Oxygen Self-Diffusion in α -Quartz

Guido Roma,^{1,2} Yves Limoge,² and Stefano Baroni^{1,3}

¹CECAM-ENS-Lyon, 46 Allée d'Italie, F-69364 Lyon Cedex 07, France ²CEA/Saclay, 91191 Gif sur Yvette Cedex, France ³SISSA/ISAS, via Beirut 2/4, I-34014 Trieste, Italy (Received 17 November 2000)

We have studied the formation energy of the simplest oxygen defects in α -quartz, the oxygen vacancy and interstitial, by an *ab initio* approach based on density functional theory in the local density approximation. We have determined the formation energies and entropies and the migration paths and energies. From our results we can conclude that oxygen diffuses in quartz by an interstitial mechanism: the interstitial has a dumbbell structure; one of the constitutive atoms jumps towards a neighboring oxygen site. The activation energy amounts to 4.7 eV in the intrinsic regime and 2.8 eV in the extrinsic regime.

DOI: 10.1103/PhysRevLett.86.4564

PACS numbers: 61.72.Ji, 66.30.Hs, 82.20.Pm, 82.60.Cx

Silicon dioxide, in its various crystalline and amorphous phases, is a widely used material in many technological domains, from microelectronics to nuclear waste storage as the main component of nuclear glasses.

Point defects play two important roles, both affecting the electronic properties of the material and contributing to the kinetics; the latter has to be known for predicting the long term behavior of heavily irradiated glasses.

The study of point defects in SiO₂, using modern first principles techniques, has been primarily driven by an interest in the electronic properties [1-4], focusing on the E'-type centers, which are paramagnetic defects observed in irradiated SiO₂, both crystalline and amorphous. Few studies have been devoted to the oxygen interstitials, and apart from the recent study by Hamann [5], the mechanisms and the energy of migration of oxygen defects have not been studied in the neutral state. The present study is entirely devoted to kinetic properties of solid SiO₂ and appears as the first comprehensive ab initio study of the self-diffusion mechanism in this system. Both empirical models [6,7] and first principles [8,9] approaches show that the short range tetrahedral arrangement of quartz is conserved in the amorphous phase, suggesting that their defect properties are similar. However, the former models are unable to properly take into account the homopolar bonds. From thermodynamical arguments [10,11] it is possible to estimate upper bounds for defect formation energies, but no clue is given on migration, nor any insight at the atomic level.

On the experimental side, E'-type defects have been identified due to their paramagnetic activity, but other defects show their presence only as traps for carriers or through diffusion data. This is the case for the neutral oxygen vacancy and interstitial. Experimental techniques can measure activation energies for self-diffusion but do not shed any light on the mechanisms responsible for formation and migration of point defects. Moreover, the only experimental result for self-diffusion in silica pertaining clearly to network oxygen [12] shows an activation energy of 4.7 eV and very low diffusion coefficients, in patent disagreement with previous works, where the activation energy is found to be much lower. For a recent review of diffusion data, see [13].

In this Letter we address the problem of formation and migration of neutral oxygen defects in α -quartz through first principles techniques. A complete account and details of methods used will be given in a forthcoming publication on silicon and oxygen diffusion.

We performed plane wave pseudopotential calculations of the total energy of various supercells, with and without point defects, in the framework of density functional theory (DFT) with the local density approximation (LDA). Our choice of the LDA is justified by the fact that it has been shown to accurately describe the structure of α -quartz even in the case of surface reconstructions [14], and by a recent detailed study [15] showing that it is globally more reliable than generalized gradient approximation, especially for energy ordering of tetrahedrally coordinated polytypes. The pseudopotentials used were standard norm conserving ones [16]. Most of the the calculations were done in an orthorhombic supercell corresponding to 2 \times 2×1 α -quartz trigonal unit cells, containing 36 (or 35/37) atoms. We checked the effect of the choice of various supercell sizes and of various special point sets. In all calculations the plane wave energy cutoff was fixed at 80 Ry, where our calculations fully converge. We performed calculations at zero pressure, relaxing atomic positions, volume, and cell shape by a conjugate gradient method, but keeping the orthorhombic symmetry. The relaxation was performed up to a force level on the atoms of the order of 10^{-4} a.u. and stresses of 10^{-5} a.u. We calculated formation entropies from eigenmodes obtained by density functional perturbation theory [17], sampling the Brillouin zone with the sole Γ point; this is expected to give accurate results, especially for the formation entropy, where only differencies are involved. To calculate the migration paths and energies we used a method proposed a long time ago by Bennet [18]; this relies on a series of constrained relaxations, where the projection of the position of the migrating atom on a given direction is fixed in the reference system of the center of mass. Each step of the migration is built from the fully relaxed configuration of the preceding step, so as to follow possible tortuous migration paths. The choice of the jump direction is not crucial, as the system has wide relaxation freedom. Since only one degree of freedom is constrained out of 3N (Nbeing the number of atoms), the moving atom can relax freely in the plane perpendicular to the jump direction, at the above mentioned level of forces and stresses, and thus allow the true saddle point to be determined.

The oxygen tracer self-diffusion coefficient in an isotropic oxide is given by $D_0^* = \sum_i \nu_0^i a_i^2 f_i c_i \Gamma_i$, where the summation runs over the possible oxygen defects—here vacancies and interstitials—whose concentration is c_i , a_i is the jump length, f_i is the correlation factor, ν_0^i is a typical attempt frequency, and Γ_i is the jump frequency. Quartz is not an isotropic crystal, so we should distinguish diffusion coefficients in the xy plane and in the z direction. However, we did not see a significant energy difference between different jump directions. Moreover, we compare our results with silica, the quartz value being not available, which is isotropic indeed.

Defects in oxides depend on formation conditions and chemical potentials. Let us first consider closed systems where intrinsic defects are formed in a homogeneous way and, therefore, as complexes of defects preserving the stoichiometry. Among these complexes, in SiO₂ one can observe Frenkel pairs of oxygen, transport occurring via either the vacancy or the interstitial, or both. In open conditions (heterogeneous formation) the system can create extrinsic defects by reacting with the oxygen gas; their equilibrium concentrations are

Vacancies,
$$c_V = \exp\left[\frac{\Delta S_{quartz}^V}{K_B} - \frac{\Delta E_f^V}{K_BT}\right] \exp\left[\frac{S_{O_2}(p_{O_2})}{2K_B}\right];$$

Interstitials, $c_I = \exp\left[\frac{\Delta S_{quartz}^I}{K_B} - \frac{\Delta E_f^I}{K_BT}\right] \exp\left[-\frac{S_{O_2}(p_{O_2})}{2K_B}\right];$

where we have separated the entropy contribution of the gas, $S_{O_2}(p_{O_2})$, from that of the solid, $\Delta S_{quartz}^{defect}$, to show the dependence on the oxygen partial pressure p_{O_2} . The temperature dependence is driven by the formation energy of the defects $(\Delta E_f^V, \Delta E_f^I)$. The formation free energy (which corresponds to the free enthalpy at zero pressure) depends on the oxygen chemical potential, i.e., on the reference state of the oxygen. Here we have chosen as the reference state the oxygen gas. Let us take the vacancy as an example: $\Delta E_f^V = E(N - 1) - E(N) + \frac{1}{2}E(O_2)$, where E(N) indicates the energy of the perfect crystal with N oxygen atoms and E(N-1) is the energy of the crystal with one oxygen vacancy; $E(O_2)$ is the energy of the oxygen molecule in the gas. To improve the reliability of the energy of the oxygen molecule, we calculated with the present approach the formation energies of several oxides and compared them to the experimental values in order to deduce $E(O_2)$. The jump frequency term is given by $\Gamma_i =$

 $\exp[\Delta S_{\text{mig}}^{i}/K_{B}]\exp[-\Delta E_{\text{mig}}^{i}/K_{B}T]$. To calculate the diffusion coefficient, we need the formation and migration free energies of both defects. In the closed mode the Frenkel pair concentration is given by $c_{\text{FP}} = \exp\frac{1}{2}[(\Delta S_{\text{quartz}}^{V} + \Delta S_{\text{quartz}}^{I})/K_{B} - (\Delta E_{f}^{V} + \Delta E_{f}^{I})/K_{B}T]$ which no longer depends on the oxygen partial pressure. Thus the activation energy Q for oxygen self-diffusion can be deduced from the formation and migration energies of defects. Taking as an example Frenkel pairs formation and vacancies migration we get $Q = \frac{1}{2}(\Delta E_{f}^{V} + \Delta E_{f}^{I}) + E_{\text{mig}}^{V}$. At standard Fermi levels the neutral defects are by far

At standard Fermi levels the neutral defects are by far the most probable ones. This result, already known in the literature [1,3], has been confirmed by our results on charged vacancies and interstitials and will be presented in a forthcoming publication.

Our results for crystalline quartz agree with experimental results within usual DFT-LDA errors. In all cases our calculations give lattice parameters whose difference with the experimental value (4.9160 Å [19]) never exceeds 1%. The four symmetry parameters, defining all the atomic positions in the cell, are also reproduced with the same precision. Releasing the symmetry constraint, in the orthorhombic unit cell, a small relaxation occurs; this is less than 0.1% on the cell parameters. The values of the bond lengths are also in good agreement with the recent results found by Pacchioni, the Si-O distances being 1.620 Å and 1.625 and 3.076 Å the Si-Si one [2]. The formation energy of quartz amounts to 9.23 eV, the experimental value being 9.37 eV (result of Ref. [20] extrapolated to 0 K).

For both defects, our results are in good agreement with the same author. For the vacancy we observe the formation of a Si-Si bond, whose length is 2.393 Å (to be compared with 2.34 Å in bulk Si); as in [2] we find a slight increase of the O-Si bonds adjacent to the vacancy (1.626, 1.638, and 1.657 Å). We find an increase of b/a by 1%, a decrease of 0.5% for c/a, and a total volume decrease of 2.5%. For the interstitial defect we find a dumbbell structure; the bond lengths are 1.501 Å in the dumbbell O-O, 1.659 and 1.671 Å for the Si-O bonds, giving a slight increase of the Si-O bonds of the oxygens involved in the defect. The formation of the interstitial corresponds to an increase of the b/a ratio by 6% and an increase of 0.7% for c/a, for a total volume increase of 3.5%. We found some metastable minima which we discuss in connection with defect migration. The results for the formation energies are 5.4 eV for the vacancy and 1.6 eV for the interstitial, which gives a formation energy of 7.0 eV for a Frenkel pair. The absolute error on these formation energies, which comes from the technical aspects of the calculation, set of special points, and size of the supercell, can be estimated from our detailed calculations to be of the order of 0.2 eV, coming mainly from the supercell size and elastic interactions between defects.

The determination of the vibrational entropy is based on the harmonic approximation: we calculate the phonon spectra of the perfect and defected quartz and deduce their entropy using a standard textbook formula [21], neglecting the temperature dependence of the eigenfrequencies.

Low energy phonons, which contribute significantly to the entropy, are slightly hardened for the vacancy and slightly softened for the interstital; this can be seen from the densities of states plotted in Fig. 1. The effect, being around 30% of the frequency, is largely beyond the error expected in SiO₂ [22]. This softening of the lattice is well known in the compact metallic structures where the interstitial gives rise to localized low frequency modes. However, in these cases the decrease is much larger, of the order of a factor of 10 [23]. As far as we know this is the first determination of the lattice softening/hardening of quartz by point defects. The solid contribution to the formation entropy is, taking the values at 1000 K, $\Delta S_{quartz}^I = 6.6K_B$ and $\Delta S_{quartz}^V = -3.5K_B$. The most important contribution to the formation en-

The most important contribution to the formation entropy is due to the oxygen molecule, becoming as large as $44K_B$ when p_{O_2} is 10^{-10} bars (at 1000 K). The effects of the solid and gas parts of the formation entropy compete, the former favoring interstitial formation with respect to vacancies, and the reverse for the latter.

We have computed the migration energy by looking at jump events in a few directions that are equivalent by symmetry in the perfect crystal, checking that we get the same value. For the vacancy we find an almost symmetric path, with a saddle point 3.2 eV above the minimum. For the interstitial we find a much smaller energy, amounting to 1.2 eV, in good agreement with Hamann's result [5]. At the end of the migration we found the system in a metastable minimum in the vicinity of the stable one, within 0.1 eV approximately, for both defects. From an analysis of atomic positions, we conclude that the two minima differ by a rearrangement of Si-O-Si angles, while the distribution of nearest neighbor distances and of O-Si-O angles remains almost identical.



FIG. 1. Vibrational density of states for the perfect and the two defected crystals, obtained by Gaussian broadening of frequencies at Γ , excluding the three zero frequencies ($\sigma = 10 \text{ cm}^{-1}$). The inset zooms in on the low frequency spectrum.

From our results we deduce that four diffusion regimes can be expected; Fig. 2 shows them at 1000 K as a typical case. First of all in the closed mode, diffusion will be driven by interstitial migration from Frenkel pairs. In this case the activation energy amounts to 4.7 eV. In the open mode the dominant mechanism will change with the oxygen partial pressure. At ambient pressure the molecular oxygen mechanism dominates; its contribution varies linearly with the oxygen pressure. We estimate, from experimental results on oxygen [13] and rare gases diffusion trends, the most probable activation energy to be 1.3 eV. Below the pressure threshold labeled P_1 , estimated around 10^{-4} athm, the mechanism switches towards the interstitial one, the defects being formed from the gas phase. The activation energy amounts then to 2.8 eV, with a square root dependence of D_0^* on the oxygen partial pressure. This regime will dominate down to P_3 , of the order of 10^{-24} athm, where the high vacancy concentration will outweigh the mobility ratio. The activation energy goes up to 8.6 eV in this regime, and D_0^* has an inverse square root dependence on p_{O_2} . In principle also Schottky triplets could play a role, but the formation energies for the silicon vacancy and interstitial are big enough to hide this contribution [24]. Anyway, the behavior observed in experiments depends on the environment of the sample during measurements and when it was prepared. Whenever the sample is in equilibrium with an oxygen reservoir, then equilibrium concentrations are heterogeneous ones; the contributions to diffusion corresponding to the two lines crossing at P_3 come from interstitial (dash-dotted line) and vacancy (long-dashed line) heterogeneous diffusion, respectively. When not in equilibrium with an oxygen reservoir, as in the experiment by Mikkelsen [12], defects are



FIG. 2. Contributions to oxygen diffusion coming from different kinds of defects at 1000 K. The vertical dashed line is an estimate of the dissociation pressure of quartz. Transition pressures P_{1-4} are discussed in the text.

always formed as Frenkel pairs, and their contribution to diffusion will be given by the solid line in Fig. 2, unless an excess of residual heterogeneous defects remains from the preparation of the sample. This leaves open the possibility of dominant mechanism change with temperature.

Speaking of α -quartz, we are not aware of experimental works able to separate the contribution of network oxygen to diffusion and giving the corresponding activation energy. We can nevertheless compare our scenario to amorphous SiO₂ data, at least on a semiguantitative basis. Mikkelsen [12] found an activation energy of 4.7 eV and relatively low prefactor D_0^* of the order of 2.6 cm² sec⁻¹. His results are in contradiction with previous ones (cited in [12]), giving activation energies of 1.3 eV (Williams), 3.4 eV (Sucov), and 2.5 eV (Haul/Dumbgen). These remarkable discrepancies, in our opinion, can be partly attributed to the fact that it is difficult to prevent molecular oxygen from contributing to the measured diffusion coefficient. In order to be able to track only network oxygen, Mikkelsen coated his sample with two silicon nitride protective layers. Prior to coating, the sample was treated under vacuum conditions, thus at very low partial oxygen pressure. The result obtained by Mikkelsen has certainly to be compared to the Frenkel pair regime, since the heterogeneous mode of formation is hindered by the silicon nitride coating, and the concentration of heterogeneous interstitials has been kept very low during the deposition of silica. On the contrary Williams and Sucov are working under standard oxygen pressure, from 0.1 to 4 athm, where the permeation regime of molecular oxygen clearly dominates the lattice oxygen diffusion. An estimation of the crossover pressure is 10^{-4} athm. A more precise value entails calculation of the enthalpy and entropy of dissolution and migration of molecular oxygen in quartz. Given the relatively low values of the solid part of the entropy terms, we can quite safely state that this picture will not be changed significantly by the effect of the migration entropies. Similar experimental results on crystalline SiO₂ would be very interesting, to understand the influence of the disordered arrangement of SiO₄ tetrahedra on the diffusion of network oxygen.

In conclusion, we have calculated activation energies for diffusion of the oxygen vacancy and interstitial in α -quartz. We find activation energies of 2.8 and 8.6 eV for the interstitial and vacancy in the open mode, respectively, and 4.7 eV for diffusion in the closed mode. We reconcile some apparently contradictory experimental results by analyzing the dependence of diffusion on the partial oxygen pressure.

- C. M. Carbonaro, V. Fiorentini, and S. Massidda, J. Non-Cryst. Solids 9812, 1 (1997).
- [2] G. Pacchioni and G. Ieranò, Phys. Rev. B 56, 7304 (1997).
- [3] K. C. Snyder and W. Beall Fowler, Phys. Rev. B 48, 13 238 (1993), and references therein.
- [4] D. C. Allan and M. P. Teter, J. Am. Ceram. Soc. 73, 3247 (1990).
- [5] D.R. Hamann, Phys. Rev. Lett. 81, 3447 (1998).
- [6] N. Mousseau, G. T. Barkema, and S. W. de Leeuw, J. Chem. Phys. **112**, 960 (2000).
- [7] J. Horbach and W. Kob, Phys. Rev. B 60, 3169 (1999).
- [8] F. Liu et al., Phys. Rev. B 49, 12528 (1994).
- [9] J. Sarnthein, A. Pasquarello, and R. Car, Phys. Rev. Lett. 74, 4682 (1995); Phys. Rev. B 52, 12 690 (1995).
- [10] Y. Limoge, in *Diffusion in Materials*, edited by A.L. Laskar, J.L. Bocquet, G. Brébec, and C. Monty, NATO ASI, Ser. E, Vol. 179 (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1990), p. 601.
- [11] G. Boureau and S. Carniato, Solid State Commun. 99, i-iv (1996).
- [12] J.C. Mikkelsen, Appl. Phys. Lett. 45, 1187 (1984), and references therein.
- [13] M.A. Lamkin, F.L. Riley, and R.J. Fordham, J. Eur. Ceram. Soc. 10, 347 (1992).
- [14] G-M. Rignanese et al., Phys. Rev. B 61, 13250 (2000).
- [15] Th. Demuth, J. Phys. Condens. Matter 11, 3833 (1999).
- [16] The pseudopotentials were generated according to the Troullier-Martins recipe for oxygen and Von Barth–Car for silicon.
- [17] S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. 58, 1861 (1987).
- [18] C. H. Bennet, in *Diffusion in Solids, Recent Developments*, edited by A. S. Nowick and J. J. Burton (Academic, New York, 1975), p. 73.
- [19] L. Levien, C. T. Prewitt, and D. J. Weidner, Am. Mineral.65, 920 (1980).
- [20] W.D. Good, J. Phys. Chem. 66, 380 (1962).
- [21] See, for example, W. Jones and N. H. March, *Theoreti-cal Solid State Physics* (Dover, New York, 1985), Vol. 1, p. 237.
- [22] X. Gonze, D. C. Allan, and M. P. Teter, Phys. Rev. Lett. 68, 3603 (1992).
- [23] H. J. Wollenberger, in *Physical Metallurgy*, edited by R. W. Cahn and P. Haasen (North-Holland, Amsterdam, 1996).
- [24] O. Jaoul, F. Béjina, F. Élie, and F. Abel, Phys. Rev. Lett. 74, 2038 (1995).