

Supplementary section: Diffusion coefficient in presence of defects and amorphous zones

Role of Defects and Radiation Damage on He Diffusion in Magnetite: Implication for (U-Th)/He Thermochronology

Fadel Bassal ¹, Jérôme Roques ¹, Marianna Corre ², Fabrice Brunet ², Richard Ketcham ³, Stéphane Schwartz ², Laurent Tassan-Got ¹ and Cécile Gautheron ^{4,*}

¹ IJCLab, Université Paris-Saclay, CNRS/IN2P3, 91405 Orsay, France; fadel.bassal@live.fr (F.B.); jerome.roques@universite-paris-saclay.fr (J.R.); tassango@ijclab.in2p3.fr (L.T.-G.)

² ISTERre, Université Grenoble Alpes, Université Savoie Mont Blanc, CNRS, IRD, Université Gustave Eiffel, 38000 Grenoble, France; marianna.corre@univ-grenoble-alpes.fr (M.C.); fabrice.brunet@univ-grenoble-alpes.fr (F.B.); stephane.schwartz@univ-grenoble-alpes.fr (S.S.)

³ Jackson School of Geosciences, The University of Texas at Austin, Austin, TX 78712, USA; ketcham@jsg.utexas.edu

⁴ Geosciences Paris Saclay (GEOPS), Université Paris Saclay, 91404 Orsay, France;

* Correspondence: cecile.gautheron@universite-paris-saclay.fr

Random walk over a periodic lattice

We consider a 3D lattice in which the interstitial sites for He are regularly spaced. This situation is representative of a flawless crystal. We consider a direction joining as closely as possible those sites. Along this direction, we name it x , we find an alternance of sites and saddle points, and the distance between the sites is denoted a_x . We denote also B_x the barrier height, say the energy difference between the saddle point and the potential minimum located at the site.

When the He atom is in one site its rate of jumping toward either sides, due to the thermal shaking, is Γ_x . This does not preclude jumps in perpendicular directions (y and z), but the motions are independent, and we can disregard those motions when studying the diffusion along x . The scheme is depicted by Figure S1.

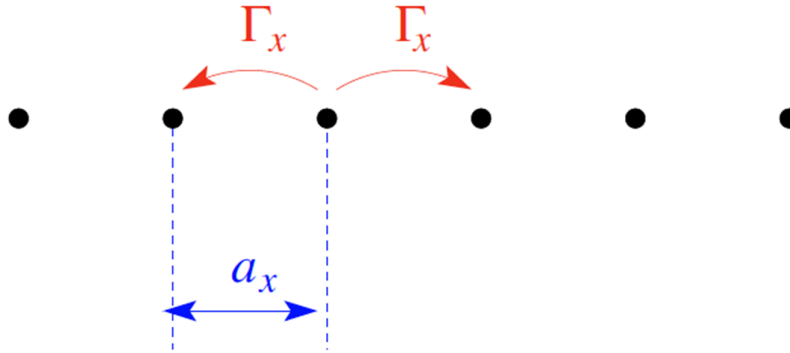


Figure S1. The computation of the diffusion coefficient along the above mentioned direction D_x , can be carried out in the following way.

We consider N jumps along the axis. As they are random, in one way or the opposite the spread of the arrival points (variance of the coordinate) is:

$$\sigma_x^2 = Na_x^2 \quad (1)$$

and the average time needed to perform the N jumps is:

$$\langle t \rangle = N \frac{1}{2\Gamma_x} \quad (2)$$

The definition of the diffusion coefficient is:

$$\sigma_x^2 = 2D_x \langle t \rangle \quad (3)$$

Combining (1), (2), (3) one gets:

$$D_x = a_x^2 \Gamma_x \quad (4)$$

According to the transition state theory (TST) we get:

$$\Gamma_x = \nu_x e^{-B_x/kT} \quad (5)$$

where ν_x is a frequency resulting from the ratio of the 3 eigen-frequencies in the potential well, and the 2 real eigen-frequencies at the saddle point. We get finally:

$$D_x = a_x^2 \nu_x e^{-B_x/kT} = D_{0x} e^{-B_x/kT} \quad (6)$$

which is the Arrhenius dependence of the diffusion coefficient. It should be kept in mind that equations (4) to (6) are valid whatever happens in the directions y and z . The diffusion can be fast, slow or blocked along those directions, without affecting D_x when a_x , Γ_x and B_x are given, due to the independence of the jumping probabilities.

Random walk over a crystal with point-defects

Now we assume that a fraction f of the sites are traps, that's to say they are more bound, and they have a higher barrier Bt to overcome: $Bt > B$, as depicted in Figure S2 where the open circles represent the trapping sites.

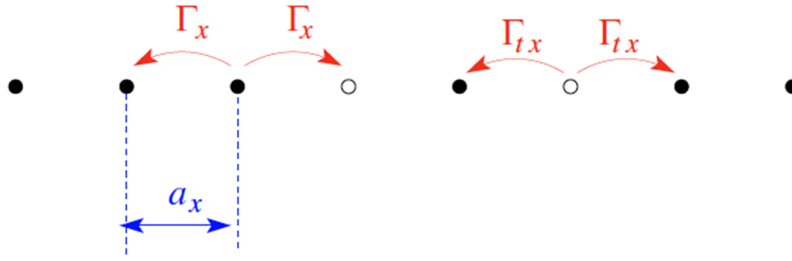


Figure S2. Again, we can update the steps done in the previous section. We consider N jumps among which statistically fN are from traps and $(1 - f)N$ are from normal sites. We denote Γ_{tx} the jumping rate from a trap site on each side.

Relations (1) and (3) still hold. However, relation (2) has to be modified. The time needed to make the $(1 - f)N$ normal jumps is $(1 - f)N/2\Gamma_x$ and the time for the fN trapping jumps is $fN/2\Gamma_{tx}$. Therefore, the average time to make the N jumps is:

$$\langle t \rangle = \frac{N}{2} \left(\frac{1-f}{2\Gamma_x} + \frac{f}{\Gamma_{tx}} \right) \quad (7)$$

At the end one obtains:

$$\bar{D}_x = \frac{a_x^2}{\frac{1-f}{2\Gamma_x} + \frac{f}{\Gamma_{tx}}} \quad (8)$$

If the trapping fraction is $f=0$ the untrapping formula (4) is retrieved. If all sites are traps ($f = 1$) one gets the same formula with the parameters of the trapping sites.

Again, from TST one can put:

$$\Gamma_{tx} = v_{tx} e^{-B_{tx}/kT} \quad (9)$$

and (8) takes the trapping Arrhenius form:

$$\bar{D}_x = \frac{a_x^2}{\left(\frac{1-f}{v_x} \times e^{B_x/kT} + \frac{f}{v_{tx}} \times e^{B_{tx}/kT} \right)} \quad (10)$$

If we denote D_x the trapless diffusion coefficient, as expressed by (6), one may express the trapping coefficient with this quantity:

$$\bar{D}_x = \frac{D_x}{1 + f \left(\frac{v_x}{v_{tx}} \times e^{\Delta B_x/kT} - 1 \right)} \quad (11)$$

where $\Delta B_x = B_{tx} - B_x$. The ratio v_x/v_{tx} lies between a fraction of unit and a few units. As $\Delta B_x \gg kT$ the main value of the trapping term is driven by the exponential. As ΔB_x is positive the diffusion is reduced by the traps. Again f is the fraction of trapping sites.

Random walk over a crystal with amorphous zones

In the case of point-defects the trapping sites are very similar to normal sites as the jumps are possible only to neighboring sites. In other words, although the rates are different the topology of jumps is exactly the same, as a consequence of the small sizes of the traps. Consider 3 parallel lines in x , as shown in Figure S3, where the trap sites have been numbered.

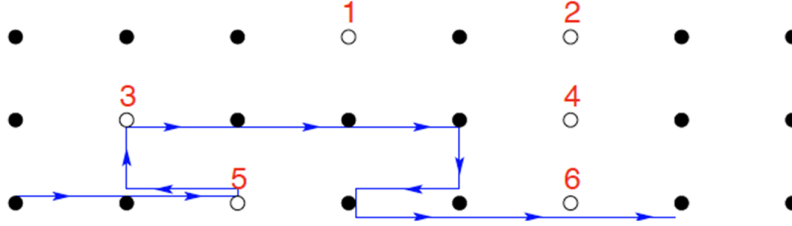


Figure S3. Diffusion along x can follow any of the 3 lines and run over them by segments as illustrated by the blue path. Again, although jumps may occur in the vertical direction (y) they do not impact diffusion along x , because the 3 lines are statistically identical regarding the density of trapping sites.

The trapping sites 2, 4 and 6 are neighbors but nothing special occurs there and their proximity has no particular effect.

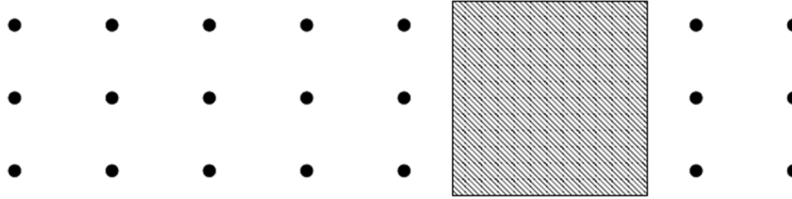


Figure S4. In the case of amorphous zones induced by recoil damage the situation is different due to the spatial dimension of the amorphous domain covering several lines, as illustrated in Figure S4, where the amorphous domain is depicted by the hatched square.

In this square the energy is much lower, so that the activation energy rises and just emphasizes the trapping effect already operating in point defects. Additionally, inside the amorphous zone the diffusion atom is supposed to have a free motion. In the case of figure 4, as the domain intercepts 3 lines its density should be weighed by a factor 3. This can be generalized to 3D.

If f represents the density of amorphous zones and n is the average number of lines (in x) connected to this zone the diffusion coefficient is:

$$\overline{D}_x = \frac{D_x}{1 + f n \left(\frac{v_x}{v_{tx}} \times e^{\Delta B_x / kT} - 1 \right)} \quad (12)$$

where ΔBx refers to the energetics of the amorphous zone.

Example of magnetite

In the case of magnetite when an α decay happens the α particle creates in average 230 point-defects with a maximal linear density along the track of 0.025 d/Å. With this low density it is safe to assume that the crystal remains intact and that the point defects remain as they have been created.

On the other hand, the recoiling daughter produces 1600 point defects over a range of 200-300 Å with a maximal linear density of 7 d/ Å, meaning that along the track the distance between defects is smaller than the inter-atomic distance. In such conditions it is plausible that the crystal collapse locally producing an amorphous domain, then we can assume that from the 1600 point-defects we are left with a single amorphous domain. The volume of the domain can be inferred approximately from the number of displaced atoms. A crystal cell is a cube of length 8.5 Å containing 56 atoms, so that 1600 displacements involve $1600/56=28.6$ cells which collapse into disorder. The domain shape is likely an elongated cylinder, but for sake of convenience and taking into account all the orientations we represent it as a cube of size $28.6^{1/3}=3$ units of cell size. As each cell intercepts 4 lines of a given direction (4 sites per cell) the number of lines intercepted by the amorphous zone is $3^2 \otimes 4 = 37$. Therefore, we get $n = 37$ in equation (12).

As a conclusion from an initial point-defect number $fp = 1600$, we get an equivalent number of defects of 37, meaning that a factor $g = 37/1600 = 0.023$ should be applied to the initial point defect density to get the equivalent density of the amorphization.