Theory of Diffusion Controlled Reactions of Point Defects in Metals

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1. Introduction

The importance of point defects like vacancies, interstitials and impurity atoms for the understanding of many features of real crystals has motivated extensive research /1.1/. The structure and vibrational behaviour of point defects, the influence of mechanical properties and their role in diffusion and solid state reactions have been studied. Many aspects can be found in Flynn's book on "Point Defects and Diffusion" /1.2/. The static structure and vibrational behaviour of point defects have recently been reviewed by DEDERICHS et al. /1.3/, and a microscopic picture for the elementary diffusional jumps of point defects has been discussed by YOUNG /1.4/ and FRANKLIN /1.5/. Diffusion in ideal crystals and the information about point defects obtained from tracer diffusion experiments and mechanical relaxation methods have been discussed by MANNING /1.6/, PETERSON /1.7/, and NOWICK and BERRY /1.8/. Microscopic methods like neutron scattering /1.9/, nuclear magnetic resonance /1.10/ and Mössbauer technique /1.11/ have proven particularly fruitful to study the behaviour of point defects.

We shall briefly review the work on diffusion in ideal lattices in Sect.2 and particularly emphasize the influence of the discrete lattice on point defect diffusion. We shall discuss the Green's function for diffusion on a lattice in some detail because its knowledge is necessary for the interpretation of experiments. The analytical properties, the asymptotic behaviour and the transition to continuum diffusion are discussed. We give a brief survey of experimental methods to determine the geometry and kinetics of diffusion.

Point defects can interact with lattice inhomogeneities like other point defects, dislocations, precipitations, etc. (Sect. 3). In metals the elastic interaction due to the strain field connected with point defects in solids is most important; in
semiconductors and ionic crystals the Coulomb interaction has to be considered for charged defects. The elastic interaction always has attractive direction indicating a general trend towards agglomeration of defects.

In Sect. 4 we describe the diffusion of point defects in external fields. It turns out that one has to distinguish two interactions, one for the stable configuration and one for the saddle point configuration of the mobile defect /1.12/. Whereas the stability of a complex (binding energy) and the stationary distribution of point defects around sinks are determined by the interaction in the stable configuration, the change of the diffusion rate is determined by the interaction in the saddle point configuration alone; the diffusion tensor can become anisotropic even in cubic materials for defects with cubic symmetry in the equilibrium configuration.

Due to the interaction defects can react with each other (and with sinks) as soon as they become mobile. Such reactions are usually described by kinetic equations using phenomenological rate constants /1.13,14/. In Sect. 5 we review the description of diffusion limited reactions, limiting our presentation to stationary situations. First we discuss the phenomenological theory which describes the interaction by a reaction radius $R_a$ and the motion of the defects by continuum diffusion with diffusion constant $D_0$. In the dilute limit (independent sink approximation) the reaction rate $K$ can be expressed in terms of these parameters /1.15/ by $K = 4\pi D_0 R_a$. The influence of larger sink densities is discussed briefly.

In Sect. 6 we show that the concept of a reaction radius remains valid if one takes into account the discrete nature of diffusion on a lattice. One obtains an explicit expression for the reaction radius for each set of reaction sites. If the reaction sites form a compact set, e.g., one site and its nearest neighbours, the results agree quite well with continuum theory with $R_a$ being approximately equal to the separation of the outermost reaction site from the center of the set /1.16/.

Finally in Sect. 7 we discuss the influence of long range potentials between sinks and mobile defects on the reaction rate. Vibrational principles are set up which yield upper and lower limits for the reaction radii. Due to the interaction the effective reaction radius becomes temperature dependent. The explicit form is determined by the radial dependence of the interaction whereas the absolute value depends on the strength and the anisotropy of the interaction /1.17/. For potentials with attractive directions the reaction radius is approximately given by the distance at which the potential energy gained by the defect in the saddle point configuration equals the thermal energy. A critical discussion of the applicability of the available theories concludes the paper.