Diffusion of muonium and hydrogen in diamond

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(Dated: February 2, 2008)

Jump rates of muonium and hydrogen in diamond are calculated by quantum transition-state theory, based on the path-integral centroid formalism. This technique allows us to study the influence of vibrational mode quantization on the effective free-energy barriers $\Delta F$ for impurity diffusion, which are renormalized respect to the zero-temperature classical calculation. For the transition from a tetrahedral (T) site to a bond-center (BC) position, $\Delta F$ is larger for hydrogen than for muonium, and the opposite happens for the transition BC $\rightarrow$ T. The calculated effective barriers decrease for rising temperature, except for the muonium transition from T to BC sites. Calculated jump rates are in good agreement to available muon spin rotation data.

PACS numbers: 61.72.-y, 66.30.Jt, 71.55.Cn, 81.05.Uw

Hydrogen has been studied for many years as an impurity in solids. Due to its low mass, this impurity has posed some challenging problems to both experimentalists and theorists [1]. An important property of hydrogen in insulating and semiconducting materials is its ability to form complexes and passivate defects [2], as was found in the case of diamond [3]. A large amount of information has been obtained by studying muonium (formed by a muon $\mu^+$ and an electron), which behaves as a light isotope of hydrogen, with $m_\mu \approx m_p/9$. In particular, muon spin rotation (µSR) experiments have provided us with invaluable information on the behavior of muonium (Mu) in semiconductors [4].

An interesting topic is the diffusion of Mu and H in crystalline materials. This problem turns out to be difficult due to the combination of quantum effects with lattice relaxation around the impurity (polaron effect). In fact, zero-point motion influences the excitation energy from the ground state to the top of the diffusion barrier. Also, tunneling of the impurities can be enhanced by phonons, and lattice distortions may depend on the isotopic mass of the impurity.

Two types of isolated Mu centers have been observed in elemental semiconductors, and are characterized by their isotropic or anisotropic hyperfine interaction. The former is accepted to consist of Mu at an interstitial tetrahedral (T) site, while the latter corresponds to Mu at a bond-center (BC) site, midway between two nearest host atoms. Muon implantation experiments in diamond, as well as various theoretical approaches, have shown that this impurity is metastable at the T site, and has its lowest energy at or around the BC site, as a result of a large lattice relaxation [1, 5, 6]. An important fraction of the implanted muons form Mu$_T$, and the transition to Mu$_{BC}$ has been observed by $\mu$SR [4]. This transition T $\rightarrow$ BC, and the opposite BC $\rightarrow$ T are also expected to be important for the diffusion of hydrogen in diamond, as derived from the energy barriers calculated with several theoretical methods [7].

In diamond there is the additional problem that H and Mu may exist in different charge states, and moreover a change of state may occur in combination with hopping. Density functional (DF) theory calculations predict H$^+$ to be stable off-axis in a buckled bond-centered configuration, in contrast to the BC site for neutral H [4, 7]. Also, calculated diffusion barriers were found to change appreciably with the impurity charge state [4, 7]. Here we will concentrate on high-resistivity diamond, where the non-paramagnetic fraction does not play an important role [1], and thus we will study neutral H and Mu.

In earlier works, hydrogen diffusion in diamond has been studied theoretically in the classical (high-temperature) limit [4, 8]. However, quantum effects are important for hydrogen-related defects in this material at relatively low temperatures [9]. Thus, we study in this Letter the diffusion of H and Mu in diamond by explicitly considering the impurities as quantum particles. The main question to be answered is the dependence of hopping rates on both temperature and impurity mass. In this respect, there is a vast literature about theoretical models for quantum diffusion of light particles in solids, and metals in particular [10]. Due to the complexity of this problem, such computations have been typically based on model potentials for the impurity-lattice interactions.

Here we calculate the jump rate of hydrogen and muonium by quantum transition-state theory [11], using path-integral molecular dynamics (PIMD) simulations. We employ a realistic interatomic potential, derived from DF theory calculations. This method allows us to calculate jump rates for this nonlinear many-body problem, including lattice relaxation, zero-point motion, and phonon-assisted incoherent tunneling.

In the path-integral formalism of statistical mechanics, a quantum particle can be represented as a cyclic chain of $L$ beads coupled by harmonic springs ($L$, Trotter number). This formalism has been employed earlier to study equilibrium properties of H and Mu in sili-
con [12] and diamond [13], by using Monte Carlo simulations. In this context, there exists a quantum extension of classical transition-state theory for calculating rate constants of infrequent events [11]. It relates the jump rate \( k \) to the probability density of the center-of-gravity (centroid) of the quantum paths of the jumping impurity, and particularly to the ratio \( P_c \) between the equilibrium probability of finding the centroid at a saddle-point (say \( r^* \)) and at a stable site (say \( r_0 \)) [11]. Namely: \( k = P_c / 2l \), where \( l \) is the distance between \( r_0 \) and \( r^* \) and \( P \) is a weakly temperature-dependent factor. 

\[
\Delta F = -\int_{r_0}^{r^*} f(\mathbf{x}) d\mathbf{x},
\]

where \( f(\mathbf{x}) \) is the mean force acting on the impurity with its centroid fixed on \( \mathbf{x} \) at temperature \( T \): 

\[
f(\mathbf{x}) = -\langle \nabla_x V(\mathbf{R}) \rangle_{\mathbf{x}}.
\]

Here \( V(\mathbf{R}) \) is the potential energy, \( \mathbf{R} \) being in our case a \( 3(N+1) \)-dimensional vector (\( N \) host atoms plus one impurity). The reliability of this method to calculate free-energy barriers and jump rates was discussed in [11] [14].

We use the Born-Oppenheimer approximation to define a potential energy surface \( V(\mathbf{R}) \) for the nuclear coordinates. Since true \textit{ab-initio} potentials require computer resources that would enormously restrict the size of the simulation cell, we have found a compromise by using an efficient tight-binding (TB) Hamiltonian, based on DF calculations [15]. With this interaction potential we found the BC site to be the absolute energy minimum for \( \text{H} \) [13], and the energy surface is similar to that derived from earlier DF and TB calculations [6].

To sample the configuration space we employed the PIMD method in the \( NVT \) ensemble [13] [16]. Simulations were carried out on a \( 2 \times 2 \times 2 \) supercell of the diamond face-centered cubic cell with periodic boundary conditions, including 64 C atoms and one impurity. To assure the right convergence of the path integrals, we took a Trotter number \( L \propto 1/T \), with \( L = 20 \) for \( \text{H} \) and 60 for \( \text{Mu} \) at 300 K. For given impurity mass and temperature, the mean force \( f(\mathbf{x}) \) was calculated at 14 points along the integration line between \( r_0 \) and \( r^* \) in Eq. 1. For a centroid position \( \mathbf{x} \), the nearest and next-nearest neighbors of the impurity (up to a total of 13 host atoms) are treated quantum-mechanically to obtain \( f(\mathbf{x}) \), as in [17]. For each point in the integration paths, we generated 5000 configurations for system equilibration, and 3 \( \times 10^3 \) configurations to calculate ensemble average properties. More technical details are given elsewhere [13] [16].

In Fig. 1 we present the free-energy barrier \( \Delta F \) for impurity diffusion from a T site to a neighboring BC site as a function of temperature. Data derived from line integration of the mean force are shown as a function of temperature for hydrogen (solid circles) and muonium (triangles). In this plot, one notices first that \( \Delta F \) is higher for \( \text{H} \) than for \( \text{Mu} \). At low temperature, the dependence of \( \Delta F \) upon impurity mass is related to the change in internal energy \( E \) of the defect complex along the diffusion path. To compare \( \text{Mu} \) and \( \text{H} \), we note that \( E_{\text{Mu}} \) is always larger than \( E_{\text{H}} \), but the difference \( E_{\text{Mu}} - E_{\text{H}} \) changes from 0.96 eV at a site T to 0.83 eV at the transition state, thus giving \( (\Delta F)_{\text{H}} - (\Delta F)_{\text{Mu}} = 0.13 \pm 0.01 \) eV. Second, in the case of \( \text{H} \), one observes a slight decrease in \( \Delta F \) for increasing \( T \), contrary to the rise in effective free-energy barrier for muonium. At high \( T \), one converges to the other, as expected for the classical limit. These migration barriers are on the order of that obtained earlier from DF-TB calculations in Ref. 8 (0.4 ± 0.1 eV).

For the opposite jump (impurity from BC to T), the effective barrier is higher for \( \text{Mu} \) than for \( \text{H} \). This is shown in Fig. 2 where symbols correspond to \( \Delta F \) derived from our PIMD simulations at several temperatures. (Note the different vertical scales in Figs. 1 and 2.) In this case, \( E_{\text{Mu}} - E_{\text{H}} \) changes at low temperature from 0.64 eV at a BC site to 0.83 eV at the transition state, giving: \( (\Delta F)_{\text{H}} - (\Delta F)_{\text{Mu}} = -0.19 \pm 0.01 \) eV. The low-temperature energy barriers obtained here for \( \text{H} \) and \( \text{Mu} \) are comparable to those found from DF theory (1.6 eV) [3] and earlier DF-TB calculations (2.0 ± 0.1 eV) [8]. Our simulations yield, however, an important decrease in \( \Delta F \) as temperature is raised.
This impurity transition between BC and T sites is asymmetric in a double sense. First, it happens between a local minimum of the energy surface and the absolute energy minimum. Second, the lattice relaxations involved in both impurity positions are very different. At BC, the nearest host atoms relax strongly (∼0.4 Å), whereas at a T site the relaxation of the C atoms is much weaker (0.08 Å). This second asymmetry is relevant for the temperature dependence of the free-energy barriers shown in Figs. 1 and 2. For diffusion across static barriers, it is known that ΔF increases with temperature [18]. In our case, the barrier ΔF depends on lattice relaxation and vibrational modes, and the larger the relaxation, the more important is the change in ΔF with temperature. For the transition BC → T, ΔF is controlled by the energy surface around BC, in which the lattice relaxation changes appreciably from the BC site to the transition point, and thus ΔF decreases fast for rising T. On the contrary, ΔF for the jump T → BC is controlled by the path between T and the transition point, which does not involve important host-atom relaxations, and ΔF changes slowly with T. In particular for increasing T, ΔF decreases for H but rises for Mu, as a consequence of the smaller lattice relaxation for Mu (closer to a static barrier).

In Fig. 3 we show the muonium jump rate from a T site to a neighboring BC site, as derived from the probability Pτ given by the calculated barriers ΔF (open squares). One observes a certain departure from linearity in the Arrhenius plot, due basically to the change in effective barrier as a function of temperature (see Fig. 1). The solid line in Fig. 3 displays the transition rate derived by Odermatt et al. [19] from μSR experiments. A triangle shows the spin relaxation rate of MuT in insulating diamond containing vacancies, and measured at room temperature [20]. In that work, it was found a rather constant relaxation rate at T < 100 K, which could indicate the appearance of coherent tunneling between T sites. For comparison, we also give in Fig. 3 the Mu jump rate from BC to T sites, as derived from the free-energy barriers shown in Fig. 2. At room temperature, and even at T ∼ 1000 K, this jump rate is several orders of magnitude smaller than that for the transition T → BC. From the jump rate derived from our simulations at 300 K (kMu = 3.4 × 10^6 s⁻¹), one expects that a muon implanted in diamond at a site T will likely diffuse to a BC site before decaying (with mean lifetime τμ = 2.2 μs).

We now turn to the diffusion of H in the diamond bulk. There are a number of possible migration trajectories, as suggested by earlier theoretical works [4]. For neutral hydrogen, according to the energy surface derived in our calculations, one can think of two main diffusion paths for hydrogen. The first one (denoted as path I) consists of a jump from BC to a neighboring T site, followed by a transition to another BC site. This is the process envisioned in Ref. 8 from (classical) locally-activated Monte Carlo simulations. For both atomic jumps, we obtain the effective free-energy barriers shown in Figs. 1 and 2. An alternative path (called II) moves H from a BC site to a nearest BC site, having a transition state at a point...
with C$_{2v}$ symmetry close to the so-called C site. This path is similar to that employed earlier in a calculation of the jump rate of H in silicon, but in diamond the energy barrier is much higher. In fact, for classical point atoms at $T = 0$ we find a barrier of $2.1 \pm 0.1$ eV, close to 1.8 eV obtained from DF calculations and 1.9 eV derived from semi-empirical cluster calculations. Concerning these energy barriers, it is worth noting that seemingly simple atomic jumps can actually involve coupled barriers, as clearly indicated in Ref. 23. Thus, to obtain the barrier in path II we considered a coupled motion of H and the C atom lying between both BC sites.

Going to the results of our finite-temperature simulations of H in diamond, we find for path II at 1000 K a jump rate from BC to BC sites of 160 s$^{-1}$, much lower than that obtained in path I for the transition from BC to T ($k = 2.5 \times 10^9$ s$^{-1}$). Taking into account the rate for the opposite process T $\rightarrow$ BC ($k = 4.6 \times 10^{10}$ s$^{-1}$), and the relative residence time of hydrogen at BC and T sites, we obtain at 1000 K a diffusion coefficient along path I of $D_H = 3.1 \times 10^{-12}$ cm$^2$ s$^{-1}$. This indicates that H diffusion from BC to BC sites will mainly happen via short visits of tetrahedral T sites, or their associated attraction basins in configuration space.

Experimental investigations on hydrogen diffusion in diamond have been so far scarce. Popovici et al. studied the diffusion of several species in diamond at 1130 K, and found that the diffusion coefficients for N, O, and H are very similar. They concluded that the diffusion process of these impurities is probably affected by crystal defects that would trap the diffusing species. Hence the value for hydrogen found by these authors [$D_H = (2.4 \pm 0.3) \times 10^{-13}$ cm$^2$ s$^{-1}$] has to be considered as a lower limit for diffusion in a perfect diamond crystal.

In summary, path-integral molecular dynamics simulations provide us with a good tool to study quantum effects on the jump-rate of muonium and hydrogen in diamond. Renormalization of the classical diffusion barriers due to these effects is appreciable. In particular, we have found that the effective free-energy barrier for muonium can be smaller or larger than that for hydrogen, depending on the diffusion process under consideration. For muonium, we find jump rates from T to BC sites on the order of $\mu$SR data. For hydrogen, the most probable diffusion path involves BC and T sites.

These calculations were performed at the Barcelona Supercomputing Center (BSC-CNS). This work was supported by M.E.C. (Spain) through Grant FIS2006-12117-C04-03. E.R. Hernández is thanked for helpful discussions.

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