E_s$) is in the order of [28]

$$\Delta E_s \approx 25 k_B T_s,$$

The pre-factor of the thermal energy, $k_B T_s$, is not necessarily 25 but depends on the heating rate, the kinetic parameters of the traps (or generally defects) and the recombination kinetics. Instead of 25, values in a broader range mainly between 20 and 30 are possible. Attributing maxima of glow curves and thermally stimulated conductivity to $T_s$ one can estimate in the temperature interval $200 \text{ K} < T_s < 2000 \text{ K}$ energies of about $0.43 \text{ eV} < \Delta E_s < 4.3 \text{ eV}$ for possible electronic transitions. This estimation of the expected electronic transition energies fits reasonably well to the experimental data of the activation energy of diffusion, $Q_{\text{diff}}$. The energy $\Delta E_s$ corresponds to electronic transitions between traps and valence or conduction band as well as to different localised levels. It also applies to electronic transitions between occupied to unoccupied states of metals in the continuum of their density of states of the outer electrons. Thus, electronic transitions with energies just mentioned occur in the temperature range of diffusion experiments.

Such electronic transitions below the melting temperature $T_m$ also contribute to the temperature dependence of the specific heat capacity [26, 29]. Data of the molar specific heat capacity $C_{p,\text{sol}}$ of the solid (crystalline) chemical elements are represented as a function of the element number and the sequence of the last orbital occupied by an electron (electron configuration of the atom) in Figure 5. The data of $C_{p,\text{sol}}$ are taken from the temperature interval just below the melting temperature, $T_m$, as published in [30]. The data on the electron configuration are from [31]. The data of the specific heat
Figure 5. Lower part: The molar specific heat capacities $C_{p,\text{sol}}$ and $C_{p,\text{melt}}$ of the solid and molten chemical elements as a function of the element number and the sequence of the last orbital occupied by an electron (constant ambient pressure of 101 kN/m$^2$). The data of $C_{p,\text{sol}}$ and $C_{p,\text{melt}}$ are taken from the temperature interval just below or above the melting temperature $T_{\text{melt}}$, respectively, as published in [30]. The data on the electron configuration are from [31]. Upper part: The contributions of conduction electrons $\gamma T_{\text{melt}}$ to $C_{p,\text{melt}}$ as obtained from an analysis of the specific heat capacity of metals at temperatures near absolute zero. In that range of temperature the molar specific heat capacity due to the lattice vibrations decreases with the temperature as $\delta T^3$, whereas the heat capacity due to the electronic excitations of the degenerate electron gas decreases as $\gamma T$, [32–34]. Since $\delta T^3$ tends to zero faster than $\gamma T$ with decreasing temperature, both contributions can be separated. The electronic contribution $\gamma T$ to $C_{p,\text{sol}}$ is extrapolated to the melting temperature, $T_{\text{melt}}$ using the data of $\gamma$ collected in [35].

Bild 5. Unterer Teil: Molare spezifische Wärmekapazitäten $C_{p,\text{sol}}$ und $C_{p,\text{melt}}$ der chemischen Elemente im festen (kristallinen) und geschmolzenen Zustand in Abhängigkeit von der Ordnungszahl und der Folge des zuletzt besetzten elektronischen Orbitals (unter konstantem Druck von 101 kN/m$^2$). Die Daten von $C_{p,\text{sol}}$ bzw. $C_{p,\text{melt}}$ beziehen sich auf den Temperaturbereich unmittelbar unterhalb bzw. oberhalb der Schmelztemperatur $T_{\text{melt}}$ Ref. [30]. Die Daten der Elektronenkonfiguration stammen aus [31]. Oberer Teil: Der Beitrag der Elektronen $\gamma T_{\text{melt}}$ zur molaren spezifischen Wärmekapazität $C_{p,\text{sol}}$ bei der Schmelztemperatur nach einer Analyse der molaren spezifischen Wärmekapazität der Metalle im Bereich tiefer Temperaturen in der Nähe des absoluten Nullpunkts. In diesem Bereich nimmt die spezifische Wärmekapazität der Gitterschwingungen wie $\delta T^3$ mit der Temperatur ab, wohingegen die Wärmekapazität auf Grund elektronischer Anregungen des entarteten Elektronengases der Metalle wie $\gamma T$ abnimmt, [32–34]. Da $\delta T^3$ mit abnehmender Temperatur schneller gegen Null geht als $\gamma T$, können beide Anteile getrennt werden. Der elektronische Beitrag $\gamma T$ wurde auf die Schmelztemperatur $T_{\text{melt}}$ extrapoliert, wobei für $\gamma$ die Daten aus [35] verwendet wurden.
capacity just above the melting temperature, $C_{p, \text{melt}}$, are included in Figure 5 for comparison. These data considered as a function of the element number are qualitatively similar to $C_{p, \text{sol}}$.

In the temperature range near $T_m$, one can clearly separate the specific heat capacity $C_{p, \text{sol}}$ of homogeneous materials into two dominant storage capabilities: One is the storage capacity due to the excitation of vibrations and the other is due to electronic transitions and excitations. The molar specific heat capacity due to vibrations of the solid state above the Debye temperature is $3R$ if the volume of the sample is constant. Textbooks on thermodynamics or solid-state physics usually indicate the difference between the molar specific heat capacities at constant pressure $C_p$ and constant volume $C_V$ ([32], e.g.). Accordingly, near the melting temperature

$$C_p = C_V + \alpha_v^2 T_m V_{\text{mol}}/\kappa$$

$$\geq 3R + \alpha_v^2 T_m V_{\text{mol}}/\kappa. \quad (16)$$

Herein, $T_m$ is the melting temperature, $\alpha_v$ the thermal volume expansion coefficient at constant pressure, $V_{\text{mol}}$ the molar volume and $\kappa$ the isothermal compressibility near $T_m$.

At high temperature near $T_m$ the theoretical $C_{V, \text{sol}}$ is $3R$ neglecting the electronic part of $C_{V, \text{sol}}$. If the electronic part of $C_{p, \text{sol}}$ can be neglected for the minimum values in Figure 5 (then the relevant part is due to vibrations only), one estimates from the experimental data the value $R/2$ as the upper limit of the difference $C_{p, \text{sol}} - C_{V, \text{sol}} = \alpha_v^2 T_m V_{\text{mol}}/\kappa$ in the temperature ranges below and above $T_m$ (compare also the minimum data of $C_{p, \text{melt}}$). Thus, the part of the specific heat capacity $C_{p, \text{sol}}$, which can be attributed to vibrations, is at most $(3R + R/2)$. Because experimental data near the melting temperature $T_m$ are compared, possible anharmonic vibrational effects are taken into account automatically near $T_m$ of the solids and the melts.

To suppress the contribution of the phonons to the specific heat capacity and focus on the storage capacity by exciting electronic transitions, the starting point of the $C_{p, \text{sol}}$ and $C_{p, \text{melt}}$-axes of Figure 5 can be shifted by $3R$ to $3.5R$. The molar specific heat capacity in excess of $(3 \text{ to } 3.5)R$ correlates well with the number of electrons in the outer shell of the atoms of the chemical elements: There are at most two electrons in an $s$ sub-shell, six in a $p$ sub-shell, ten in a $d$ sub-shell and fourteen in an $f$ sub-shell. This correlation demonstrates clearly that electronic excitations and transitions take place in solids with noticeable rates.

Further evidence of the electronic contributions to $C_{p, \text{sol}}$ arises from an analysis of the specific heat capacity of metals at temperatures near absolute zero. In that range of temperature the molar specific heat capacity due to the lattice vibrations decreases with the temperature as $\delta T^3$, whereas the capacity due to the electronic excitations of the degenerate electron gas decreases as $\gamma T$ [33, 34]. Since $\delta T^3$ tends to zero faster than $\gamma T$ with decreasing temperature, both contributions can be separated clearly. With the data of $\gamma$ collected in [35] the electronic contribution $\gamma T$ is extrapolated to the melting temperature, $T_m$. The results of $\gamma T_m$ are depicted in the upper part of Figure 5. Despite of the huge temperature interval of the extrapolation from temperatures near liquid helium (He) to several hundred or thousand Kelvin one obtains the right order of the electronic contribution to the molar specific heat capacity near $T_m$. Thus, there is no doubt that electronic transitions are excited with an increasing rate approaching the melting temperature, $T_m$.

Available data of the molar activation energy of diffusion, $Q_{\text{diff}}$, have been tentatively plotted versus the element number (and atomic electron configuration) and compared with data of the molar melting enthalpy $\Delta H_{\text{melt}}$, Figure 6. The pattern is roughly similar to the electronic part of the molar specific heat capacities, which indicates a correlation of $Q_{\text{diff}}$ to the occupancy of the outer shells of the chemical elements and the electronic transitions, Figure 5. This gives a strong hint that the activation energy of the diffusion constant relates to electronic transitions in chemically bonded systems. This is not surprising, since the strength of the bonding depends on the electronic structure of the atoms. Using logarithmic scales, we compare $Q_{\text{diff}}$ with the molar melting enthalpy, $\Delta H_{\text{melt}}$, Figure 7. The curves indicate that $Q_{\text{diff}}$ is roughly $(15 \pm 5)$ times as much as $\Delta H_{\text{melt}}$ mentioned already in [36] with the claim that the entropy of fusion and the melting temperature have a governing influence on the self-diffusion rates in solids. However, the correlation with electronic transitions has
not been considered in [36]. The qualitative similarity between $\Delta H_{\text{melt}}$ and $Q_{\text{diff}}$ as a function of the atomic number of the chemical elements seems to be surprising. The reason is that data of $\Delta H_{\text{melt}}$ are the relatively small differences between the molar enthalpies of the molten and the solid state in thermal equilibrium at the melting temperature, $T_m$, whereas data of $Q_{\text{diff}}$ are much larger activation energies of dynamic processes to overcome the potential barriers due to spontaneous fluctuations within temperature intervals below $T_m$. Therefore, $Q_{\text{diff}}$ is not necessarily expected to be related to the relatively small energy difference $\Delta H_{\text{melt}}$ between two equilibrium states of the sample at $T_m$.

In fact, the net energy difference between two equivalent places of a diffusing particle is zero on average: The energy necessary to overcome the barrier between two neighbouring equivalent places is redistributed during the relaxation of the diffusing particle, Figure 3. Thus, there is no net energy $Q_{\text{diff}}$ stored by the diffusing particle.

The difficulty to understand the similarity between $\Delta H_{\text{melt}}$ and $Q_{\text{diff}}$ as a function of the atomic number of the chemical elements, in particular the fact $Q_{\text{diff}} \gg \Delta H_{\text{melt}}$, can be removed by the following considerations visualised schematically in Figure 8: In a recent paper, it was shown that the melting of chemically bonded solids is induced by electronic transitions [26]. Chemically bonded crystals melt if sufficient electrons make transitions from bonding states $E_0$ to excited states $E_1$ and relax into lower electronic states $E_0$ of the disordered melt. The electrons in the excited states have a diff-
different probability distribution as compared to their bonding states and force the neighbouring core ions to accept new places. In the steady molten state, sufficient electrons are thermally excited to \( E_1 \) and drive core ions to new places and finally relax together with core ions to new (in the molten state disordered) positions \( E'_0 \). The melting energy needed is in the order of \( E_0 - E_0 \) per particle. The molar melting enthalpy, \( \Delta H_{\text{melt}} \), and entropy, \( \Delta S_{\text{melt}} = \Delta H_{\text{melt}} / T_m \), are essentially stored in the new configuration. During diffusion, however, the overall configuration remains constant, but the transitions of electrons to excited states with much larger energy \( E_1 - E_0 \gg E_0 - E_0 \) and the subsequent relaxation induce reordering of the diffusing core ions and drive the local diffusion processes. Thus, the activation of the diffusion process requires transitions to excited electronic states with transition energies per particle, \( Q_{\text{diff}} \gg \Delta H_{\text{melt}} \), which are not stored in the material, whereas the molar melting enthalpy, \( \Delta H_{\text{melt}} \), corresponds to the difference between the initial crystalline state and the relaxing ground states in the melt. The melt as a new configuration of the system stores \( \Delta H_{\text{melt}} \), but the larger activation energy \( Q_{\text{diff}} \) is taken from the lattice and released back to the lattice of the sample. Then, the correlation between \( \Delta H_{\text{melt}} \) and \( Q_{\text{diff}} \) as functions of the atomic number is not surprising but expected, if melting and diffusion are caused by transitions of the same bonding electrons over similar barriers or excited states.

7 Inducing electronic transitions separately and independently of the temperature

In the preceding sections, it has been qualitatively described how diffusion is driven by both vibrations of the atoms and core ions and by electronic transitions. Since diffusion is usually investigated at constant temperature in the samples in equilibrium, the effects of the vibrations are simultaneously coupled to those of electronic transitions. Thus, it is not obvious how to separate both kinds of driving effects in experiments of diffusion. Therefore, one needs to vary the rate of electronic transitions separately and independently of the temperature and the vibrations in the solid. Such a possibility is given by irradiating the samples with photons and transferring electrons to levels at higher energy. Then, the rate of electronic transitions can be varied independently and separated from atomic and ionic vibrations. This technique has already been applied for decades or even centennials to induce diffusion. Examples how applications and technique drew profit are given in the following subsections.

7.1 Decomposition of silver halides

The powder of crystallites of the silver halides AgCl (silver chloride) and AgBr (silver bromide) are usually white if they are produced freshly and kept in the dark. If the crystallites are irradiated by photons with energies larger than their band-gap (typically in the blue and near UV spectral regions), they become grey and – after extended irradiation – finally black. This well-known photolytically induced reaction is the basis of silver halide photography. An uncounted number of publications can be found in the literature. References [37–40] represent an arbitrary selection.

The photons absorbed by the silver halide crystallites induce transitions of electrons from states in the valence band to the conduction band leaving
holes in the valence band. The electrons in the conduction band can be trapped on the surface of the silver halide crystallites to form silver (Ag) atoms. The holes are trapped in hole traps for charge compensation (such as changing the charge state from Cu$^+$ to Cu$^{++}$) or transform selected Cl$^-$ and Br$^-$ ions into atoms and finally Cl$_2$, Br$_2$ or ClBr molecules, which escape from the surface of the crystallites into the atmosphere because they are volatile. With increasing duration of the irradiation, the whole silver halide crystallite can be decomposed photolytically into metallic silver particles (small specks and wires) and volatile halogen. This process is called “printing out”.

In today’s silver halide photography it is sufficient to create a latent image by diffusion of silver atoms to form small clusters of just four Ag atoms on the surface of each irradiated grain or crystallite [39]. The process of diffusion is initiated by the photoelectrons released by the irradiation. Such a small Ag cluster allows the crystallite to be fully decomposed or reduced into silver (Ag) specks and halogens by a chemical developer. Without silver (Ag) cluster on its surface the developer does not decompose remarkably the silver halide crystallite. The silver cluster on the surface lowers the barrier for the chemical development (which is also an effect of diffusion). Then, the reduction of the silver halide grains proceeds much faster by orders of magnitude. The process of chemical development increases the sensitivity of darkening roughly by the ratio of all silver ions in the grain to about four atoms of the initial silver cluster on the grain.

### 7.2 Photochromism of oxide glasses doped with silver halides

Armistead and Stookey invented and described commercial photochromic sunglasses [41, 42]. The darkening and regeneration kinetics is summarized with further details on electronic and coupled ionic processes and the respective references in [43, 44]. Accordingly, most commercial photochromic glasses consist of a transparent glass matrix (sometimes it may be additionally coloured by absorbing ions in the glass) with silver halide precipitations as photochromic centres. The silver and halogen ions are dissolved as isolated ions in the melt and in the glass right after cooling the melt. The photochromic centres are created by phase separation or demixing of the homogeneous glass upon a heat treatment or striking process at temperatures above the glass transformation temperature $T_g$. The centres have diameters preferentially in the range of 10 nm to 25 nm. They consist mainly of mixed Ag-(Cl, Br) with some copper halide to increase the sensitivity of the photochromism.

The silver halide centres do not absorb appreciably in the visible spectrum unless they are exposed to blue, violet or ultraviolet (UV) radiation. Photons from those parts of the spectrum are absorbed and create simultaneously photo-electrons in the conduction band and photo-holes in the valence band of the photochromic centres. Photo-electrons diffuse to the surface, where they are trapped in surface states of the photochromic centres. They attract Ag$^+$ ions from the interior of the centres, recombine with them and form neutral Ag specks by repeating this process many times. If a speck has grown large enough, it has metallic properties. It may form an Ag layer on the surface of a photochromic centre. Such Ag layers cause broad absorption bands in the visible (VIS) spectral range, which darken the glass. This reaction is similar to the printing out in silver halide photography mentioned in section 7.1, however with the possibility to reverse the effect if the darkening radiation is switched off, since the reaction products of the photolysis remain close together in the photochromic centres of the glass matrix. The photoholes in the valence band as the counterparts of the photo-electrons are trapped in hole traps (partly Cu$^+$ / Cu$^{++}$) or neutralize the halogen ions in the interior of these centres. Simultaneously to the forward reaction a reverse reaction takes place, which increases approximately with the square of the deposited silver atoms [43]. Since the decomposition products cannot escape, the photolytic decomposition is reversed to form again Ag(Cl, Br), which is transparent in the visible (VIS) spectral region, if the darkening irradiation is switched off. The diffusive processes in the photochromic centres are clearly driven by electronic transitions initiated by the irradiation.
7.3 Photo-induced nucleation in lithium-alumo-silicate glass

Glasses are obtained if crystallisation is hindered during cooling of melts. This can occur essentially if the melting entropy is small enough and if sufficiently directed bonds are present in the melt [45]. The barriers for crystallisation are overcome more or less effectively if nuclei are formed on which crystallites can be grown. Nuclei are grown from special nucleating ingredients, such as (titanium dioxide) TiO$_2$, (zirconium dioxide) ZrO$_2$ or materials precipitating as metallic particles in inorganic glasses at temperatures near the transformation temperature $T_g$. Growing metallic particles as nuclei can also be induced by irradiating glasses of special compositions in particular in the UV spectral region.

A typical composition (in % of the mass) of the commercial photosensitive glass FOTURAN™ of SCHOTT AG, Mainz, is (75–85) % SiO$_2$, (7–11) % Li$_2$O, (3–6) % Al$_2$O$_3$, (3–6) % K$_2$O, (1–2) % Na$_2$O, (0–2) % ZnO, (0–1) % B$_2$O$_3$, (0.2–1) % Sb$_2$O$_3$, (0.1–0.3) % Ag$_2$O and (0.01–0.2) % CeO$_2$ [46]. The glass is roughly a lithium-alumo-silicate glass with adjusted stability against spontaneous crystallisation by replacing part of the Li$_2$O by K$_2$O and Na$_2$O. The components ZnO and B$_2$O$_3$ are added to better control the melting temperature and the chemical stability of the glass. Sb$_2$O$_3$ is used to adjust a sufficiently large amount of cerium (Ce) in the valence state 3+. The small amounts of Ag$_2$O and CeO$_2$ are necessary ingredients for photosensitivity to induce nucleation. Further details of the process and applications are described in the literature [47–50].

The transformation temperature, $T_g$, of this glass is about 455°C [46]. If a glass specimen, such as a sheet glass, is irradiated at room temperature in the UV spectral region (the manufacturer recommends the range of wavelength around 320 nm) electrons are split off from Ce$^{3+}$ to form Ce$^{4+}$ leaving a hole (or empty state) behind. The photo-electrons are trapped in trapping centres (also cerium in its 4+ valence state or fully oxidised Ce$^{4+}$ in the glass matrix) and may transform silver ions, Ag$^+$, into neutral silver atoms, Ag. As the photo-electrons do not recombine immediately with the Ce$^{4+}$ ions from which they have been split off by the irradiation, the electron system of the irradiated volume stores photo-electrons and photo-holes in the volume irradiated by photons in the UV. The charge distributions is stable at low temperature. If the specimen is subsequently heated to temperatures in the range of about 450°C to 500°C, electrons are split off from traps, Ag atoms and Ce$^{3+}$ and trapped again to form silver atoms and Ce$^{3+}$ ions before finally recombining with holes. In the neutral state, the silver atom carries a trapped electron which corresponds to a localized negative charge in the glass. Thus, it attracts positive ions, such as other Ag$^+$ ions in the neighbourhood, and starts as an Ag$_2^+$ dimer, which is neutralized capturing an electron split off thermally from other electron traps, Ce$^{3+}$ ions or single isolated silver (Ag) atoms. Repeating these steps, small metallic silver clusters are formed which act as nucleation centres for crystallising the former irradiated volume. The net balance of the electrons corresponds to the shift of electrons from Ce$^{3+}$ ions (forming Ce$^{4+}$ ions) to Ag$^+$ ions (forming Ag clusters). The diameter of the silver clusters is in the range of few nm [46]. Such silver clusters cause yellow to orange-yellow colouring of the clear glass. (Such clusters show also up in the yellow coloured glass in window paintings of medieval cathedrals.) In the present case, these silver (Ag) clusters serve as nuclei to catalyse crystal growth in the irradiated volume.

Further heating to temperatures above $T_g$ (the typical range is from 560°C to 600°C) makes lithium-metasilicate (Li$_2$SiO$_3$) crystals grow on the silver nuclei just in the volume irradiated with UV-light before. These crystals can be etched by hydrofluoric acid, whereas the glassy material in the non-irradiated volume is not crystallized and therefore does not dissolve remarkably in the etching process. Here we see how the electronic transitions in the irradiated volume initiate diffusion and nucleation to be exploited for the subsequent shaping of glass by etching.

7.4 Photo induced reactions of colour centres in alkali halides

The (1 0 0) plane of an alkali halide crystal with face centered cubic (fcc) structure is represented schematically by the arrangement of plus and minus signs in Figure 9. The minus signs symbolize the position of halide ions and the plus signs the al-
F-centres are readily created in crystalline alkali halides if the crystals are irradiated by nuclear radiation. Such radiation may create a bunch of different defects in the crystals with different superposing absorption bands. To study their absorption bands and other properties or effects alone, F-centres are introduced into alkali halide crystals by heating the crystals in alkali vapour under pressure in the range between about $10^2$ Pa to $10^4$ Pa near or above $2/3$ of the melting temperature of the respective alkali halide. The technical procedure of this additively colouring process is described in [51, 52]. The mechanism of additive colouring is understood as follows: During the heating of an alkali halide crystal, the alkali from the vapour bonds to the surface of the crystal as an alkali ion. The electron compensating the positive charge of the ion diffuses into the crystal where it is trapped in a halogen ion vacancy and forms an F-centre. The electron trapped in a halogen ion vacancy inside nearby establishes electrical charge neutrality. Adding further alkali ions to the surface of the alkali halide crystals, the number of vacancies must also increase. As the halogen vacancies trap electrons, the number of pure vacancies would decrease. Thus, further halogen ion vacancies form and are filled with electrons to fulfil chemical equilibrium for a specified vapour pressure of alkali.

F-centres in freshly coloured and quenched alkali crystals are stable at low temperature and in the dark. With increasing temperature and time duration F-centres aggregate and build aggregate centres of many different kinds. Surveys on the defect chemistry are found in [53–57]. The aggregation of colour centres is enforced if the centres are irradiated with photons. The first in the series of aggregate centres is the F$_2$-centre (sometimes also called M-centre). It consists of two neighbouring F-centres, Figure 10. It can be detected by its absorption band of the dipole transition in [1 1 0] direction and equivalents (M$_1$ absorption band). The maximum of its absorption band shifts with respect to the F absorption band roughly by a factor of $\sqrt{2}$ to longer wavelengths. The M$_1$ band can be interpreted as a vibrational mode of two electrons coupled along the axis of the pair of vacancies. The other transitions perpendicular to that direction (M$_2$...
and M₃ absorption bands) superpose the absorption band of the F-centre.

With increasing photon irradiation into the F-band, F-centres continue to aggregate and form F₂ and F₃-centres (also called R- and N-centres with their different R₁, R₂, N₁ and N₂ absorption bands depending on the arrangement and the orientation with respect to the axes of the crystals). Such colour centres may capture an additional electron or loose an electron (equivalent to capturing a hole). This considerably increases the series of different possible colour centres. The general nomenclature is X if the centre is not charged (each of the aggregated vacancies contains an electron), X⁺ if the centre lost an electron and X⁻ or X' if the centre trapped a surplus electron. The absorption bands of the F- and F-aggregate centres have been extensively investigated and the position of the maxima are given in the literature (for a survey see [53–57]). Data of several absorption bands of F-aggregate centres in different alkali halides are collected from the literature and interpreted as local vibrational modes of captured electrons in [58], because the energies of the absorption band maxima vary similar to the frequencies of the local vibrational modes of isolated H– and D–ions (called U-bands) replacing halogen ions in alkali halides [59].

Obviously, the aggregation of the F-centres occurs by diffusion. It is well known that the aggregation can be considerably enhanced by irradiating the doped alkali halides in the F-band. Thus, the diffusion is enhanced by the irradiation directly or by changing the charge state of the centres and creating X⁺ and X⁻ centres.

For a reaction scheme in a band diagram, it is assumed that only F-centres are present in the alkali halide crystal at the beginning of the irradiation. A scheme of energy levels visualizes the electronic transitions induced in an alkali halide crystal if a photon is absorbed in the F-absorption band, Figure 11 [60, 61]. As a first step, the electron of the F-centre is excited by a photon of energy hνᵢ from its ground state to the excited state F⁺, Figure 11 (transition 1a). The energy hνᵢ is about 1.8eV < hνᵢ < 3.6eV depending on the composition of the alkali halide. The electron of the F-centre relaxes in its excited state and emits phonons to the crystalline lattice. At low temperatures the electron transits from its relaxed excited state F⁺ to the ground state emitting a photon of energy hνᵢ < hνᵢ or radiationless with excitation and emission of further phonons (transition 1b). If sufficient thermal energy is available, the electron can be emitted from the excited state F⁺ into the conduction band (transition 2). If the electron escapes the F-centre, a halogen vacancy or α-centre is left.

Electrons in the conduction band can be captured by other F-centres, which become F’-centres (transition 3a). F-centres are stable at sufficiently low temperature (e.g. below 180K in potassium.

![Figure 10](image1.jpg)
**Figure 10.** An F₂- or M-centre consists of two F-centres bound together.

![Bild 10](image2.jpg)
**Bild 10.** Ein F₂- oder M-Zentrum besteht aus zwei aneinander gebundenen F-Zentren.

![Figure 11](image3.jpg)
**Figure 11.** Transitions of electrons between F-centres in their different charge states and the conduction band. The transitions of electrons are defined in the text.

![Bild 11](image4.jpg)
**Bild 11.** Übergänge von Elektronen zwischen F-Zentren in ihren unterschiedlichen Ladungszuständen und dem Leitungsband. Die Übergänge der Elektronen sind im Text beschrieben.
chloride or KCl further vacancies are created by continuing irradiation ready to be filled with electrons). This means that a photoelectron can contribute to photoconductivity only until it is captured by an F-centre. At higher temperatures (higher than 180K in KCl), however, the F'-centres become unstable. They emit one of their electrons back into the conduction band if enough thermal energy is available from lattice vibrations (transition 3b): The higher the temperature the larger the rate of re-emission of electrons from the F-centres. Capture into F-centres and reemission from the F-centres into the conduction band occurs multiple times until the photoelectrons are finally captured by α-centres (or “empty F-centres”) via the excited state F* reversing the transitions 2 and 1a or directly radiationless into the ground state, Figure 11 (transition 4). The rate equations of the reaction kinetics described have been established and discussed as a function of temperature, photon flux density and F-centre concentration [61]. The theoretical results have been tested and verified by experiments of both the photoconductivity of the electrons in the conduction band and photochromy due to the induced absorption band of the F-centres as a function of time using rectangular photon pulses [62, 63].

Aggregation of added colour centres and their combination with deliberately added impurities in the alkali halides depends also on diffusion. The kinetics of the diffusion can be investigated and followed by determining the absorption constants of the participating centres as a function of time. The enhancement of the transformation reactions due to irradiation with photons in selected absorption bands has been intensively investigated in the past. For simplicity one can assume that in such experiments at sufficiently low temperatures diffusion without irradiation can be neglected. The formation of F₂-centres (also called M-centres) has been investigated without a definite conclusion whether the vacancy (α-centre) or the F-centre or both are the diffusing particles [53, 64]. Surveys on different investigations are given in [54–57]. In any case, the α- and F’-centres attract each other as they are oppositely charged centres with respect to the alkali halide lattice.

If electronic transitions are supposed to initiate a step of a diffusing particle to a neighbouring equivalent place, in principle all electronic transitions in Figure 11 have to be considered. However, one can estimate that the rate of transitions 3a/3b would be sufficient to account for the aggregation of F’-centres with F-centres (forming M’-centres which lose their surplus electrons) under irradiation. Without irradiation M-centres do not form in the range of low temperatures considered. It is interesting to note that the multiple capture process of electrons into F-centres (indicated in Figure 11) has not yet been considered as a possible reason for the diffusion of F’-centres. The energy released locally during the capture transition 3a of an electron from the conduction band into the F-centre is in the order of typically 0.3eV to 0.5eV of thermal energy. Such values could be sufficient for rearranging the atoms around the centre and for diffusing. In principle, one must also take into account electronic transitions 4 in Figure 11 enhancing the diffusion of colour centres. In this case, much larger amounts of energy are liberated but much less frequently than by transitions 3a/3b.

8 Qualitative description of the diffusion induced by electronic transitions

The basic idea that diffusion is enhanced by capture and emission from energy levels of electrons – or for short by electronic transitions – has already been described in section 5e of [26] together with the reasons for melting chemically bonded solids, the glass transition $T_g$ and their increased thermal expansion coefficient in the range above $T_g$. Accordingly, electronic transitions seem to initiate these effects.

Electronic transitions in chemically bonded melts, glasses and solids require typical activation energies in the range of about $0.4eV < \Delta E_{diff} < 6eV$. (For metals and superionic conductors the lower limit tends to zero.) Therefore, it is hard to understand why electronic transitions assisting diffusion are disregarded until now.

In the preceding section 7 several examples are presented how electronic transitions and recombination processes initiated by photons induce or at least enhance diffusion at constant temperature. In these cases, the electronic transitions are due to photon irradiation and the rate of electronic transitions is varied without changing the possible con-
tribution to diffusion by thermal phonons. The reason for these examples was that the changes of the electron states, their electronic wave functions and their probability distribution in space induce the steps of diffusion. Of course, we can try to switch off the contribution of the photons and try to test only the influence of the phonons without irradiation. However, this does not exclude that concomitant electronic transitions induce and contribute to the diffusion even in the dark. Without irradiation, the temperature must be increased to replace the action of photons. To estimate the effect of the photons to diffusion one needs the kinetic parameters of the electronic transitions. These parameters can be determined from photoelectronic relaxation and generation-recombination noise spectra, e.g.

Also important is considering that the photon irradiation changes the charge state of the diffusing particles and new particles or new mixing components arise in the system by exchanging electrons between different states. Then, we induce additional local electrical driving forces to enhance the diffusion, i.e. the transport of the particles of the different components (see section 10.3). However, the probability density distribution of the electric charges changes temporarily and locally, but over distances longer than a few lattice constants the average net charge is close to zero and the electrical potential does not change. The different components created by the photon irradiation are not in thermal equilibrium, which is perceived experimentally by the relaxation to the thermal equilibrium after switching off the irradiation. If electrons occupy different energy levels even in thermal equilibrium, we have a mixture of different components, since the position of different charge states is fluctuating in space. Such an effect can be seen in investigations of fluctuations of the charge carrier concentration in the valence and conduction band (generation-recombination noise), which depends on the fluctuation of the occupancy of the different local levels or the amount of each component [65–67].

The configuration around the atoms relaxes during both the capture and emission processes of electrons and holes into the local electron states, as their wave functions and charge distributions adjust to the initial and the final states of the charge carriers. Both processes can rearrange the local configuration of the atoms in a solid or a melt and induce diffusion. In a capture process, however, excess energy is released, whereas in a reemission process energy is needed to achieve the transition of the electron. Since diffusion normally requires activation energy, a jump or step of the diffusing particle is more likely during capture than during re-emission of charge carriers. One must point out that assistance of phonons to perform the steps of diffusion is certainly necessary and has to be included.

The transition of an electron into a different state with its changed probability density distribution in space has an important dynamical effect: The electron system and the position of the core ions are out of full local equilibrium. Thus, the core ions rearrange and cause the particles to move to new positions or to diffuse during the subsequent relaxation period. In this case, the driving force for diffusion results less from the extended vibrations of the diffusing atom and its environment but rather from the localized transition of the electron to a different state with new probability density distribution in space. If an electron with its wave function extended over the single crystal is captured to a lower local energy level, the transition energy is liberated on site. Then, the activation energy of diffusion is not coupled to average energies of extended phonons or average thermodynamic quantities such as the melting or boiling enthalpies, but to fluctuations of local electronic transitions and to kinetic parameters, such as transition energies, densities of states, bandgaps and capture cross sections (or recombination coefficients) of electrons and holes. This would be a true dynamic and not an average static effect. Such fluctuations of electronic transitions occur with higher rates with increasing temperature and require that the local crystalline lattice rearranges. Finally at sufficiently large temperature, the lattice breaks down and the solid melts. Thus, one might expect that the activation energy of self-diffusion would rather be related to a multiple of the average thermal equilibrium energy needed for melting (Figure 8), since all bonds of a diffusing atom must be broken. To test this assumption, we compare the activation energy of self-diffusion with the melting enthalpy, $\Delta H_{\text{melt}}$, as a function of the element number together with the last orbitals occupied by an electron (Figure 6). In fact, the number of electrons in the uppermost shell of the atoms controls the activation energy of self-
diffusion as well as the melting enthalpy. This gives a strong hint that $Q_{\text{diff}}$ relates to electronic effects. In this case, the coefficient of self-diffusion is driven by local fluctuations of both the chemical and electrical potential or - for short - the local fluctuations of the electrochemical potential.

9 Basic quantitative description of the diffusion induced by electronic transitions

9.1 Qualitative interpretation of the diffusion coefficient

The general traditional interpretation of the diffusion constant focuses on the movement of atoms, ions, defects, larger entities like molecules and the coupling of the diffusing species to phonons (see section 4). The diffusion constant for a special mechanism is basically build of three factors: $v_x$: trial, jump or escape rate (one should avoid frequency, as these events are not necessarily periodic) of a diffusing particle of kind $x$ to overcome the barrier, $P_x$: probability of the particle to overcome the barrier successfully and to reach a different position in a special direction, expressed essentially by Boltzmann’s factor $\exp\left(-\frac{Q_{\text{diff}}}{k_B T}\right)$, $a^2_x$: average jump width squared.

Then, the diffusion constant has the form

$$D_x \propto v_x P_x a^2_x.$$  \hspace{1cm} (17)

Refinements by correlation and entropy factors and coupling of different diffusing species may be included if necessary. This can be generalized to different paths, mechanisms and kind of particles.

Applying relation (17) to interpret diffusion data one needs to know the average jump width squared $a^2_x$, the probability to overcome the barriers into a special direction $P_x$ and the trial rate, $v_x$, or a reasonable estimate of these quantities.

To interpret the diffusion coefficient by electronic transitions the activation energy $Q_{\text{diff}}$ results partly from breaking chemical bonds by transitions of electrons from bonding to antibonding states. Indications of such an effect are given and discussed for silicon and germanium in the subsequent section 9.2. The trial rates arise from the capture and reemission rates of electrons or holes from local energy levels into conduction and valence bands and vice versa. These rates contribute to the pre-exponential factor $D_0$ and their possible activation energy may be part of the activation energy, $Q_{\text{diff}}$. On the other hand, the successful trial rates can be driven by the energy released during the capture of charge carriers into defect levels or by band-to-band recombination of the carriers. Also energy from the phonon bath of the solid or the melt may contribute. Therefore, a general prediction is not yet possible. Dealing with electronic transitions, one may take profit of the rate description of dynamic processes in semiconductor devices and photoconduction [68, 69] to be discussed in section 9.3.

9.2 Interpreting the activation energy of the coefficient of self-diffusion in silicon and germanium

Silicon and germanium atoms are bound to their neighbours 4-fold in their respective crystals. Therefore, four bonds must be opened in order an atom may diffuse. A single bond opens by a transition of an electron from a local bonding state in the valence band to a local anti-bonding state nearby in the conduction band. It requires the thermal gap energy, $\Delta E_{\text{gap}}$. Using the energies of the indirect bandgaps at low temperature of silicon (Si) and germanium (Ge) [70, 71] four open bonds correspond to the energy $4\Delta E_{\text{gap}} = 4 \times 1.17 \text{ eV} = 4.68 \text{ eV}$ for Si and $4 \times 0.7437 \text{ eV} = 2.9748 \text{ eV}$ for germanium (Ge). These energies are close to the observed activation energies for self-diffusion of silicon (Si) and germanium (Ge), Table 1.

Pichler evaluated the tracer diffusivity of many publications and obtained for Si a mean activation energy of $Q_{\text{Si,diff}} = 4.705 \text{ eV}$ with a 90% confidence interval ranging from 4.6 eV to 4.8 eV [72]. The data $Q_{\text{Si,diff}} = 4.76 \text{ eV}$ from [73] is very close to the value determined in [72]. On the other hand, a value of $Q_{\text{Si,diff}} = 5.13 \text{ eV}$ has been determined for self-diffusion, which is outside the 90% confidence interval [74].

Experimental data on self-diffusion in germanium crystals are not as numerous as for silicon.
The diffusion for Ge in Ge yields values between $Q_{\text{diff}}$ and pre-factors $D_0$ (if available) of the diffusion coefficient of silicon (Si), germanium (Ge), acceptors and donors in silicon and germanium. Data of acceptors and donors in silicon (Si) are for the intrinsic case, i.e. if $p = p_i = n_i = n_i$.

**Table 1.** Activation energies $Q_{\text{diff}}$ and pre-factors $D_0$ (if available) of the diffusion coefficient of silicon (Si), germanium (Ge), acceptors and donors in silicon and germanium. Data of acceptors and donors in silicon (Si) are for the intrinsic case, i.e. if $p = p_i = n_i = n_i$.

![](image)

In the range of temperature in which diffusion experiments take place with Si and Ge, the bandgap narrowing is approximated linearly as indicated in Figure 12, such as

$$\Delta E_{\text{gap}}(T) = \Delta E_{0,\text{fit}} - \frac{d\Delta E_{\text{gap}}(T_{\text{fit}})}{dT} T,$$

where the initial value $\Delta E_{0,\text{fit}}$ and the average slope $m = \frac{d\Delta E_{\text{gap}}(T_{\text{fit}})}{dT}$ of the experimental temperature range are fitting parameters. $\Delta E_{0,\text{fit}}$ is 1.28 eV for silicon and 0.815 eV for germanium. Interpreting these data of $\Delta E_{0,\text{fit}}$ as $\Delta E_{\text{gap}}$ in the exponential, one obtains as the activation energy of diffusion

$$4\Delta E_{\text{gap}} = 5.12 \text{ eV for silicon and 3.26 eV for germanium, which would also be consistent with the experimental data of the activation energy.}$$

Inserting generally $(\Delta E_{0,\text{fit}} - mT)$ into the exponential to determine the activation energy from experimental results of the diffusion constant yields

$$
\Delta E_{\text{gap}}(T) = \Delta E_{0,\text{fit}} - \frac{d\Delta E_{\text{gap}}(T_{\text{fit}})}{dT} T,
$$

where the initial value $\Delta E_{0,\text{fit}}$ and the average slope $m = \frac{d\Delta E_{\text{gap}}(T_{\text{fit}})}{dT}$ of the experimental temperature range are fitting parameters. $\Delta E_{0,\text{fit}}$ is 1.28 eV for silicon and 0.815 eV for germanium. Interpreting these data of $\Delta E_{0,\text{fit}}$ as $\Delta E_{\text{gap}}$ in the exponential, one obtains as the activation energy of diffusion

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where the initial value $\Delta E_{0,\text{fit}}$ and the average slope $m = \frac{d\Delta E_{\text{gap}}(T_{\text{fit}})}{dT}$ of the experimental temperature range are fitting parameters. $\Delta E_{0,\text{fit}}$ is 1.28 eV for silicon and 0.815 eV for germanium. Interpreting these data of $\Delta E_{0,\text{fit}}$ as $\Delta E_{\text{gap}}$ in the exponential, one obtains as the activation energy of diffusion

$$4\Delta E_{\text{gap}} = 5.12 \text{ eV for silicon and 3.26 eV for germanium, which would also be consistent with the experimental data of the activation energy.}$$

Inserting generally $(\Delta E_{0,\text{fit}} - mT)$ into the exponential to determine the activation energy from experimental results of the diffusion constant yields
still larger temperatures, the activation energy increases in the case of a concave $\Delta E_{\text{gap}}(T)$-function. In fact, such a behavior can be observed [72].

In the case of a convex $\Delta E_{\text{gap}}(T)$-function, the interpretation can also be inaccurate depending on the slope $m = \frac{d(\Delta E_{\text{gap}}(T))}{dT}$ in the temperature range of the investigation. Such possible errors do not depend on how the varying activation energy in an exponential is interpreted, which accidentally is here the bandgap. Thus, it is not surprising that the measured activation energies from similar investigations show large differences, if the experimental data points to be evaluated refer to a rather small temperature range at high temperatures.

Since the experiments on diffusion take place typically between 700 K and 1400 K, one must consider bandgap narrowing and a shift of the energy levels of defects and impurities as well as reactions between defects.

The activation energies $Q_{\text{diff}}$ of the typical substitutional acceptors (boron, aluminum, gallium and indium) and donors (phosphorus, arsenic, antimony and bismuth) in silicon and germanium are smaller than those of Si in Si and Ge in Ge mentioned above, Table 1. They are mostly in the range (3 to 4)$\Delta E_{\text{gap}}$ except for the acceptor boron in germanium, which exceeds with $Q_{B, \text{diff}} = 4.5$ eV even 4$\Delta E_{\text{Ge, gap}} = 3.26$ eV.

The bonding of Si (Ge) in the Si (Ge) lattice requires according to the octet-rule four electrons per atom in $sp^3$ orbitals. A substitutional acceptor replacing Si or Ge delivers only three occupied $sp^3$ orbitals in the outer shell. The forth $sp^3$ orbital is occupied for bonding if the acceptor catches an electron from the valence band. This is equivalent for reemission of a hole from the acceptor level into the valence band. Then, it is negatively charged. Because the acceptor fluctuates between the states with four and three bonds, it needs partly three or four bonds to be broken for diffusion.

In the outer shell of the substitutional donors five electrons occupy $sp^3$ orbitals. As only four electrons are needed to complete the bonding, the fifth orbital readily emits its electron into the conduction band. The donor atom becomes positively charged. The states of the bonding electrons are part of the valence band similar to the bonding states of the acceptors, whereas the fifth $sp^3$ orbitals of the donor occupies an anti-bonding state. Thus, the donors possess effectively three or four

---

**Figure 12.** Bandgaps of germanium (Ge) and silicon (Si) as a function of temperature $T$ using Varshni’s empirical formula $\Delta E_{\text{gap}}(T) = \Delta E_{\text{gap}0} \cdot \frac{T}{T + T_0}$ with the parameters $\Delta E_{\text{Ge, gap}}(T) = 0.7437$ eV $- \frac{4.73 \times 10^{-14} T^2}{T + 235 K}$ and $\Delta E_{\text{Si, gap}}(T) = 1.17$ eV $- \frac{4.73 \times 10^{-14} T^2}{T + 235 K}$ [70, 71] (solid curves) and the linear approximations (dotted lines) in the high temperature range of the diffusion experiments $\Delta E_{\text{Ge, gap}}(T) = 0.815$ eV $- 4.607 \cdot 10^{-4} T$ and $\Delta E_{\text{Si, gap}}(T) = 1.28$ eV $- 4.036 \cdot 10^{-4} T$. 

**Bild 12.** Breite der verbotenen Bänder von Germanium (Ge) und Silizium (Si) in Abhängigkeit von der Temperatur $T$ nach der empirischen Formel von Varshni $\Delta E_{\text{gap}}(T) = \Delta E_{\text{gap}0} \cdot \frac{T}{T + T_0}$ mit den Parametern $\Delta E_{\text{Ge, gap}}(T) = 0.7437$ eV $- \frac{4.73 \times 10^{-14} T^2}{T + 235 K}$ und $\Delta E_{\text{Si, gap}}(T) = 1.17$ eV $- \frac{4.73 \times 10^{-14} T^2}{T + 235 K}$ [70, 71] (durchgezogene Kurven) und die linearen Approximationen (punktierte Geraden) für hohe Temperaturen, bei denen die Diffusionsversuche durchgeführt wurden, $\Delta E_{\text{Ge, gap}}(T) = 0.815$ eV $- 4.607 \cdot 10^{-4} T$ und $\Delta E_{\text{Si, gap}}(T) = 1.28$ eV $- 4.036 \cdot 10^{-4} T$.

$$\exp\left(-\frac{\Delta E_{0, \text{fit}} - m T}{k_B T}\right) = \exp\left(\frac{m}{k_B T}\right) \exp\left(-\frac{\Delta E_{0, \text{fit}}}{k_B T}\right) = \text{const.} \exp\left(-\frac{\Delta E_{0, \text{fit}}}{k_B T}\right).$$

Thus, one determines an activation energy that differs more or less from its actual lower value at low temperature. In the case of Figure 12, where $\Delta E_{\text{gap}}(T)$ is concave (seen from below), it is larger than the actual bandgap $\Delta E_{0, \text{gap}}$ near 0K. If the range of temperature of an investigation shifts to
bonding states depending of the occupancy of the donor level.

As the effective number of bonds fluctuates between three and four, the activation energy of the diffusion is \((3 \rightarrow 4)\Delta E_{\text{gap}}\). Further shifts of the activation energy \(Q_{\text{diff}}\) may be due to the mismatch between the substitutional atoms and the lattice atoms, since the substitutional atoms may repulse (or attract) the surrounding matrix atoms due to the mismatch of their atomic diameters. If the diffusion constants of the matrix atoms Si or Ge are determined simultaneously, their value might depend on the level of co-doping as the diffusion of the doping atoms couples to the matrix atoms. Coupling and interactions between different kinds of defects and impurities are also possible.

Summing up, there are many reasons why experimental investigations sometimes do not reproduce data of the diffusivity including the activation energy with sufficient accuracy. One reason may be that distinctive mechanisms of diffusion yield a superposition of diffusivities. Besides superposing different mechanisms also diverse minor amounts of additional impurity components (sometimes even with variable charge states) may provide different diffusivities as a function of the temperature. Many variants of such mixtures can be conceived even in the case of a single dominating mechanism. In this respect, we point at section 9.4 with an example from the literature demonstrating that the diffusivity of boron in silicon varies by a factor as large as 100 to 1000 depending on the concentration of free holes.

### 9.3 Defect centres and the appertaining transition rates of electrons and holes

Singly charged defect levels in the forbidden gap of semiconductors and insulators possess generally four different transitions from the defect level (called \(x\)-centre) to the conduction and valence band and vice versa, \(\text{Figure 13}\). The following considerations on the transition rates are based on \([68]\). They can be extended to multiply charged centres with their respective rates. The concentration of \(x\)-centres occupied by an electron is \(X_n\) and those occupied by a hole is \(X_p\). Because a singly charged defect level is either occupied by an electron or a hole, we have the sum

\[
X_n + X_p = X. \quad (18)
\]

Electrons can be captured from the conduction band, if the \(x\)-centres are occupied by a hole. Then, the capture rate of electrons into the \(x\)-centres per volume is written as

\[
nr_p X_p, \quad (19)
\]

where \(n\) is the concentration of (free) electrons in the conduction band, \(r_p\) is the recombination coefficient for the capture of an electron by an \(x\)-centre and \(X_p\) is the concentration of \(x\)-centres occupied by holes. Analogously, the capture rate of holes into \(x\)-centres occupied by electrons is per volume

\[
pr_n X_n. \quad (20)
\]

Herein, \(p\) is the concentration of free holes in the valence band, \(r_p\) is the recombination coefficient for the capture of a hole by an \(x\)-centre and \(X_n\) is the concentration of \(x\)-centres occupied by electrons.

The concentration of \(x\)-centres occupied by electrons emit electrons into the conduction band with the rate of emission (or reemission) per volume

\[
v_n \exp \left(\frac{-E_c - E_x}{k_B T}\right) X_n \quad (21)
\]
with \( v_n \) being the average trial rate and \( (E_c - E_v) \) the difference between the lower edge of the conduction band and the position of the energy level of the \( x \)-centres. \( k_B \) is Boltzmann’s constant and \( T \) is the temperature.

The \( x \)-centres occupied by holes can emit holes into the valence band. The emission rate per volume reads

\[
v_p \exp \left( -\frac{E_v - E_v}{k_B T} \right) X_p,
\]

(22)

Herein, \( v_p \) is the average trial rate for the emission of a hole from an \( x \)-centre into the valence band and \( (E_v - E_v) \) is the energy difference between the level of the \( x \)-centres and the upper edge of the valence band.

The number of independent parameters in the expressions (19) to (22) can be reduced if we consider thermal equilibrium. In this case, the principle of detailed balancing applies. This means that the capture rate equals its reversing rate, namely the corresponding reemission rate, i.e.

\[
vr_n X_p = nr_n (X - X_n)
\]

= \( v_n \exp \left( -\frac{E_c - E_v}{k_B T} \right) X_n \)

(23)

or

\[
\frac{X_n}{X} = \frac{nr_n}{nr_n + v_n \exp \left( -\frac{E_c - E_v}{k_B T} \right)} = \frac{1}{1 + \frac{v_n}{r_n} \exp \left( -\frac{E_v - E_F}{k_B T} \right)}.
\]

(24)

If the electron concentration in the conduction band and the hole concentration in the valence band are non-degenerate, we are allowed to set

\[
n = N_c(T) \exp \left( -\frac{E_c - E_F}{k_B T} \right),
\]

(25)

wherein \( N_c(T) \) is the effective density of states of the conduction band and \( E_F \) is the Fermi-energy. Inserting (25) into (24) yields

\[
\frac{X_n}{X} = \frac{1}{1 + \frac{v_n}{r_n} \exp \left( -\frac{E_v - E_F}{k_B T} \right)}.
\]

(26)

On the other hand, the occupation of the \( x \)-centres by electrons is determined in thermal equilibrium by the Fermi-function

\[
\frac{X_e}{X} = \frac{1}{1 + \exp \left( \frac{E_v - E_F}{k_B T} \right)}.
\]

(27)

Equations 26 and 27 are identical in thermal equilibrium, if

\[
v_n = r_n N_c(T).
\]

(28)

Thus, the trial rate \( v_n \) can be expressed as the product of the recombination coefficient \( r_n \) and the effective density of states of the conduction band, \( N_c(T) \). The exchange of holes from the valence band and the \( x \)-centres yields mutatis mutandis the analogous relation

\[
v_p = r_p N_v(T).
\]

(29)

Generally, the factors of degenerateness of the respective electron level, \( g_v \), must be included in (26) and (27) if necessary [69] e.g.. In the following, these factors are neglected, because they are not known in many cases and are expected to be in the order of unity.

Using (18) to (22) one can generally calculate the concentration of \( x \)-centres occupied by electrons or via (15) those occupied by holes in the steady state, both under equilibrium and in particular under non-equilibrium conditions (under irradiation, injection, depletion or extraction of charge carriers). It is given by [68, 69]
\[ X_n = \frac{nr_n + v_n \exp\left(-\frac{E_c - E_v}{k_BT}\right)}{X} \]
\[ + pr_p + v_p \exp\left(-\frac{E_c - E_v}{k_BT}\right) \]
\[ = \frac{nr_n + v_n \exp\left(-\frac{E_c - E_v}{k_BT}\right)}{nr(n + n_x) + pr(p + p_x)} X \]

and

\[ X_p = X - X_n \]
\[ = \frac{pr_p + v_n \exp\left(-\frac{E_c - E_v}{k_BT}\right)}{X} \]
\[ + pr_p + v_p \exp\left(-\frac{E_c - E_v}{k_BT}\right) \]
\[ = \frac{rp_p + nr_n r_x}{nr(n + n_x) + pr(p + p_x)} X \].

In (30) and (31) we used as abbreviations the identities
\[ v_n \exp\left(-\frac{E_c - E_v}{k_BT}\right) = r_n N_c(T) \exp\left(-\frac{E_c - E_v}{k_BT}\right) = r_n n_x \]

and
\[ v_p \exp\left(-\frac{E_c - E_v}{k_BT}\right) = r_p N_v(T) \exp\left(-\frac{E_c - E_v}{k_BT}\right) = r_p p_x \]

with the concentration of free electrons in the conduction band
\[ n = N_c(T) \exp\left(-\frac{E_c - E_F}{k_BT}\right) \]

and the concentration of free holes in the valence band
\[ p = N_v(T) \exp\left(-\frac{E_F - E_v}{k_BT}\right) \].

(35)

Analogous to the concentrations of free electrons \( n \) and holes \( p \) in the conduction or valence band, we define \( n_x \) (or \( p_x \) respectively) as the free electron (hole) concentration in the conduction (valence) band, if the Fermi-energy in the equilibrium case (and quasi-Fermi-energy in the case of non-equilibrium) coincides with the energy of the level \( \epsilon_x \) of the \( x \)-centres. Further, \((E_c - \epsilon_x) > (2 \text{ to } 3) k_B T \) and \((E_v - \epsilon_x) > (2 \text{ to } 3) k_B T \) are assumed. This means that the electron gas in the conduction band and the hole gas in the valence band are non-degenerate.

The general formulae (30) and (31) seem to be rather complicated. In practice, however, further simplifications are acceptable, as often just two of the four transitions (19) to (22) dominate. In the case of electron traps transitions (19) and (21) (capture and reemission into the conduction band) dominate and their rates are balanced in the steady state, whereas the rates (20) and (22) can be neglected. Both rates per \( x \)-centre simplify to

\[ nr_n X_p \approx v_n \exp\left(-\frac{E_c - E_v}{k_BT}\right) \frac{X_n}{X} \]
\[ \approx \begin{cases} r_n n_x \text{ if } n \gg n_x \\ r_n n \text{ if } n \ll n_x \end{cases} \]

(36)

Electron traps are expected, if the empty \( x \)-levels (concentration \( X_p \)) possess large recombination coefficients, \( r_n \), for electrons, whereas the occupied \( x \)-levels (concentration \( X_n \)) possess very small ones, \( r_p \), for holes. Preferentially, the levels of electron traps \( E_x \) are closely below the lower edge of the conduction band at \( E_C \).

In the case of a hole trap the rates (20) and (22) dominate and one obtains mutatis mutandis
Hole traps have large recombination coefficients for holes from the valence band but small ones for electrons from the conduction band. One expects hole traps at energies of the levels in a range close-ly above the upper edge of the valence band at \( E_v \). 

For typical recombination centres, the rates (19) and (20) dominate with 
\[
\frac{n_r}{X} \approx \frac{p_r}{X} \approx \frac{r_n r_p n p}{r_n n + r_p p},
\]
and (22) do not compensate each other, such as recombination centres are applicable under non-equilibrium conditions (the rates (19) and (21) or (20) and (22) do not compensate each other), such as under (strong) photo-generation or injection and depletion of electrons and holes under reverse bias of \( pn \)-junctions, respectively.

### 9.4 The diffusion coefficient as a function of the concentration of free charge carriers

Applying the results of the preceding section 9.3 we estimate now the order of the attempt rates by electronic transitions during diffusion. The recombination coefficients are in the order of 
\[
10^{-11} \text{ cm}^3 \text{s}^{-1} < r = \sigma v_{th} < 10^{-5} \text{ cm}^3 \text{s}^{-1}.
\]

By analogy to the kinetic theory of gases, the recombination coefficient \( r \) is the product of capture cross section \( \sigma \) times the average thermal velocity of an electron or a hole, \( v_{th} \), in the conduction or valence band, respectively. Above 300 K, \( v_{th} \) of a free electron is in the range of some \( 10^7 \text{ cm s}^{-1} \). The range near the upper limit of the recombination coefficient \( r \) in (40) corresponds to a charged attractive centre, whereas the range near the lower limit corresponds to a repulsive centre, as its capture cross section is smaller than the cross section of an atom. If \( r \) is in the range given in (40) and the concentration of free electrons \( n \) or \( n_x \) are in the range
\[
10^{13} \text{ cm}^{-3} < n \text{ or } n_x < 10^{19} \text{ cm}^{-3},
\]
the average trial rate of a single \( x \)-centre is
\[
10^2 \text{ s}^{-1} < r_n n \text{ or } r_n n_x < 10^{14} \text{ s}^{-1}.
\]

For transitions of holes similar considerations apply. Defects with the lower values would possess a rather low attempt rate and scarcely diffuse. However, the large values are in the order of ex-
pected trial rates. It is remarkable that $r_n n$ or $r_p n_x$ is a factor of the diffusion coefficient. This factor can be proportional to either a Boltzmann factor (if $n_x \gg n$ or $p_x \gg p$) or to the concentration of free charge carriers $n$ or $p$ (if $n \gg n_x$ or $p \gg p_x$). The transition occurs if the Fermi-energy passes the energy level of the centres. This is important for interpreting $Q_{\text{diff}}$, because the energy in Boltzmann’s factor $n_x$ or $p_x$ does not correspond to the barrier height a diffusing particle has to overcome. $Q_{\text{diff}}$ can also encompass the energy needed for the breaking of bonds such as the energy of band-to-band-transitions $\Delta E_{\text{gap}}$ or a plurality thereof depending on the number of bonds necessary to be broken (see section 9.2). Thus, it is worth revisiting and reinterpreting $Q_{\text{diff}}$ and $D_0$ of diffusing particles in insulators and semiconductors.

The present considerations yield that the diffusion coefficient $D \propto n$, if both the diffusing atom or ion is an electron trap and $n < n_x$, or $D \propto p$, if both the diffusing atom or ion is a hole trap and $p < p_x$. In fact, the diffusion coefficient of the acceptor boron, $D_{\text{boron}}$, in silicon is proportional to the free hole concentration, $p$, over two and a half orders of magnitude, Figure 14, redrawn from [76]. This proportionality has not yet been explained convincingly [76, 77]. The free hole concentration, $p$, in Figure 14 is normalized to the intrinsic free hole concentration, $p_i$, and the diffusivity of boron, $D = D_{\text{boron}}$, is normalized to the equilibrium diffusivity under intrinsic conditions, $D_i$. **Intrinsic condition** means that the free hole concentration equals the free electron concentration or $p(T) = n(T) = n_i(T) = p_i(T)$ with

$$np = n_i^2 = p_i^2$$

$$= N_e(T)N_v(T) \exp\left(-\frac{E_c - E_v}{k_B T}\right)$$

(43)

or

$$n(T) = p(T) = n_i(T) = p_i(T)$$

$$= \sqrt{N_e(T)N_v(T)} \left\{ \exp\left(-\frac{E_c - E_v}{k_B T}\right) \right\} \exp\left(-\frac{E_F - E_v}{k_B T}\right)$$

(44)

Figure 14. Diffusivity $D$ of boron and gallium in silicon as a function of free holes $p$ which is normalized to the intrinsic concentration of free charge carriers $n_i = p_i$. $D$ is normalized to the diffusivity $D_i$, if the concentration of free charge carriers equals the intrinsic concentration of free charge carriers $p = p_i = n_i$. It is assumed that the averaged experimental data $D(T)$ obtained for different temperatures of diffusion are comparable due to the normalizing to $D_i(T)$ and $p_i(T) = n_i(T)$. Redrawn from [76], Figure 5.

**Bild 14.** Der Diffusionskoeffizient $D$ von Bor und Gallium in Silizium in Abhängigkeit von der Konzentration freier Löcher $p$ bezogen auf die innere Konzentration freier Ladungsträger $n_i = p_i$. $D$ ist normiert auf die Diffusionskonstante $D_i$ von Bor und Gallium im Fall $p = p_i = n_i$. $D$ ist gleich der Diffusionskonstante, bei der die Konzentration freier Löcher gleich der innern Konzentration der Ladungsträger ist. Es wird angenommen, dass die gemittelten Messergebnisse von $D(T)$ bei unterschiedlichen Diffusions-temperaturen infolge der Normierungen auf $D_i(T)$ und $p_i(T) = n_i(T)$ vergleichbar sind. Neu gezeichnet nach [76], Bild 5.
Equations 43 and 44 define as a function of temperature, \( T \), the intrinsic concentrations of free electrons and holes, \( p_i = n_i \), and the position of the intrinsic Fermi-energy, \( E_{F,i} \), of the pure component (here: crystalline silicon) with respect to the lower edge of the conduction band \( (E_c - E_{F,i}) \) and to the upper edge of the valence band \( (E\\bar{v} - E_{F,i}) \). \( E_i \) re-names \( E_{F,i} \) in Figure 14, in agreement with [76].

Low doping levels of donors and acceptors yield \( n(T) \neq n_i(T) \), \( p(T) \neq p_i(T) \) and \( E_F \neq E_{F,i} \). However Equation 43 is still valid, if one inserts \( n(T) = N_c(T) \exp \left( \frac{-E_c - E_F}{k_B T} \right) \) and \( p(T) = N_v(T) \exp \left( \frac{-E_v - E_F}{k_B T} \right) \) into the product \( np \) on the left-hand side. Low doping level means that the concentration of free electrons (holes) in the conduction (valence) band is smaller than the effective density of states, \( N_c(T) \), (or \( N_v(T) \)) by a factor of 10 to 100. In this case, the Fermi-energy, \( E_F(T) \), is at least \( (2 \text{ to } 3)k_B T \) below (above) the lower (upper) edge of the conduction (valence) band.

Interpreting the results in Figure 14, we consider the doping with shallow donors (suffix: \( D \)) or acceptors (suffix: \( A \)) with concentrations \( X_{D \text{ or } A} \ll \frac{N_c(T)}{N_v(T)} \). Shallow means that \( (E_c - E_D) \ll \Delta E_{\text{gap}}(T) \) for donors and \( (E_A - E_v) \ll \Delta E_{\text{gap}}(T) \) for acceptors. Further, we take profit from the fact that the product \( np \) in (43) is independent of the actual position of the Fermi-level. Then, the change of the concentration of free electrons \( n \) by a factor \( f \) automatically compensates a change of the concentration of the free holes \( p \) by a factor \( 1/f \) and vice versa:

\[
fn(T)\frac{1}{f}p(T) = n(T)p(T) = n_i(T)p_i(T).
\] (45)

Depending on the kind and amount of doping atoms, the Fermi-energy in (44) shifts from the intrinsic position \( E_{F,i}(T) \) to a different position \( E_F(T) \). If \( E_F(T) > E_{F,i}(T) \), the sample is n-type, i.e. \( n(T) > n_i(T) \) and \( p(T) < p_i(T) \), otherwise it is p-type with the reversed conditions \( n(T) < n_i(T) \) and \( p(T) > p_i(T) \). The shift of the Fermi-level in Figure 14 by doping is calculated as \( 3.45k_B T \) for the p-type range (or \( E_F(T) < E_{F,i}(T) = E_i \)) and \( 2.3k_B T \) in the n-type range (or \( E_F(T) > E_{F,i}(T) = E_i \)).

The experimental results published by Fair and Pappas show a clear linear increase of the diffusion constant of boron as a function of the free hole concentration \( p \) [76], Figure 14, i.e.

\[
D_{\text{Boron}}(p) = D_{\text{Boron}}(p_i) \times \left( \frac{p}{p_i} \right)
\] (46)

\[
= D_{\text{Boron}}(p_i) \times \exp \left( \frac{E_{F,i} - E_F}{k_B T} \right).
\]

Replacing \( \frac{n_i}{n} \) for \( \frac{p_i}{p} \) (from (45)) in (46), however, one is equally allowed to claim instead of (46) the relation

\[
D_{\text{Boron}}(n) = D_{\text{Boron}}(n_i) \times \left( \frac{n}{n_i} \right)
\] (47)

\[
= D_{\text{Boron}}(n_i) \times \exp \left( \frac{E_{F,i} - E_F}{k_B T} \right).
\]

Accordingly, the diffusion constant is proportional to the inverse of the free electron concentration. Thus, we have the apparent difficulty to understand whether the decrease of the free electrons or the increase of the free holes is responsible for the increasing diffusion constant.

Boron substitutes silicon atoms in the silicon lattice and acts as an acceptor with a shallow energy level at \( E_{\text{Boron}} - E_v = 45 \text{ meV} \) just above the upper edge of the valence band. As the Fermi-energy is shifted with increasing concentration of free holes from the upper half of the forbidden gap monotonously towards the upper edge of the valence band, the concentration of holes in the boron levels increases proportional to the concentration of free holes, \( p \). This is equivalent to an increase of boron atoms in their neutral state bound by three bonds and a decrease of boron in its negatively charged state bound by four bonds. Thus, the observation is explained by the increase (decrease) of the amount of boron with three (four) bonds without difficulty [76]. The activation energy for breaking the three-bond state is about three times the bandgap of silicon, as has been mentioned already to explain the results of the intrinsic diffusion constant of boron in Table 1.

However, this does not explain the diffusion constant completely, as the three remaining bonds
of a boron atom still need to be broken. This is achieved by a large fluctuation of the holes near the boron atom replacing the bonding electrons by free holes or shifting these bonding electrons into antibonding states of the conduction band. Such fluctuations require transitions of holes or electrons in the close environment of the boron atom, as holes from the valence band and equivalently transitions of electrons into the conduction band loosen the bonds of boron atoms for the diffusion.

Such dynamic deviations from local average concentrations result in fluctuations of free charge carriers and cause generation-recombination noise in semiconductors [65–67]. Experimental investigations of the generation–recombination noise of semiconducting cadmium sulphide, e.g., demonstrate as an example that the fluctuations of the occupancy of a defect level increase if the Fermi-energy shifts towards the defect level, in agreement with the description above [66].

9.5 Interpreting the diffusivity based on transitions of electrons and holes

The considerations presented in sections 9.1 to 9.4 apply to singly charged defect or impurity levels in insulators and semiconductors. The capture and emission rates of such centres, their concentrations and their different levels as well as the position of the Fermi-level as a function of temperature are required for the evaluation of experimental investigations. These parameters are accessible by a rich variety of experimental methods characterizing defect levels. (Capture and emission of electrons and holes into and out of defect and impurity centres occur also in multiply charged defects. Then, the rate equations for the occupation of each level have to be established and solved for the different steps of the diffusion mechanism.) If intrinsic defects with varying concentration play a role, one must determine their concentration and parameters to interpret the results of diffusion experiments reliably. In practice, such experiments and calculations are difficult and cumbersome, in particular if the concentration of defects changes by recombination, reactions, stress and cycling of the temperature. Mainly, heating and cooling during the investigation may change the concentration of intrinsic defects.

10 Discussion and conclusions

10.1 General results

The present article deals with self-diffusion in chemically bonded solids, glasses and melts. The activation energy, $Q_{\text{diff}}$, in the diffusion constant (7) corresponds to a large fluctuation of thermal energy required for diffusion, because $Q_{\text{diff}}$ is much larger than the maximal average thermal energy, which is in the order of some $k_B T$. As Equation 7 does not specify the kind of activation energy, the necessary fluctuations can and have to be provided from all stored thermal energy in the internal energy, $U(S_V(T))$, at constant volume or in the enthalpy, $H(S_p(T))$, under constant pressure, such as the vibrations and the transitions between the electronic states. These storage possibilities represent the dominant contributions to the specific heat capacities either at constant volume or preferentially at constant pressure, which is the case diffusion constants of solids and melts are determined in practice. To be effective, however, the required fluctuations must be sufficiently probable and localized close to the diffusing atoms. Thermal vibrations of the constituents of the crystalline lattice, the glass or the melt as well as the wave functions of free electrons and holes in single crystals normally extend over large volumes. Therefore, they seem to initiate the diffusion of atoms rarely. However, transitions of electrons and holes between different localized states and their fluctuations within a defect centre or close to a broken bond of an atom seem to provide the driving power in systems with chemical bonding. Thus, they must be included to interpret the atomic mechanism of diffusion in such systems. Several examples in sections 6 and 7 demonstrate the kinetic effects on diffusion by electrons and holes in solids, glasses and melts of materials. Such effects have been widely ignored in the literature of diffusion until now. Several results on the diffusion constant and its activation energy of crystalline silicon and germanium have been interpreted by electronic transitions without difficulty. In the following subsections, we point at two additional effects of electronic transitions worth considering: Thermal spiking, which is also treated in appendix A, and the attraction and repulsion between positive and negative ions.
Irrespective of the mechanism in detail, the diffusion of neutral atoms, core ions (atoms without the bonding electrons), molecular groups or defect centres, any entities in crystals and melts are split into the following three essential steps:

(i) The moving atoms must break their bonds, which keep them at special sites of a matrix, lattice, network or interstitial sites of the system. Sufficiently large localized fluctuations of phonons and electronic transitions induce the bond breaking. This step requires combined actions to initiate diffusion. The activation energy is zero if the diffusing atoms are freely moving, i.e., if the interaction with their neighbours can be neglected. In the case of chemically bonded solids and melts, however, activation energy is needed. If moving particles are created (e.g., interstitials, vacancies, dissociating or combining molecules), their concentration is not constant but varies as a function of temperature. The energy to create the new species of diffusing particles should be separated from the activation energy of the diffusion constant, because it does not characterize the diffusion constant as a transport coefficient.

(ii) The motion of the diffusing particles may also require an activation energy. It depends on the interaction of the moving particles with their environment within the system. The distance between starting and arrival points may be unique (direct exchange, e.g.) or indefinite, such as for interstitials and vacancies, if one considers the distance between creating and combining of the interstitial with a vacancy.

(iii) The moving particles recombine with sites equivalent to the starting position. Then energy is released during the relaxation and phonons are emitted inducing a local thermal spike.

These three steps or actions are considered to occur for a given charge state of the particles. If varying charge states are possible, the different steps apply for particles in the respective state of charge.

10.2 Thermal spiking induced by electronic transitions

The excitation of electrons from occupied low-energy levels to non-occupied high-energy levels transfers energy into the electron system. The energy levels can be localized in or near an atom or belong to the conduction band as the high-energy level and to the valence band as the low energy level. The transitions create free electrons in the conduction band and leave unoccupied states or free holes in the valence band.

The inverse of the excitation must also occur in the steady state of thermal equilibrium. Then, the energy delivered for the excitation is released again in a relaxing local fluctuation.

The transition of an electron (hole) from an occupied (empty) level in the forbidden gap into the conduction (valence) band requires also a sufficiently large fluctuation of local thermal energy, whereas the reverse process delivers the corresponding thermal energy back to the system.

Electrons and holes interact with each other due to their electric charges. Thus, for excited carriers of opposite charges, recombination is a built-in mechanism to localize and transfer the energy stored in these excitations. The excited charge carriers can couple to core ions and to any deviation from the ideal arrangement of the building blocks in the solid during recombination. The capture of a charge carrier into a localized level or the recombination of an electron with a hole releases locally large energy densities, which can drive diffusion. For full balancing, both the acceptance as well as the release of thermal energy may cause diffusion.

We may express the local release of energy due to the recombining electron-hole pair by an increase of the local temperature and assume that the energy is released instantaneously and completely at the origin of a spherical coordinate system within an atom or a defect centre. Eqn. (A3) of Appendix A describes the distribution of the temperature increase \( u(r, t) \) as a function of time, \( t \), and distance, \( r \), from the origin using the time dependent heat equation, Figure 16. Results of \( u(r, t) \) are scaled for two typical amounts of energy released at the origin:

(a) The recombination of an electron with a hole releasing 50 meV. This corresponds to thermal low-energy transitions, Figure 16 (left-hand scale).

(b) The transition of an electron from an excited to a lower state releasing 1 eV, Figure 16 (right-hand scale). Inserting reasonable parameters of thermal conductivity, specific heat capacity and mass density one calculates that the energy dis-
10.3 Action of varying local electric charges

Electronic transitions can be radiative, i.e. emitting photons, or radiationless, i.e. emitting a cascade of phonons. The photons are effective at a different place after reabsorption, whereas the phonon cascade heats up the local environment and facilitates diffusion. The diffusion of charge carriers and their transitions from excited states to low energy states change the local charge distribution. Then, the probability density distributions of the charge carriers change also. Thus, the core ions surrounding the local transition are driven to new equilibrium places during the relaxation of the fluctuation. Together with inelastic scattering processes of the background phonons, this induces diffusion and facilitates to create defect centres.

$$\sigma_{\pm} = \frac{F(r_{12})}{\pi d^2} = \pm \frac{e_{\pm} e_0}{\pi^2 \varepsilon_0 r_{12}^2 d_0^4}.$$  (49)

If we consider two neighboring atoms, each with one elementary charge, at the distance $r_{12} = d_0$ and $r_{12} = 2d_0$ Equation 51 yields the values of the stress

$$\sigma_{\pm} = \pm \frac{e_{\pm} e_0}{\pi^2 \varepsilon_0 d_0^4}$$  (50)

and

$$\sigma_{\pm} = \pm \frac{e_{\pm} e_0}{4\pi^2 \varepsilon_0 d_0^4}$$  (51)

The absolute value of the stresses (52) and (53) decrease rather steeply as a function of the atomic diameter, $d_0$, Figure 15. For the diameters of most ions the stresses are more than an order of magnitude larger than about $10^5 \text{N/m}^2$ for which solid materials start flowing [84].

10.4 Interpreting the diffusion, old and new

Interpreting diffusion traditionally is based on the excitation of local vibrations of the diffusing particles in solids, glasses and even liquids or melts to overcome barriers between neighbouring sites. The diffusing particles are atoms, molecules, defects of the lattice, such as vacancies and interstitials, and combinations of such particles without a charge or in different charge states. Different diffusion mechanism are described in handbooks and textbooks as in survey articles such as [1–11, 14, 15]. Often the diffusing particles are considered to vibrate loosely in a potential well such as the sinusoidal well in Figure 3. This can be accepted for diffusing particles distributed with negligible bonding to the matrix such as rare gases or molecular gases in solids or melts. However, most diffusing particles are bound to the neighbours in the matrix or are part of the matrix. These bonds have to be opened in order that a particle can move as a single atom or combined with other particles (which may be defects created in the matrix).

Breaking bonds and creating defects in chemically bonded solids requires necessarily electronic
transitions. Therefore, the present paper deals with a selection of examples where electronic transitions take a decisive role to drive diffusion in contrast to the traditional atomistic models based on vibrations, only. The bonds of a diffusing particle are loosened by electronic excitations or transitions. Electrons and holes interacting with core ions drive the diffusing particles from one place to another and to a rearrangement. Such electronically induced mechanisms have been widely neglected in the literature. Peter Pichler considers such enhanced diffusion mechanisms in chapter “1.3.4 Athermal Diffusion” of [72]. On less than one page of his fundamental textbook and comprehensive collection of data on diffusion in silicon (page 38 of [72]) several publications, in particular a review article of Jacques C. Bourgoin and James W. Corbett is mentioned [85]. The following specific classification and characterization is extracted from [85] (see also the list of references therein):

(i) Electrostriction and stress enhanced diffusion, where the influence of free charges alters the diffusion mechanism (presence of electrons or holes in the conduction and valence band; change of the charge state of the diffusing defect; alternative change of the charge state of the defect, Figure 15).

(ii) Normal ionization-enhanced diffusion mechanism (IED), which occurs when two different charge states have different activation energies for thermally activated diffusion.

(iii) The Bourgoin mechanism, when different charge-states reverse the positions of their respective minima of potential energy and saddle points of the diffusion.

(iv) The recombination process and the production of electron-hole pairs.

(v) The energy-release mechanism, proposing that the energy of recombination of carriers could be sufficient to generate Frenkel pairs.

(vi) Collision-enhanced mechanism due to high-energy particles colliding with nuclei or atomic recoil in photo-electron production.

(vii) Different mechanisms for electro-migration [86].

Several of these mechanisms can be understood by considering that the diffusivity of the particle changes with the charge and its interaction with the environment. As a simple argument one may consider that the radius of a diffusing particle depends on its charge state. The change of a charge state is achieved by several mechanisms such as photo-generation, charge carrier injection or by spontaneous transitions. Further energy is released due to recombination, causing local phonon cascades to enhance diffusion.

Arguments in [85] support the idea that electronic transitions must not be neglected to interpret diffusion data correctly. Bourgoin and Corbett put it in this way: “In summary these enhanced diffusion mechanisms can occur in many systems and in many types of experiments, but the exploration...
of the full implication of these mechanisms has just begun” [85].

Thus, we have to point out what is new in the present article as compared to the previous status: The present paper shows that athermal conditions are not necessary. Athermal conditions correspond to deviations from thermal equilibrium. However, the coefficient of self-diffusion as a kinetic coefficient must depend on processes taking place even in thermal equilibrium without macroscopic gradients of the chemical or any other potential. Such processes are driven by transitions of electrons and holes with their kinetic and dynamic transition parameters since they cause sufficiently large fluctuations. These fluctuations cause much larger fluctuating local gradients than the usual experimental gradients of the potentials. The transition rates and their local fluctuations are driving the diffusion irrespective of additional gradients of temperature and other potentials. The fluctuations of the occupancy of the electronic states couple to the diffusing particles via the changing wave functions of the charge carriers in their different states, because the absolute values of the square of the wave functions correspond to the probability distribution of the charge carriers in space. The vibrations of the constituents help to localize the wave functions of electrons and holes, if the wavelengths of the vibrations correspond to the wavelengths of the wave functions of the electrons and the holes. The vibrations interacting with the charge carriers break the symmetry of the wave functions and localize electrons and holes, which otherwise would extend over the whole crystal.

10.5 Summary

The molar activation enthalpy, \( Q_{\text{diff}} \), needed for self-diffusion in chemically bonded solids and melts is much larger than the molar melting enthalpy, \( \Delta H_{\text{melting}} \), by about an order of magnitude. If the initial and final states of the diffusing particle have the same symmetry and energy, the molar activation enthalpy \( Q_{\text{diff}} \) is regained during the subsequent relaxation. Thus, a sufficiently large local fluctuation of enthalpy delivers \( Q_{\text{diff}} \) to the diffusing particle. \( Q_{\text{diff}} \) is taken from the enthalpy stored in the system. Usually, the dominant contributions to \( H(T) \) are the energies stored in vibrations and electronic excitations. Both contributions to \( H(T) \) must be taken into account to understand the results of diffusion experiments. Further shares of the enthalpy are important in special cases, such as excitations of magnetic and electric polarization, excitation of two-level systems, elastic deformation, internal and external surface effects or the formation of defects. Here, the energy released from electrons relaxing to low energy states contributes to drive the diffusion. The known literature delivers numerous examples of diffusion effects that evidence this driving mechanism without difficulties.

Appendix A: Thermal spiking as a function of time

We consider a heated crystalline or molten sample in thermal equilibrium. Then, thermal energy changes freely between the elementary states of vibrations, electronic excitations, further possible excitations, such as the creation of vacancies and interstitials, and the thermal radiation in the sample under investigation. Among other reactions, a thermally excited electron may recombine with a hole or a lower empty electron state and locally release energy \( E_v \). This transition excites vibrations of particles nearby, such as electrons and core ions, and emits or absorbs thermal radiation. We want to calculate the development of the thermal pulse or spike \( u \) with respect to the uniform average background temperature of the sample as a function of time \( t \) and distance \( r \) from the centre of the recombination as an average over time and many similar events.

As we do not know of a more detailed statistical approach, we simplistically assume that we can apply the heat diffusion equation, which is equivalent to Equation 9 above (diffusion equation or second law of Fick)

\[
\frac{\partial u}{\partial t} = a^2 \Delta u. \tag{A1}
\]

The coefficient \( a^2 = \frac{1}{c_p \rho} \) is the temperature conductivity (\( \lambda \): heat conductivity or enthalpy conductivity, \( c_p \): specific heat capacity at constant pressure and \( \rho \): mass density). We assume that these averaged parameters are independent of temperature, time and coordinates. Further, the energy is to be released locally at the origin of a spherical
coordinate system at time $t = 0$ and guided radially in the surrounding matrix that extends to infinity. Then, we need to consider only the radial part

$$\Delta u = \frac{\partial^2 u}{\partial r^2} + \frac{2}{r} \frac{\partial u}{\partial r}$$

of the Laplacian (A1) in spherical coordinates. Equation A1 transforms into

$$\frac{\partial u}{\partial t} = a^2 \left( \frac{\partial^2 u}{\partial r^2} + \frac{2}{r} \frac{\partial u}{\partial r} \right).$$

(A2)

With the boundary conditions mentioned, (A2) yields the solution for the temperature difference as a function of time, $t$, and distance, $r$, from the location of the recombination

$$u(r, t) = \frac{E_0}{c_p \rho} \frac{1}{(4\pi \frac{\lambda}{c_p} t)^{\frac{3}{2}}} \exp \left( -\frac{r^2}{4 \frac{\lambda}{c_p} t} \right).$$

(A3)

The energy released locally due to recombination spreads radially as a function of time, Figure 16. The numerical results require some caveats and must not be overestimated. First, the data of the thermal conductivity of bulk materials are valid for a continuum, not for a material that is grainy due to the atoms. Hence, one may question whether a local temperature can be defined, because the distribution of the released energy corresponds certainly to a large fluctuation deviating from long-term thermal equilibrium within the sample. Such equilibrium is a prerequisite to define temperature. A temperature might be justified under the proviso that the local energy exchanges freely back and forth between at least all local vibrational states, even those with long wavelength. Therefore, defining a local increase and subsequent relaxation of temperature may be questionable. On the other hand, the large deviation from the average temperature is due to thermal fluctuations and the coupling of vibrations, electronic excitations and radiation in the sample in thermal equilibrium. Consequently, these local fluctuations occur in thermal equilibrium.

Further, the parameters in $a^2 = \frac{\lambda}{4\pi c_p \rho}$ depend on the temperature and on the grainy structure around the local electronic transition. To avoid such a difficulty of interpretation by temperature, one may consider the temperature scale in Figure 16 as an approximation to estimate the relaxation and diffusion of the local energy as a function of $r$ after different time intervals $t$ qualitatively.

Figure 16. Average increase of temperature (in K) as a function of time and distance from the radiationless recombining electron with a hole in a lower unoccupied energy level applying Equation A3. Left scale for the temperature distribution if the energy liberated is $E_0 = 50$ meV corresponding to thermal energy of about 600 K. Right scale: $E_0 = 1$ eV corresponding to the energy of an infrared optical photon stored in the system of electrons and holes. Constant parameters applying Equation A3: $\lambda = 10^{-2}$ W/(cm · K), $c_p = 0.8$ Ws/(g · K) and $\rho = 2.5$ g/cm$^3$.

Bild 16. Mittlere Temperaturzunahme (in K) in Abhängigkeit von der Zeit und dem Abstand des Elektrons, das mit dem Loch in einem tiefer liegenden Zustand strahlungslös rekombiniert, berechnet mit Gleichung A3. Die linke Skala gilt für die Temperaturverteilung, wenn bei der Rekombination $E_0 = 50$ meV (entsprechend der thermischen Energie von ca. 600 K) freigesetzt wird. Rechte Skala: $E_0 = 1$ eV entsprechend der Energie eines Photons im infraroten Spektralbereich, die im System der Elektronen und Löcher umgesetzt wird. Konstante Parameter in Gleichung A3: $\lambda = 10^{-2}$ W/(cm · K), $c_p = 0.8$ Ws/(g · K) und $\rho = 2.5$ g/cm$^3$.

Thus, the curves in Figure 16 represent a mean local temperature fluctuation and the energy $E_0$ relaxes via the available states compatible with the
thermal equilibrium of the whole system. One may replace the temperature scale in Figure 16 by an energy density scale, if one multiplies it with the product of specific heat capacity and mass density, \(c_p \rho\) (see Equation A3).

Acknowledgements

Open access funding enabled and organized by Projekt DEAL.

Correction added on 15 February 2021, after first online publication: on pages 1580 and 1590 two unites were corrected.

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Received in final form: September 24th 2020