Atomic Transport in Solids

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This book provides the fundamental statistical theory of atomic transport in crystalline solids; that is the means by which processes occurring at the atomic level are related to macroscopic transport coefficients and other observable quantities.

The cornerstones of this treatment are (i) the physical concepts of lattice defects, (ii) the phenomenological description provided by non-equilibrium thermodynamics and (iii) the various methods of statistical mechanics used to link these (kinetic theory, random-walk theory, linear response theory etc.). The book brings these component parts together into a unified and coherent whole and shows how the results relate to a variety of experimental measurements. It thus provides the theoretical apparatus necessary for the interpretation of experimental results and for the computer modelling of atomic transport in solid systems, as well as new insights into the theory itself.

The book is primarily concerned with transport in the body of crystal lattices and not with transport on surfaces, within grain boundaries or along dislocations, although much of the theory here presented can be applied to these low-dimensional structures when they are atomically well ordered and regular.

Atomic Transport in Solids will be of interest to research workers and graduate students in metallurgy, materials science, solid state physics and chemistry.

Atomic transport in solids

To Betty and to Ann

Preface

In any area of physical science there are stages in its historical development at which it becomes possible and desirable to pull its theory together into a more coherent and unified whole. Grand examples from physics spring immediately to mind – Maxwell's electro-magnetic theory, Dirac's synthesis of wave-mechanics and matrix mechanics, the Salam–Weinberg electro-weak theory. Yet this process of unification takes place on every scale. One example of immediate concern to us in this book here is afforded by the emergence of the thermodynamics of irreversible processes, where the coming together of separate strands of theory is made plainly visible in the short book by Denbigh (1951). In connection with imperfections in crystal lattices the Pocono Manor Symposium held in 1950 (Shockley *et al.* 1952) might be said to mark another such stage of synthesis. At any rate a great growth in the understanding of the properties of crystal imperfections occurred in the years following and this carried along a corresponding achievement in understanding atomic transport and diffusion phenomena in atomic terms. Around 1980, in the course of a small Workshop held at the International Centre for Theoretical Physics, Trieste we concluded from several observations that such a stage of synthesis could soon be reached in the study of atomic transport processes in solids. First of all, despite the great growth in detailed knowledge in the area, the theory, or rather theories, which were used to relate point defects to measurable quantities (e.g. transport coefficients of various sorts) were recognizably still largely in the moulds established considerably earlier in the 1950s and 1960s, notwithstanding the advances in purely numerical techniques such as molecular dynamics and Monte Carlo simulations. There were clear limits to the quantities which could be confidently expressed in terms of the properties of point defects. Thus, despite the existence of useful and accurate theories of tracer diffusion coefficients in dilute solid solutions, other coefficients, such as intrinsic (chemical) diffusion coefficients, cross-coefficients between the flows of different chemical species, ionic mobilities, etc. were less well understood, especially in concentrated solid solutions. At the same time the Kubo–Mori theory of linear transport processes had become firmly established in other areas of the theory of condensed matter; but, although some first steps had been taken to translate this scheme to the field of atomic transport (i.e. to a stochastic, hopping type of process), it had not been shown that this provided a practical way to evaluate the transport coefficients of particular defect models. Indeed, some formulations of this Kubo–Mori theory made the prospects look decidedly unpromising!

This being the situation at that time we therefore directed part of our research towards the objective of providing a more fundamentally based and unified theory of the subject in terms of the concepts of point defects. A review which we published in 1987 (Allnatt and Lidiard, 1987b) sketched out our overall view of the theory at that later time. We felt that this indicated that a more extensive and self-contained work was necessary; the present book is the consequence.

The emphasis of the work is thus on the fundamental theory of the topic. Our aim is to establish this in a more unified and powerful form than is currently available elsewhere. The corner-stones of our treatment are threefold: (i) the physical concepts of point defects, (ii) the phenomenology of non-equilibrium thermodynamics and (iii) the various methods of statistical mechanics (statistical thermodynamics, linear response theory, kinetic theory, random-walk theory, etc.), which enable us to express measurable quantitites in terms of the properties of point defects. Inevitably there are boundaries to our narrative. Since the focus of attention is the fundamentals of atomic migration in 'bulk' crystal we are not concerned, except in passing, with surface diffusion nor with diffusion in grain boundaries or other components of the 'microstructure'. From the point of view of experimental research the distinction between processes taking place in the bulk and at interfaces often presents little difficulty. However, to the computer modeller of complex systems in which a number of distinct processes are going on, we admit that our work can help with only one part of the task: our contribution is to point to the correct phenomenology to use for those processes involving migration through the body of the crystal lattice and to show how the corresponding transport coefficients depend on circumstances (structure, thermodynamic variables, forces acting, etc.). We should have liked to do more, but space and time did not allow.

Let us now turn to the structure and content of the book in more detail. Firstly the text is inevitably fairly mathematical. Nevertheless, it has been our intention that it should be of interest to all concerned with this subject, for we believe that there are scientific gains to be made by viewing the subject in the unified way we present here. We therefore offer some suggestions to readers about how they may wish to approach the book. These must obviously be different for different classes of reader.

Chapters 1–5 are essentially introductory. Chapter 1 describes the quantities of concern – diffusion coefficients, ionic mobilities, loss factors, relaxation times, dynamical structure factors, etc. Chapter 2 summarizes the physical basis of the theories of atomic migration; this may be studied more casually by those who have a basic knowledge of structural imperfections in crystals.

The rest of this book describes the theory of the quantities introduced in Chapter 1 as it is based upon the ideas and models of point defects described in Chapter 2. Chapter 3 describes several particular calculations of the thermodynamic equilibrium concentrations of point defects as well as certain more general results used later. The particular calculations should present no difficulty to those familiar with the basic ideas of statistical thermodynamics. This chapter also touches on the mobility of point defects within the same framework. The more experienced reader may need to concentrate only on the later more general parts of this chapter.

Chapters 4 and 5 provide discussions of the phenomenology of non-equilibrium thermodynamics and of the form it takes for crystalline solids containing point defects. The first of these two chapters is more formal; the second is more physical and contains basic examples and certain 'physical' extensions. Both probably merit study, for they provide the natural framework for the results of the microscopic statistical theory as we develop it.

Chapter 6 is the heart of the work, whence it follows that all readers need to understand the way the ideas are expressed mathematically. In principle all that follows this chapter flows from the master equation (6.2.1). At a first reading §§6.2 and 6.5 (as well as the introduction) would suffice, with a more complete reading later in time for Chapter 9. Theoreticians will probably want to tackle this chapter in its entirety.

The remainder of the book illustrates and applies the concepts and methods of Chapter 6 in a variety of ways. Chapters 7–12 are principally concerned with solids in which the concentrations of defects are small but Chapter 13 is specifically devoted to highly disordered solids. Chapter 7 deals with dielectric and mechanical relaxation processes associated with complex point defects and is mathematically similar to the more abstract formalism of Chapter 6. It can therefore be viewed as an illustration of this formalism. The beginner could well study this as a way of establishing confidence with the formal structure of Chapter 6. Chapter 8 extends the approach of Chapter 7 to diffusion processes. A first reading should include §§8.2 and 8.3 and a review of the results in §8.5

Chapters 9–11 present the random-walk approach to the calculation of diffusion coefficients and of the *L*-coefficients more generally. Theoreticians may want to read all three coherently but experimentalists may find it more profitable at a first reading to turn to the second part of Chapter 11 where expressions for the L-coefficients for various models are gathered together and discussed in relation to experimental results. This shows how models may be confirmed and their characteristic parameters inferred. Chapter 12 emphasizes the corresponding calculation of relaxation times arising in nuclear magnetic relaxation. In particular, it compares different theories using some of the results obtained in Chapter 9. It will be necessary then to refer back to this chapter if the details of the comparison are to be fully understood. On the other hand the conclusions can be employed without that understanding.

The last chapter (13) addresses the more difficult task of calculating transport coefficients of concentrated and highly defective systems. It is in essentially two parts: (i) analytic, limited to concentrated random alloys and solid solutions and (ii) Monte Carlo, which describes the use of the technique and the results obtained on models of order–disorder alloys and like systems.

Next we set down one or two caveats. Firstly, in connection with notation, nomenclature and units we have tried to follow the recommendations of I.U.P.A.P. and I.U.P.A.C. as recorded by Cohen and Giacomo (1987) and by Mills *et al.* (1988). Among other things this implies that we use SI units; the only exception is the electron-volt (1 eV equals 96.49 kJ/mol), which is so well matched to the magnitude of the defect energies we shall be concerned with that not to follow current use of it would seem perverse. Lists of our mathematical notation follow this Preface. To simplify the mathematical arguments we have limited some of them to cubic solids, but, the fact that, for the transport coefficients of most solids of practical concern, one can define principal axes (Nye, 1985) means that the bulk of our results apply directly to the component coefficients along individual principal axes. We assume that the reader is familiar with certain areas of mathematics (e.g. Cartesian vectors and tensors, matrix manipulation, Fourier and Laplace transforms) although in no case are more than the basic ideas required. We have tried to ensure that all the mathematical arguments presented can be followed either as they stand or with the aid of a very little pencil and paper work. The longer derivations are given in appendices.

Lastly, we should like to acknowledge our indebtedness to various institutions and individuals. Our own research on the topics described here has been supported in the main by the Underlying Research Programme (now the Corporate Research Programme) of the U.K.A.E.A. and by the Natural Science and Engineering Research Council of Canada, but we have also received assistance from the U.K. Science and Engineering Research Council and the Royal Society of London. This work has been aided also by the hospitality of the Department of Theoretical Chemistry of the University of Oxford, the Department of Physics of the University of Reading, the Interdisciplinary Centre for Chemical Physics at the University of Western Ontario, the Institut für Physikalische Chemie und Elektrochemie of the University of Hanover and the former Theoretical Physics Division of the U.K.A.E.A. at Harwell. One of us (A.B.L.) would particularly like to acknowledge the support of Dr R. Bullough and Dr A. W. Penn of AEA Technology. In connection with the book itself we have benefited enormously from the encouragement, advice and comments of many friends to whom we wish to record our very warm thanks. They include: Professor D. Becker (Hanover), Dr A. H. Harker (Harwell), Professor P. Heitjans (Hanover), Dr M. J. Hutchings (Harwell), Professor P. W. M. Jacobs (London, Ontario), Professor C. W. McCombie (Reading), Professor J. Mahanty (Canberra), Professor N. H. March (Oxford), Dr G. Martin (Saclay), Professor H. Schmalzried (Hanover), Professor C. A. Sholl (Armidale) and Professor J. Strange (Canterbury). The generosity of Professor March and Professor Schmalzried in time, ideas and in other ways is to be especially recorded. We are also grateful to authors and the following publishers for permission to reproduce diagrams from works as cited: Academic Press, Akademie Verlag, American Institute of Physics, American Physical Society, ASM International, Elsevier Science Publishers, Elsevier Sequoia, the Institute of Physics, the Minerals, Metals & Materials Society, Pergamon Press, Plenum Publishing Corporation, Taylor & Francis and VCH Verlag.

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Principal symbols

Capital Roman

$\mathbf{A}$	matrix of relative jump probabilities
A, B	particular species of atom
$\mathbf{B}$	magnetic induction (vector)
D	diffusion coefficient (tensor)
$\mathbf{D}$	electric displacement (vector)
E	electric field (vector)
F	Helmholtz free energy
F_j	force on species j
G	Gibbs free energy
$G(\mathbf{r}, t)$	position correlation functions
$G_{\beta\alpha}$	propagator matrix derived from $P_{\beta\alpha}$
H	enthalpy
I	interstitial species (goes with A, B)
I	nuclear spin
$I(\mathbf{q}, t)$	intermediate scattering function
$\mathbf{J}_i$	flux (vector) of component, i
$\mathbf{J}_q$	flux (vector) of heat
L_{ij}	transport coefficient (species i and j)
$\mathbf{M}$	nuclear magnetisation (vector)
N_i	number of species i in the volume of the system
N_m	number of stoichiometric cells ('lattice molecules') in the volume of the system
$N_{\beta\alpha}$	diagonal matrix derived from the $p_\alpha^{(0)}$
P	pressure
$\mathbf{P}$	electric polarization (vector)
$\mathrm{P}_{\beta\alpha}$	matrix from the master equation

Q	Arrhenius activation energy
Q_i^*	heat of transport of species, i
Q_{pq}	matrix derived from P_{pq}
S	Entropy
S_i	Soret coefficient
$S(\mathbf{q}, \omega)$	neutron scattering dynamical structure factor
$S_{\beta\alpha}$	symmetrized $P_{\beta\alpha}$ matrix
T	thermodynamic (absolute) temperature
T_1, T_2, etc.	*N.M.R.* relaxation times
U	internal energy
$U_{\beta\alpha}$	matrix derived from the propagator $G_{\beta\alpha}$
$U(\mathbf{l}, y)$	generating function for random walks
V	volume of the system
V	designation of vacancy (like A, B and I)
$W(\mathbf{q})$	Debye–Waller factor
$\mathbf{X}_i$	thermodynamic force on species i
$\mathbf{X}_q$	thermodynamic force due to a temperature gradient
X, Y	kinetic quantities (Chap. 6)
Z	partition function
Z_i^*	effective charge number for species i (electrotransport)

Lower case Roman

a	lattice parameter
$\mathbf{a}^{(\nu)}$	νth eigenvector of $\mathbf{S}$
b	neutron scattering length
c_i	relative concentration of species i $(=N_i/N_m)$
e	proton charge
f	Helmholtz free energy per atom, defect etc.
f	also correlation factors and functions
g	Gibbs free energy per atom, defect, etc.
h	enthalpy per atom, defect, etc.
i	$\sqrt{-1}$
$i, j, k \ldots$	species in the system (atoms, vacancies, etc.)
k	Boltzmann's constant
$\mathbf{k}$	wave-vector in Fourier transforms
$\mathbf{l}$, $\mathbf{m}$, $\mathbf{n}$	sites in a lattice
n	number of 'lattice molecules' (sites) per unit volume $(=1/v)$
n_i	number density of species i
p, q, r	configurations of complex defects (pairs)

p_α	probablity that the system is in state α
$\mathbf{q}$	scattering vector
q_i	electric charge on unit of i
r, s, t	types of defect in an assembly of defects (Chap. 3)
$\mathbf{r}$	position vector (x, y, z)
s	entropy per atom, defect, etc.
$\mathbf{s}$	elastic compliance tensor
s, t	time variables
u	internal energy per atom, defect, etc.
u	electrical mobility
v	volume per lattice molecule
v_K	Kirkendall velocity
$w_{\beta\alpha}$	rate of transition $\alpha \to \beta$
x, y, z	Cartesian co-ordinates
x_i	mole fraction of species i
z	number of nearest neighbours
z_i^*	electron wind coupling constant for species i

Lower case Greek

$\alpha, \beta, \gamma \ldots$	states of the whole system
$\alpha^{(\nu)}$	νth eigenvalue of $\mathbf{S}$
γ	nuclear gyromagnetic ratio
γ	natural line-width (Mössbauer)
γ_i	activity coefficient of i
δ	loss angle
δ	with argument, Kronecker and Dirac functions
δ	deficiency in chemical composition
ε	electric permittivity tensor
ε	strain tensor
ε_F	Fermi energy
θ	polar angle
θ	thermoelectric power
θ	Heaviside and other step functions
κ, λ, μ	Cartesian indices with vectors and tensors
κ	conductivity tensor
κ_D	Debye–Hückel screening length
λ	Laplace transform variable
$\lambda_{\alpha\beta}$	elastic dipole strain tensor
μ_i	chemical potential of species i

ν	index for eigenvalues of $\mathbf{S}$
ν	mean number (exchanges, visits, etc.)
ν	pre-exponential factor in transition rate
π, ϖ	probabilities
ρ	occupancy variable
$\boldsymbol{\sigma}$	stress tensor
σ	rate of entropy production
σ	scattering cross-section
τ	relaxation time
$\boldsymbol{\tau}$	column matrix (to effect summation)
ϕ	azimuthal angle
ϕ	electric potential
ψ	probability function (Chap. 13)
ω	angular frequency

Capital Greek

$\Gamma(\mathbf{q})$	half-width at half-maximum
Γ	mean number of jumps per unit time
Δ	difference operator
Π	product operator
Σ	summation operator
$\boldsymbol{\Phi}$	response function (tensor)
Ω	number of distinct configurations of a given energy

Contents