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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Limits of the Ratios of Tracer Diffusivities for the Vacancy-Pair Mechanism with Application to Compound Semi-Conductors

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1. Introduction

Many years ago, it was demonstrated convincingly that bound vacancy-pairs make a very significant contribution to diffusion in alkali halides [1]. However, the contribution of vacancy-pairs to diffusion in other materials where separate sublattices exist, such as certain intermetallics and compound semiconductors, is still rather controversial. From measurements of tracer diffusion of a component alone it is generally not possible to determine the role of vacancy-pairs vis à vis diffusion by mono-vacancies, although a small curvature of an Arrhenius plot should in principle be in evidence because the formation energies and migration energies for the vacancy-pair are different from the mono-vacancy. There are however a number of experimental ways of demonstrating the contribution of vacancy-pairs to diffusion such as the isotope effect experiment, measurement of tracer diffusivities an alkali halide doped separately with divalent cations and anions and the ratio of the component tracer diffusivities, the topic of this paper.

The vacancy-pair mechanism puts quite strict upper and lower bounds on the ratio of the tracer diffusivities of the two atomic components assuming that diffusion is carried principally by vacancy-pairs. However, these limits are not known as precisely as they should be. The difficulty in determining these limits is that tracer correlation effects of the vacancy-pair mechanism are much more prominent than in any other diffusion mechanism. Indeed, it is the correlation effects inherent in the vacancy-pair mechanism that lead to the extremely strong coupling of the overall tracer diffusivities of the two components. Small approximations in the calculation of the tracer correlation factors can lead to large errors in the determination of the limits of the ratio of the tracer diffusivities.

Here, we are interested in the tracer correlation behaviour, and the corresponding limits of the ratio of the tracer diffusion coefficients, for diffusion by vacancy-pairs in the NaCl, CsCl structures and, especially, in the zinc blende structured II-VI and III-V compound semiconductors.

There have been a number of analytical calculations of the tracer correlation factors for the NaCl and CsCl structures. Howard [2] gave the limits for the ratio of the tracer diffusion coefficients D_A/D_B in the NaCl structure as:

$$6.1^{-1} < (D_A/D_B)^{NaCl} < 6.1 \tag{1}$$

and in the CsCl structure (as interpolated by Le Claire [3]):

$$12.1^{-1} < (D_A/D_B)^{CsCl} < 12.1 \tag{2}$$

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Using a modified matrix method Bakker *et al.* also determined correlation factors for diffusion via vacancy-pairs in the CsCl structure [4]. They showed that the limits of the ratio of the diffusion coefficients are given by:

$$13.3^{-1} < (D_A/D_B)^{CsCl} < 13.3 \qquad (3)$$

Only one study has addressed the calculation of tracer correlation factors for diffusion via vacancy-pairs in the zinc blende structure. Weiler and colleagues [5] calculated the tracer correlation factors using a modified matrix method. They found that the limits for the ratio of the tracer diffusion coefficients are given by:

$$2.59^{-1} < (D_A/D_B)^{zinc\ blende} < 2.59 \qquad (4)$$

Using the Monte Carlo method [6], we performed high precision calculations of the tracer correlation factors in the NaCl, CsCl and zinc blende structures. We also employed the matrix method to calculate correlation factors for the CsCl structure.

2. Results of numerical simulations

Monte Carlo simulation results for the limits of the tracer diffusivities are:

NaCl structure:

$$5.7^{-1} < (D_A/D_B)^{\mathrm{NaCl}} < 5.7 \qquad (5)$$

CsCl structure:

$$11.2^{-1} < (D_A/D_B)^{\mathrm{CsCl}} < 11.2 \qquad (6)$$

Zinc blende structure:

$$2.6^{-1} < (D_A/D_B)^{zinc\ blende} < 2.6 \qquad (7)$$

We see that Monte Carlo simulation results agree very well for the theoretical results for the zinc blende structure and slightly deviate for the NaCl structure. On the other hand, the simulation results differ significantly for the CsCl structure (11.2 compared with 13.3 given in [4]). However, our new matrix method calculations for this structure give:

$$11.316^{-1} < (D_A/D_B)^{\mathrm{CsCl}} < 11.316 \qquad (8)$$

which is in very good agreement with the Monte Carlo data.

The present results support the view that the experimental results for the ratios of the diffusivities in the III-V compound semiconductors InSb and GaSb are probably consistent with the vacancy-pair mechanism but not those for the II-VI compounds HgCdTe and CdTe.

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