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DIFFUSION IN CRYSTALLINE SOLIDS

EDITED BY

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Foreword

Arthur Nowick and I both started research in the field of diffusion in solids some 35 years ago. The intervening period has made us, with certainty, much older, only arguably much wiser. This area of research has proved remarkably durable for its fundamental interest to both condensed-matter physicists and materials scientists, as evidenced by the contents of this volume, which contains contributions from sexagenarians (like Nowick and me) along with those from young research workers a third our age. It is perhaps in the nature of the beast that the elementary diffusional process is so very fundamental and ubiquitous in the art and science of dealing with matter in its condensed phase that it never ceases to be *useful* but, at the same time, is a problem which is never really *solved.* It remains *important* by any measure.

Interest in diffusion is as old as metallurgy or ceramics, but the scientific study of the phenomenon may probably be dated from the classic papers of H. B. Huntington, which appeared in the *Physical Review* some four decades ago. These papers were the first to attempt to identify the basic underlying atomistic mechanisms responsible for mass transport through solids by a quantitative theoretical analysis of the activation energies required for diffusion by exchange, interstitial, and vacancy mechanisms in copper. Prior to this time, there had been little concern with treating diffusional phenomena on a microscopic basis, and most research was concerned with fairly crude observations of overall bulk transfer processes at junctions between regions with strong compositional differences.

Although large masses of experimental data were prevalent in the literature—to the extent that whole books dealing with diffusion had already appeared by the late 1940s—experimental techniques were largely limited to optical microscopic observations of changes in color and texture and wet chemical analysis of layers near diffusion boundaries. Most numerical values of diffusion coefficients were deduced from the familiar (but painfully imprecise) Matano–Boltzmann method of analysis. It was not until the late 1940s, with the availability of reactor-produced radioisotopes of high purity and high specific activity, that measurements of real precision became possible. The scientific developments since that time have been extraordinary. With precise data available, it became possible to find answers to precise questions.

Steve Rothman, who wrote the first chapter of this volume, is one of the pioneers who developed the optimal experiment methods for measuring the diffusion coefficient by means of radiotracer techniques. No one can expound with greater authority on this vital aspect of the subject. Since so much of the past progress, as well as the future, of this field of research is reliant on acquisition of data of high precision, it is entirely fitting that the book begin with a review of measurement techniques.

For the first few decades of *scientific* study of the subject, attention was focused on identifying the atomistic mechanism or mechanisms which could be invoked to explain diffusion in the simplest of systems: pure, monatomic, monocrystalline metals, simple cubic salt crystals, etc. The lattice vacancy emerged as the dominant defect in most substitutional lattices, with the singular exception of the silver halides. However, even the simple vacancy turned out to be more than the ideal *point* defect calculated by Huntington; there were relaxation effects which involved a large number of its lattice neighbors. Neither was it clear that the vacancy acted only singly; there was good evidence for pairs and higher-order clusters of vacancies in some systems.

More recently, interest has centered on extending the earlier studies to the diffusional behavior of more complex systems and structures. Some of the most exciting recent work is reported in this volume by some of the world's leading experts: elemental semiconductors, by Frank, Gösele, Mehrer, and Seeger; oxides, by Nowick; concentrated alloys, by Bakker; diffusion along grain boundaries, by Balluffi.

Progress in theory has been somewhat less dramatic than that in experiment over the four decades. It has been difficult to expand following Huntington's original models, which involved *ab initio* calculations of the total energies of ground and saddle-point states with and without defects. Only the differences between these two large energies could be compared with the activation energies actually measured for diffusion. The *theoretical errors* in the calculated differences were far larger than the experimental uncertainties in the activation energies, even if no relaxation effects were considered. If these are included—to be consistent with experimental findings—lattice symmetry is lost in the vicinity of the defects, and even ground-state energies are nearly impossible to calculate with any degree of precision. Certain critical areas, however, have yielded to the ingenuity of theorists. I am pleased to see the review by Le Claire and Rabinovitch of the mathematical analysis of diffusion along dislocations.

The advent of modern, high-speed computers has made possible a new kind of theory, inconceivable four decades ago. It is now possible to perform large-scale simulations of diffusional motions inside the mathematical "lattice" of a computer's memory. There, one can follow individual atomic jumps and sequences of jumps and try to correlate this microscopic behavior with observed macroscopic tracer motion. Murch's chapter brings us up to date on these methods.

One of the bases for all diffusion theories is the so-called theory of absolute reaction rates, initially introduced by Wigner and Eyring as a means to describe chemical reactions between systems *in equilibrium*. Activation energies and entropies are equated to differences in Gibbs free energies between ground and excited saddle-point states, and the manipulations of normal thermodynamics are used to relate calculated parameters to experiment. A basic question, most often avoided by theorists, is why should such parameters, deduced for an equilibrium system, be valid descriptions for diffusion, which is patently a nonequilibrium process? The connection between the kinetic theory of the process, which involves consideration of the enormous spectrum of lattice modes which must enter into both formation and motion of defects, and the reaction-rate parameters has only very recently been brought into focus by the exciting work of C. P. Flynn and some of his co-workers, including G. Jacucci. It is fitting that the final chapter in this volume gives us Jacucci's up-to-date account of these new developments.

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Preface

This book is a sequel to "Diffusion in Solids: Recent Developments," edited by A. S. Nowick and J. J. Burton and published in 1975 by Academic Press. By following the aims of the original work, we have chosen to focus upon some of the most active areas of diffusion research. Although the editors' choice must inevitably be somewhat subjective, we have endeavored to select those subjects which, in our opinion, have matured to the extent that there is general agreement on their scope and interpretation.

The backbone of diffusion is undoubtedly the precise measurement of diffusion coefficients. In the first chapter, S. J. Rothman has compiled extensive information on the measurement of diffusion coefficients with radioisotopes. The following three chapters consider diffusion in materials of substantial technological importance for which, in addition, considerable basic understanding has developed. W. Frank, U. Gösele, H. Mehrer, and A. Seeger deal with diffusion in silicon and germanium and A. S. Nowick with atomic transport in oxides of the fluorite structure, while H. Bakker analyzes diffusion in concentrated alloys, including intermetallic compounds.

The next two chapters delve into diffusion along short-circuiting paths. A. D. Le Claire and A. Rabinovitch analyze the effect of diffusion down dislocations on the form of the tracer concentration profile, while R. W. Balluffi deals with the mechanisms of diffusion in grain boundaries in metals by invoking considerable work done on grain-boundary structure.

In recent years computer simulation has made a substantial contribution to diffusion theory. The last two chapters are concerned with the two main streams of such activities. In the first, G. E. Murch describes the application of the Monte Carlo method to the calculation of random-walk-related quantities. In the final chapter, G. Jacucci focuses on machine calculations of the fundamental atomic migration process by reviewing some state-of-the-art calculations for defect energies and the topology of the saddle surface.

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The Measurement of Tracer Diffusion Coefficients in Solids*

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I. Introduction

A. GENERAL REMARKS

The first measurement of diffusion in the solid state was made by Roberts-Austen (1896). Many measurements, especially of chemical diffusion in metals, were made in the 1930s; the field was reviewed by Mehl (1936), Jost (1952), and Seith (1955). Diffusion research increased after World War II; the increase was motivated by the connection among diffusion, defects, and radiation damage and helped by the availability of many artificial radiotracers. It was at this time that suggestions on how to carry out high-precision, highly reproducible diffusion experiments were first put forward (Slifkin *et al.*, 1952; Tomizuka, 1959).

The three major factors that determine the quality of a diffusion measurement are

1. the method used,
2. the care taken in the measurement, and
3. the extent to which the material is specified (Nowick, 1951).

The most accurate method has, in general, been considered to be radiotracer sectioning (Tomizuka, 1959), and most of this article is devoted to this method, especially to points for which special care must be taken; these are the measurement of temperature, the accuracy of sectioning, and the reproducibility of counting the radioactivity.

The importance of specifying the material cannot be overstated. The measured diffusion coefficient depends on the chemistry and structure of the sample on which it is measured. Impurities, nonstoichiometry of compounds, grain boundaries, and dislocations can give apparent values of the diffusion coefficient that are different from, and usually larger than, the true value.

The objective of this chapter is to describe some experimental techniques that are useful in carrying out diffusion measurements. We have organized the chapter around general principles that are applicable to all materials, and then listed the particulars. The materials we consider are mainly inorganic solids, especially metallic materials; however, organic solids are also mentioned. The effect of pressure on diffusion is omitted. Previous reviews covering mainly metals and inorganic crystals have been given by Hoffman (1951), Tomizuka (1959), Čadek and Janda (1957), Adda and Philibert (1966, Chapter 4), Lundy (1970), and Benière (1983). Chadwick and Sherwood (1975) have reviewed techniques for organic crystals.

Radioactive tracers are essential to many of the experiments described in this article. Radioactive tracers are hazardous materials, and the experimenter who uses them is under the strongest moral obligation to avoid exposure of his colleagues and contamination of his environment.

B. THE RELATION OF DIFFUSION EXPERIMENTS TO THE MATHEMATICS OF DIFFUSION

For measurable diffusion to take place a gradient of some kind is necessary. Diffusion is a consequence of the hopping motion of atoms through a solid. The diffusion coefficient D is defined in Fick's first law (Fick, 1855; Manning, 1968),

$$\mathbf{J} = -D\,\nabla C + C\mathbf{V} \tag{1}$$

where $\mathbf{J}$ is the flux of atoms, C their concentration, and $\mathbf{V}$ the velocity of the center of mass, which moves due to the application of a force such as an electric field or a thermal gradient. A number of different diffusion coefficients exist, e.g., for the diffusion of a radioactive tracer in a chemically homogeneous solid in the absence of external forces,

$$\mathbf{J}^* = -D^*\,\nabla C^* \tag{2a}$$

where the asterisk denotes the radioactive species. For diffusion in a chemical gradient,

$$\mathbf{J} = -\tilde{D}\,\nabla C \tag{2b}$$

where $\tilde{D}$ is the interdiffusion or chemical diffusion coefficient. Any of these equations can be combined with the equation of continuity

$$\partial C/\partial t = -\nabla\cdot\mathbf{J} \tag{3}$$

to yield Fick's second law

$$\partial C/\partial t = \nabla\cdot(D\,\nabla C) \tag{4a}$$

where the mass flow term has been omitted. For a tracer in a homogeneous system,

$$\partial C^*/\partial t = D^*\,\nabla^2 C^* \tag{4b}$$

Equations (4a) and (4b) describe the types of diffusion experiments discussed in this article.

The tracer diffusion coefficient is given also in the atomistic form

$$D^* = \gamma a^2 \Gamma f \qquad (5)$$

where γ is a geometric factor, a the jump distance, Γ the atomic jump frequency, and f the correlation factor (Bardeen and Herring, 1951; Manning, 1968). It is thus possible, in principle, to measure D^* by measuring Γ in a resonance experiment of some kind (Nowick and Berry, 1972; Wolf, 1979). This kind of experiment will not be treated here.

We are concerned here with diffusion measurements where the diffusion coefficient is obtained via Fick's second law, i.e., from a solution of the diffusion equation. Fick's second law is used rather than his first because concentrations are easier to measure than fluxes and because the magnitudes of D in the solid state are so small that the required steady state is seldom reached.

In order to obtain a solution of the diffusion equation, the initial and boundary conditions (IC and BC) must be known. The IC correspond to the distribution of the diffusing substance in the sample before the diffusion anneal, and the BC describe what happens to the diffusing substance at the boundaries of the sample during the diffusion anneal. If the experimental IC and BC correspond to the mathematical conditions, the mathematical solution to the diffusion equation $C(x, y, z, t)$ will describe the distribution of the diffusing substance as a function of position in the sample and of annealing time. The diffusion coefficient is finally obtained by fitting the experimentally determined $C(x, y, z, t)$ to the appropriate solution of the diffusion equation with D as a parameter. This chapter describes some methods for setting up the IC, maintaining the BC as well as the implicit conditions mentioned later in this section, and determining $C(x, y, z, t)$.

Most laboratory experiments are arranged so that diffusion takes place in one dimension. The solution of the diffusion equation is then $C(x, t)$. One most often determines $C(x)$ at constant t, i.e., the concentration distribution along the diffusion direction after a diffusion annealing time t. It is also possible to determine $C(t)$ at a constant x (e.g., the concentration at a surface) or $\int\int C(x, t)\,dx\,dt$ (e.g., the weight gain of a sample as a function of time).

The IC, BC, and solutions to the diffusion equation (for $D = \text{const}$) for some common geometries are described below. These, and solutions for other cases, are given by Crank (1975) and Carslaw and Jaeger (1959).

(i) Thin Layer or Instantaneous Source Geometry (Fig. 1a). An infinitesimally thin layer ($\ll (Dt)^{1/2}$) of diffusing substance is deposited on one surface of a semi-infinite ($\gg (Dt)^{1/2}$) solid. The initial condition is

$$C(x, 0) = M\delta(x) \tag{6}$$

where δ is the Dirac delta function and M the strength of the source in atoms per unit area. The boundary condition is

$$\frac{\partial C}{\partial x}(0, t) = 0 \tag{7}$$

i.e., there is no flux through the surface (impermeable boundary). The solution is

$$C(x, t) = (M/\sqrt{\pi Dt}) \exp(-x^2/4Dt) \tag{8}$$

One determines $C(x)$ for constant t.

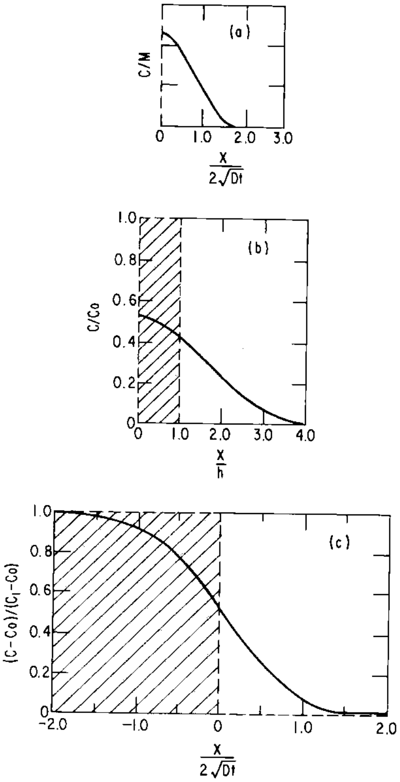

Fig. 1. Concentration distributions for different initial conditions. Dotted line is for $t = 0$, solid line is for a finite t. (a) Thin layer geometry [case (i)]; (b) thick layer geometry [case (ii)], solid curve for $Dt = h^2$; (c) infinite couple [case (iii)]. [After Crank (1975).]