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Diffusion of interstitial species (H and O atoms) in fcc systems (Al, Cu, Co, Ni and Pd): contribution of first and second order transition states.

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We present a discussion on the influence of high-order transition states on interstitial diffusion in fcc systems using first-principles calculations. In earlier works, only first-order transition states (1TS) were used to compute the diffusivity at the atomic-scale: the direct diffusion between tetrahedral (t) and octahedral (o) sites has been proposed to describe atomic-scale diffusion mechanisms. However, we show here that if this direct diffusion makes it possible to reproduce displacements remarkably well, neglecting higher-order transition states induces an underestimation of the diffusion coefficient at high temperature. We hereinafter revisit the diffusion coefficient of interstitial species in different fcc-systems. The effect of these configurations on atom diffusion in Al, Co, Cu, Ni and Pd, whose only stable sites are the tetrahedral and octahedral positions (H and O atoms) is thus discussed here. We show that if the correction is low, taking into account higher-transition states can modify the diffusivity values at high temperature.

INTRODUCTION

The diffusion mechanisms of atoms in interstitial position are now commonly studied in solid-state physics, as the growing amount of work [1–5] on the matter indicates. If the possibility of forming clusters with vacancies, the interactions with defects or the interfaces of the network are ignored, the atomic process of diffusion of interstitial species is controlled, in first-order approximation, by the energy landscape defined by the network. Atoms then diffuse from one stable site to another. However, these stable sites are not necessarily equivalent from a geometrical standpoint. In the case of fcc systems, where tetrahedral and octahedral sites are often the most stable sites, direct diffusion between t and o sites is (almost) systematically used to describe and predict atomic-scale diffusion. Wimmer *et al.* [2] proposed an explicit diffusion coefficient formula taking into account these two stable sites with a single jump, using the jump rates from o to t sites, "Γ_{o-t}". In the literature, various authors have considered that direct transitions between first-nearest neighboring octahedral or tetrahedral sites should be ignored in the calculation of the diffusion coefficient, due to a high migration energy. As shown by David *et al.*[4], this transition state is always set in the M site, which is located exactly between two nearest octahedral sites, between two nearest tetrahedral sites and between two fcc sites (see Fig. 1). From a geometrical standpoint, when an interstitial atom is located an M site, it can move directly into four different stable sites.

By studying the vibrational properties of interstitial atoms in different positions, results have shown that, in Al [4], these calculated transition states necessarily present two imaginary branches associated with the moving atom. These mechanisms should therefore be included in the transition theory in addition to the direct o-t path. However, most solid-state physics works do not discuss the possibility of interstitial diffusion through these configurations. Most expressions of diffusion equations generally do not include this option.

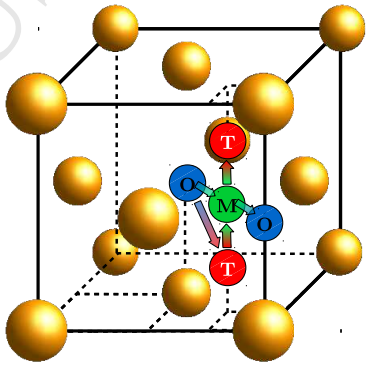

Figure 1. Position of main specific sites in fcc structures: octahedral (o), tetrahedral (t), and M sites. The different diffusion paths are also depicted.

In this paper, we look back at the often overlooked question of taking these paths into account. We compare the diffusion mechanisms between t and o sites found in two proven cases (H and O atoms) by taking into account the first-order transition state (direct diffusion path between o and t) but also second-order transition states (2TS) by taking into account M site or not. The case of H atoms in Al, Cu, Co, Ni and Pd, and O atom in Ni, Cu, Co and Pd are suitable cases to illustrate our point. This study also entails the opportunity of a detailed discussion on H and O diffusion mechanisms in various fcc metals, which, in some cases, has never been carried out. Our study was conducted by examining the mechanisms of diffusion at the atomic scale using first-principles calculations, and using the Eyring theory, with explicit equation of diffusion coefficients. We hereby study the effect of including 2TS in the atomistic process of diffusion.