Oxygen Self Diffusion in SiO$_2$: An *Ab-Initio* Approach

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Abstract. We present a first principles study of oxygen self-diffusion in α-quartz. By supercell calculations, in the DFT-LDA framework, with plane waves and pseudopotentials, we have determined the energy of formation for the simplest oxygen defects, the vacancy and the interstitial oxygen. We have also calculated the vibrational spectrum, which allowed us to obtain the formation entropies for these defects, as well as the migration energies, using a constrained minimisation procedure. The results of our first principles calculations allow us to evaluate the contributions to diffusion of these defects in open and closed formation modes. We discuss the possible diffusion regimes depending on experimental conditions, in particular on the oxygen partial pressure, explaining some discrepancies between the experimentally available results.

1   Introduction

Quartz and its amorphous counterpart, silica, are constantly under investigation as materials for a wide range of technological applications, ranging from microelectronics to nuclear industry. The fundamental research is also very much interested in silica for its prototypical glass properties, for example, or, as other silicates, for its role in the dynamics of the earth mantle. For all the quoted fields the knowledge of self-diffusion in quartz and silica is an important point, as it is linked to ionic conductivity and to the viscosity of the glass. In this communication we present the results of a study focused on oxygen self-diffusion in α-quartz driven by point defects. Our approach is based on standard reaction-rate theory where we applied first principles techniques to investigate the formation and migration of oxygen vacancies and interstitials. First principles techniques have already been applied to crystalline and amorphous silicon dioxide, but almost always investigating the electronic properties of the materials [1, 2] rather than the kinetics of the atoms. An exception in this regard is the recent article by Hamann [3], devoted to the migration of interstitials. On the other hand, first principles techniques has already been applied with satisfactory results to the study of diffusion in other materials, either to metals [4, 5] or to insulators and semiconductors [6], including oxides [7]. For this reason we think that this approach can be very fruitful and will lead to a deeper understanding of self-diffusion in quartz and silica. We should also remark that empirical potentials and classical molecular dynamics fails to account for the breaking and reforming of bonds which are very likely in the formation and migration of defects in silica. This happens because, besides the partly ionic character of bonding in quartz, some homopolar bonds can appear when the local tetrahedric order is broken, due to the presence of defects. These microscopic details are generally not within reach of

experiments focused on the measurements of diffusion coefficients. The interpretation of diffusion coefficients on the basis of microscopic mechanisms seems particularly desirable in the case of oxygen diffusion in silica, because the large number of experimentally available data [8] is often difficult to explain. One of the reasons is certainly related to the presence of a multiplicity of mechanisms, including heterogeneous and homogeneous defect formation and the diffusion of oxygen in molecular forms, as well as the dependence of the latter on several experimental conditions. For example an activation energy as small as 1.3 eV [9] has been reported, which should probably be attributed to molecular diffusion; at the same time some older results give activation energies of 2.5 or 3.4 eV ([10] and [11] respectively). In order to clarify this puzzling situation in 1985 Mikkelsen [12] drew his attention on network oxygen diffusion. To achieve this goal he performed an experiment where the sample was prepared under ultrahigh vacuum and then coated with a protective layer, in order to prevent molecular oxygen to contribute to the oxygen self-diffusion constant. The activation energy which was found was even higher, 4.7 eV. In this paper we wish to address these discrepancies and to explain the result obtained by Mikkelsen.

2 Formation

We have calculated the formation energies for the oxygen vacancy and the oxygen interstitial defect in α-quartz. Our tools are density functional theory (DFT) in the local density approximation (LDA) and pseudopotentials for total energy calculations. We have performed totally relaxed (atomic positions and volume) total energy calculations for an orthorhombic supercell corresponding to 2x2x1 primitive cells of quartz, sampling the Brillouin zone by the only Γ point. We developed the electronic wave functions in plane waves up to 80 Rydberg cutoff energy.

Our results for the formation energies are 5.4 eV for the vacancy and 1.6 eV for the interstitial. The structure of these defects is in good agreement with previous calculations: Si-Si bond for the vacancy and a peroxy-bridge for the interstitial. These results are certainly affected by usual errors of DFT-LDA calculations, the magnitude of which cannot be established apriori; but we made several test a posteriori [14], which allows us to evaluate them around ±0.1 eV. At last we have to add errors coming from the finite size of the supercell and all technical parameters of the calculation (energy cutoff, k-points) which we estimate to be of the same order.

We are interested in the equilibrium concentration of defects, which stems from the chemical equilibrium between species and involves also formation entropies. For this reasons we calculated the vibrational entropies for the perfect and defected crystals. Through the evaluation of the eigenmodes at the Γ point for the perfect crystal and defected supercells using state of the art linear response first principles methods (the so called density functional perturbation theory, DFPT [13]). We used the vibrational frequencies in the standard formula:

$$S = k_B \sum_{\mathbf{q}\nu} \left\{ \frac{\hbar\omega_{\mathbf{q}}^{\nu}}{2k_B T} \coth\left(\frac{\hbar\omega_{\mathbf{q}}^{\nu}}{2k_B T}\right) - \ln\left[2\sinh\left(\frac{\hbar\omega_{\mathbf{q}}^{\nu}}{2k_B T}\right)\right] \right\} \tag{1}$$

where the frequencies are considered independent of temperature. Our results for the vibrational densities of states issued from our phonon calculations are shown in figure 1. Here we can see that the vacancy induces a hardening and the interstitial a softening of the network. The effect is anyway not as relevant as in some metallic systems.

Energies and entropies of formation of defects can thus be calculated in the homogeneous and heterogeneous formation modes, provided, for the latter, that we know energy and entropy
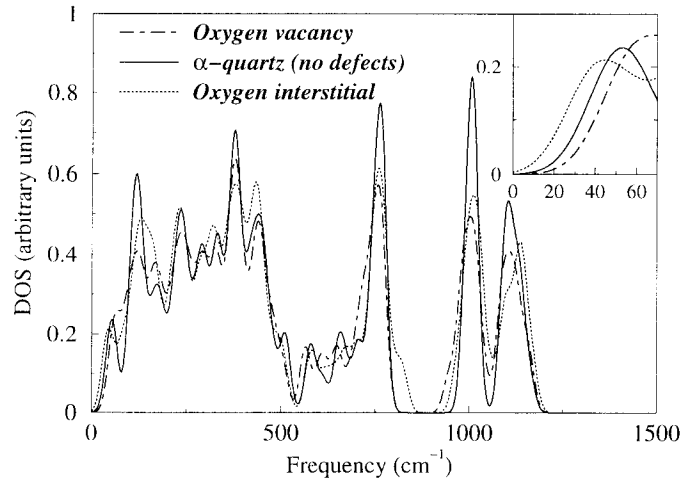
Fig. 1. The effect of oxygen defects on the vibrational spectrum of SiO_2. We show the calculated density of states for the perfect and defected crystal. The upper left inset shows a zoom on the low frequency region, where are the modes whose influence on entropy is crucial.

of the oxygen molecule. The entropy of the oxygen molecule is crucial in our analysis, because it contains a dependence on the oxygen partial pressure —through the configurational entropy of the gas. The higher the partial oxygen pressure, the higher the concentration of interstitials, and vice versa for the vacancy. We can then calculate a pressure at which the concentration of
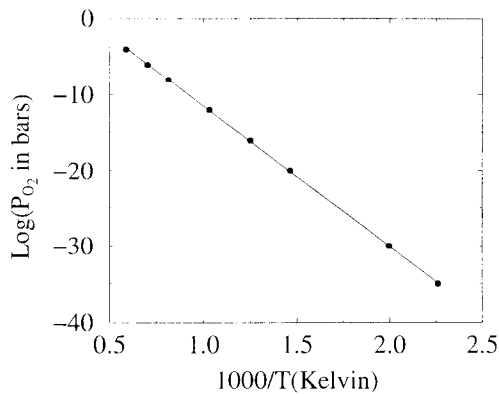

Fig. 2. The pressure at which the concentration of vacancies equals the concentration of interstitials is shown as a function of temperature.

interstitials equals the concentration of vacancies (equal to the concentration of Frenkel pairs). This pressure, that will be important in the discussion of diffusion regimes, is

$$P_{O_2} = e^{-\frac{(F_{vac} - F_{int})}{K_B T}}$$

where F_{vac} and F_{int} are the formation free enthalpies for the two defects. It's dependence on

temperature is shown in figure 2; this shows that at sufficiently low, but not unattainable, values of the oxygen pressure, vacancies are more abundant than interstitials, reversing the order expected on the basis of formation enthalpies.

3 Migration

In order to model the diffusion of network oxygen in quartz, we studied the migration of defects in quartz. The *ab-initio* approach has already been used in diffusion problems with satisfactory results [15]. Nevertheless the computational load of such calculations remains very high, excluding the possibility of an investigation of multiples migration paths. The challenge is then to find the most favourable one. We chose a method [16] consisting in "dragging" the migrating atom step by step towards the end position, relaxing all the others degrees of freedom at each step. In other words this means constraining the projection of the position of the migrating atom (relative to the center of mass) on a given direction; we chose this direction to be the one connecting the starting and the ending points. The resulting energy path is shown
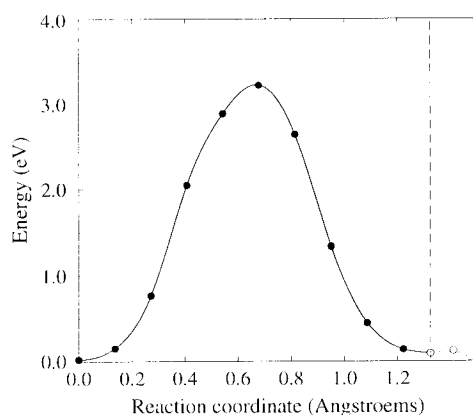

Fig. 3. The energy profile during the migration of an oxygen vacancy in quartz; the black circles are calculated values, the line is a guide for the eye. The white circles, out of the x scale, represent the small barrier that the system has to overcome to reach the real minimum from the metastable position where it is trapped at the end of the migration. Refer to the text for details

in figure 3, where our reaction coordinate is the value of the constraint. For the vacancy we chose one of three atoms which are nearest to the Si-Si bond of the vacancy, and we forced it to migrate towards the vacancy [17]. In fact the system does not fall into a position which is exactly equivalent by symmetry to the starting one, but which is slightly higher in energy (~ 0.1 eV). To reach the real minimum a small barrier has to be overcome; this is shown in figure 3 with the empty circles connected by the dashed line. The values of the reaction coordinate on these points is almost the same, it wouldn't be readable on the scale of the graph. The analysis of the atomic positions suggests that this barrier is associated to the tilting of one or few Si-O-Si angles, which are known to be easily deformable. The energy that we find for the migration of the vacancy is 3.2 eV: for the interstitial we find a much smaller migration energy of 1.2 eV. For the interstitial, as for the vacancy, we find metastable positions near the minimum, which are also within 0.1 eV from the lowest stable minimum.

4   Conclusions: heterogeneous versus homogeneous regimes

The contributions to the diffusion coefficient have the form of a product of a concentration by a jump factor, which is essentially the Boltzmann factor of the migration energy. We neglect in this stage the migration entropy and geometric prefactors. We will consider the contribution of
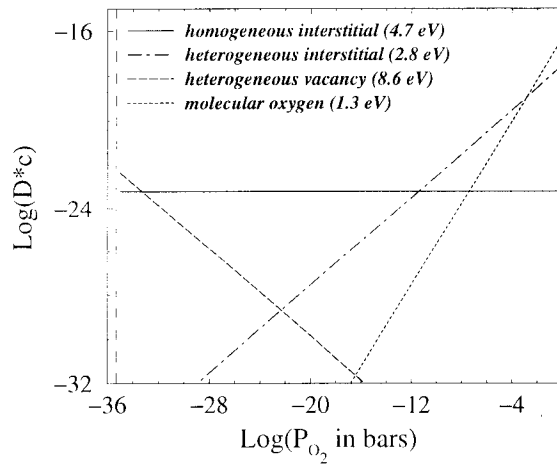

Fig. 4. Contributions to oxygen diffusion from several kinds of defect, at the temperature of 1000K, as a function of the oxygen partial pressure; the vertical dashed line is a crude estimate of the dissociation pressure of quartz.

oxygen vacancies and interstitials, either created in the open mode (also called heterogeneous formation) by interaction with an oxygen gas, or in the closed mode (homogeneous formation) as Frenkel pairs —in principle also Schottky triplets could play a role, but we think that the formation energy of the silicon vacancy is large enough to hide this contribution [18]; the same thing should hold for interstitial silicon. The results of our analysis are shown in figure 4; here we present the contributions to the self-diffusion coefficient coming from different kinds of defect at 1000K. On the horizontal axis is the oxygen partial pressure, P_{O_2}. Together with the results of our *ab-initio* calculations we have included the contribution due to molecular oxygen diffusion; this contribution is a rough estimate from experimental results on activation energy [9]. The contribution coming from Frenkel pairs is independent on P_{O_2}.

It has to be kept in mind that if the sample is in contact with an oxygen atmosphere, then the equilibrium concentration will be the heterogeneous one, and so the contributions to diffusion; but if the sample is not in contact with a reservoir of oxygen molecules, then the concentration of defects will be the Frenkel pairs equilibrium concentration added to the concentration of defects which were present when the sample was prepared. The way to read the diagram is from right to left, as if we were performing a diffusion experiment and progressively lowering the pressure.

At ambient pressure molecular diffusion is dominant (activation energy $E_{act} = 1.3$ eV. Then, at around $P_1 = 10^{-4}$ bars interstials formed in the open mode become the most important contribution ($E_{act} = 2.8$ eV). If we are in heterogeneous formation conditions this regime will continue up to $P_3 \sim 10^{-20}$ bars where vacancies begin to be dominant ($E_{act} = 8.6$ eV). But if the open mode of formation is forbidden, which happens in Mikkelsen experiment [12], then interstitials from Frenkel pairs can become the leaders of oxygen diffusion, with $E_{act} = 4.7$ eV, which compares very well with Mikkelsen result. This regime is expected for samples prepared

in a large range of pressures, from $P_2 \sim 10^{-11}$ bars to $P_4 \sim 10^{-33}$ bars, if ever this pressure, very close to the dissociation pressure of quartz, is attainable. P_2 is, in fact, the pressure which depends on temperature as shown in figure 2.

To conclude we remark that Mikkelsen samples were prepared in ultra high vacuum; thus it is very likely that the concentration of interstitials before coating was very low, much smaller than the homogeneous concentration of Frenkel pairs, and so indeed in the range between P_2 and P_4; this explains the value of the activation energy, which is higher than previous experimental results which were obtained at much higher partial oxygen pressure.

In summary, from the calculation of formation free enthalpies and of migration enthalpies for oxygen point defects in α-quartz, we present a scenario of several diffusion regimes, depending on experimental conditions. In particular we show the leading role played by the oxygen partial pressure, which explains the discrepancy between Mikkelsen experiment and previous ones.

References

[1] J. Sarnthein, A. Pasquarello and R. Car, Phys.Rev.Lett. **74**, 4682 (1995).

[2] G. Pacchioni and G. Ieranò, Phys. Rev. B **56**, 7304 (1997).

[3] D.R. Hamann, Phys.Rev.Lett. **81**, 3447 (1998).

[4] W. Frank, U. Breier, C. Elsässer, and M. Fähnle, Phys.Rev.Lett. **77**, 518 (1996).

[5] F. Willaime, A. Satta, M. Nastar, and O. Le Bacq, Int. J. of Quantum Chem., in print.

[6] Peter E. Blöchl, Enrico Smargiassi, R. Car, D.B. Laks, W. Andreoni, and S.T. Pantelides, Phys.Rev.Lett. **70**, 2435 (1993).

[7] A. De Vita, M.J. Gillan, J.S. Lin, M.C. Payne, I. Stich, L.J. Clarke, Phys.Rev.Lett. **68**, 3319 (1987)

[8] M.A. Lamkin, F.L. Riley, and R.J. Fordham, J. Europ. Ceram. Soc. **10**, 347 (1992).

[9] E.L. Williams, J.Am.Ceram.Soc. **48**, 190 (1965).

[10] R. Haul and G. Dumbgen, Z. Elektrochem. **66**, 636 (1962).

[11] E.W. Sucov, J.Am.Ceram.Soc. **46**, 14 (1963).

[12] J.C. Mikkelsen, Appl.Phys.Lett. **45**, 1187 (1984).

[13] S. Baroni, P. Giannozzi, A. Testa, Phys. Rev. Lett. **58**, 1861 (1987).

[14] Guido Roma, Yves Limoge, and Stefano Baroni, submitted to Phys. Rev. Lett. .

[15] R. Nieminen, DIMAT2000 Proceedings

[16] C.H. Bennett in "Diffusion in Solids, Recent Developments", ed. by A.S. Novick, J.J. Burton, Academic Press, (1975) p.73.

[17] The choice of this direction is not crucial, as our constraint is extremely loose (only one degree of freedom is constrained out of $3 \times \#$ of atoms). For the vacancy the endpoint is choosen as the midpoint of the Si-Si bond of the vacancy. For the interstitial we simply chose the z direction.

[18] O. Jaoul, F. Béjina, and F. Élie, Phys.Rev.Lett. **74**, 2038 (1995)

Jaoul: What about hydrogen or hydroxyl?

A: I am aware that a paper recently published in Nature claims that the presence of hydrogen enhances oxygen diffusion in Si O_2 by forming hydroxyl group. Though this is certainly an effect that can be studied by first principles calculations, we did not introduce any hydrogen atom in our calculations, also because we had in mind the experiment by Mikkelsen, in which the sample was dehydrated in ultrahigh vacuum and then coated with a protective layer to keep the hydrogen concentration to a negligible value.