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Long time scale evolution of radiation-induced defects in Er_2O_3

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ABSTRACT

The diffusion of point defects after an irradiation event in Er_2O_3 is considered. It is shown that saddle point finding methods find one transition that is a rank-2 saddle and a method is proposed to determine the attempt frequency for the transition in this case. Different methods were used to study the point defect transitions which showed good agreement at the lower temperatures but which diverged at high temperature due to anharmonic effects. The diffusion coefficients for the point defects were calculated which indicated that the calculated values could differ by up to a factor of 3 if the exponential prefactor in the Arrhenius expression was not accurately determined. Point defect diffusion in a perfect crystal was shown to be independent of direction.

1. Introduction

Many metal oxide materials are radiation tolerant and in a previous paper [1] we investigated the radiation damage induced by collision cascades and calculated the energy barriers for point defect diffusion in Er_2O_3. The motivation for that study was to investigate how radiation damage in oxide materials having the bixbyite structure differed from other materials such as spinel [2–4] and MgO [5,6]. Materials with the bixbyite structure have been extensively investigated by the group of Sickafus et al. [7–10]. The main difference was the higher energy barriers for point defect diffusion in Er_2O_3 and the fact that the oxygen vacancy was the point defect with the lowest energy barrier whereas in MgO and spinel the isolated interstitials had the lowest energy barriers. In that paper the cascades were analysed by molecular dynamics (MD) over picosecond time scales after which the dynamics is dominated by rare events. The motion of the point defects which remained at the end of the cascade were then investigated in more detail and the point defect diffusion coefficients were calculated by temperature accelerated dynamics (TAD) [11]. Using this method the diffusion pathways are determined and as the system hops from one basin of attraction to the next, the energy barriers are accurately calculated by the nudged elastic band (NEB) or climbing image nudged elastic band method (CINEB) [12,13].

The TAD method is based on the assumption of harmonic transition state theory with the hopping rate v being given by

$$v = v_0 \exp(-E/kT)$$

for a given energy barrier E where v_0 is the (often assumed constant) prefactor, T is temperature and k is Boltzmann's constant. The method works well when there are not lots of small energy barriers surrounding a local minimum energy configuration and takes into account that events which occur at a high temperature may not necessarily occur in the same order as at a lower temperature. The method can be fairly expensive on computational time and an alternative method to TAD would be to determine the transitions by a method that finds the saddle points surrounding a local minimum energy configuration by more direct means, e.g. the dimer, ART or RAT methods [14–16] and then determine the prefactor v_0 by the Vineyard method [17]. This should in theory give the same values as those previously determined by TAD and be computationally less expensive, provided the methods can find all relevant transitions so that a full rate catalogue can be produced. In the Vineyard method the prefactor v_0 is calculated from the ratio of the product normal frequencies v_i associated of the positive eigenvalues λ_i (where $\lambda_i = (2\pi v_i)^2$) of the Hessian matrix of the potential energy function at the minimum and the saddle. For a system on N atoms,

$$v_0 = \frac{\prod_i^{3N} v_i^{\min}}{\prod_i^{3N-1} v_i^{\text{saddle}}},$$

where the negative eigenvalue at the saddle point does not occur in the product. There is thus an immediate assumption that the saddle point must be rank-1, i.e. have only one negative eigenvalue. This point will be explored later. However, it is worth noting that rank-2 saddles are being increasing investigated in the literature, see for example [18].

Since the main point defect diffusion processes and barriers were determined in the previous paper [1] we concentrate here

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on the defects with the lowest energy barriers for diffusion, namely the O vacancy and O interstitial with the main purpose of the paper therefore to compare the different methods (i.e. TAD and saddle finding plus Vineyard) to see if there are any issues involved with either approach and then to use these methods to determine the associated diffusion coefficients of these point defects, more accurately than previously calculated in [1] where a constant prefactor was assumed.

2. Methodology

The potential used in the simulations is a classical fixed charge potential whose parameters are all given in the original paper describing the collision cascades [1]. The Coulombic part of the potential was evaluated both by Ewald summation and by the fast multipole method. For the Vineyard method only atoms which had moved more than 0.01 Å between the minimum and the saddle point were included in the calculation. This was typically around $N = 600$ atoms giving a Hessian matrix of dimension 1800×1800.

In calculating the prefactor by the Vineyard method, the eigenvalues at the saddle and the minimum point need to be determined. However, in the lowest energy transition of the oxygen vacancy in Er_2O_3, we found two negative eigenvalues at the saddle point determined by the NEB method. Use of the string method [19] also found this rank-2 saddle and despite increasing the number of images in the NEB and string methods, we were unable directly to find a rank-1 saddle between the two states. Further investigation revealed that such saddle points exist when the potential energy surface is very flat, almost ridge-like near the transition point and when the rank-2 saddle lies on a symmetric pathway. When this occurs, the normal frequencies of vibration at the saddle point provide only $3N - 2$ values. The saddle point, which has two negative eigenvalues, is normally called a rank-2 saddle point while the normal saddle point which has one negative eigenvalue is the rank-1 saddle point. Murrell and Laidler [20] give an example of a saddle point that has more than one negative eigenvalues from the calculation of the rate constant in a chemical reaction and show that between any two minima joined by a path that passes through a rank-2 saddle there will be a lower energy path passing through a rank-1 saddle. Rank-2 saddles have also been found by others studying defect diffusion, e.g. for H diffusion on the Fe surface [21]. We also found these for one of the O interstitial diffusion pathways in MgO and $MgAl_2O_4$ so this situation where the rank-2 saddle dominates over the nearby rank-1 saddle is a not uncommon occurrence that needs to be addressed.

We use a new approach to investigate this situation. Since the Vineyard method can be used at the rank-1 saddle point and by the Murrell–Laidler theorem a rank-1 saddle exists between two separate minima then we will determine the rank-1 saddle in a straightforward way by moving the system from the rank-2 saddle point along the eigenvector direction of the small negative eigenvalue. Generally the two negative eigenvalues have a large difference in size, typically around a factor of 10 so we call them the large negative eigenvalue and the small negative eigenvalue. The system will be moved until the minimum point is found and at that point the Hessian matrix should have only one negative eigenvalue. The prefactor and rate constant are then calculated at this point and compared to the values that TAD gives.

In the TAD simulations a lattice containing ≈640 atoms is used with T_{high} at 3000 K and T_{low} varying between 300 and 2000 K, depending on the type of defect and magnitude of the energy barrier. For the NEB and CINEB methods typically between 8 and 13 images were taken along the path. In addition to TAD, a few full high temperature MD simulations were performed using the LBOMD code [22] with a larger lattice containing 5311 atoms and the multipole method utilised for calculating the electrostatic part. The purpose of this was to investigate the possibility of correlated events.

3. Results

3.1. Oxygen vacancy

Of all the point defects investigated, the oxygen vacancy has the smallest energy barrier for diffusion. The possible transition pathways and energy barriers of the oxygen vacancy are shown in Fig. 1. The transitions of energy barriers of 0.8, 1.0 and 1.36 eV (see Fig. 1(a)–(c)) occur via a direct exchange of the oxygen vacancy with a neighbouring oxygen atom. These are the dominant transitions and almost all transitions of oxygen vacancy at the temperatures studied here involved one of these transitions. The last three energy barriers are rarer events with higher energy barriers of 1.94, 1.97 and 2.31 eV (see Fig. 1(d)–(f)). Rather than a direct exchange mechanism, these movements use the lattice structural vacancy (16c) as an intermediate site to which the replacing oxygen first moves.

In each transition, equivalent pathways can be observed. If the two transitions are symmetry transitions, they have identical transitions and the same energy barrier. For example in Fig. 1(b), the transitions in the same direction of arrows are the symmetry transitions with an energy barrier of 1 eV. The number of symmetry transitions of the oxygen vacancy are shown in Table 1. From simulations by TAD, the lowest energy barrier results in the oxygen vacancy moving in the lattice as a repeating movement between two neighbouring states. Therefore, in order for oxygen vacancy to diffuse through the lattice, a barrier greater than 0.8 eV needs to be overcome and the minimum diffusion barrier is the second lowest energy barrier of 1.0 eV.

Fig. 2 shows the movement of the atom which moves to the oxygen vacancy (labelled I) following eigenvectors of the large (a) and small (b) negative eigenvalues. The figures start from the saddle point (a2 and b2) and move following the directions of the eigenvectors. The movement along the eigenvector of the large negative eigenvalue shows the same initial transition pathway observed from the simulation in Fig. 1(a) while the movement following the eigenvector of the small negative eigenvalue makes another transition which has the same saddle point but the oxygen atom is moved perpendicular to the first pathway in a direction towards the structural vacancy.

Graphs (a) and (b) in Fig. 3 shows the total energy of the system following the eigenvectors of the small and large negative eigenvalues, respectively. For the small negative eigenvalue, the energy drops by only 0.01 eV at a separation distance of 0.4 Å. For the large negative eigenvalue, the energy is reduced 0.25 eV at the minimum point with a separation distance of 0.75 Å. This is not the same as the real minimum, i.e. the starting point for the NEB calculations, so all this plot shows is that the real minimum energy path deviates from that of the quadratic approximation as we move away from the saddle point (i.e. the eigenvector direction at the saddle no longer follows the minimum energy path).

The minimum points on the small negative eigenvalue graph are expected to be close to the rank-1 saddles. We have calculated the Hessian matrix at the minimum points of graph 3(a) and the result is that indeed only one negative eigenvalue is found at these points which are symmetrically located close to the rank-2 saddle. In other cases that we tested, the nearby rank-1 saddle could be determined in this way and in all cases the energy difference between the symmetric path rank-2 saddle and the nearby rank-1 saddle was always small.