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Published in:
Physical Review B Condensed Matter

Link to article, DOI:
[10.1103/PhysRevB.61.12590](https://doi.org/10.1103/PhysRevB.61.12590)

Publication date:
2000

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Lægsgaard, J., & Stokbro, K. (2000). Local chemistry of Al and P impurities in silica. *Physical Review B Condensed Matter*, 61(19), 12590-12593. <https://doi.org/10.1103/PhysRevB.61.12590>

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Local chemistry of Al and P impurities in silica

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(Received 21 December 1999)

The local structure around Al and P impurities in silica is investigated using density-functional theory. Two distinct cases are considered: impurities substituting for a Si atom in α quartz, and impurities implanted in a stoichiometric α -quartz crystal. Both impurity elements are found to have similar stable substitutional configurations; however, when they are implanted the geometries are quite different: While P prefers to stay in the interstitial region, Al tends to substitute for a Si atom, which in this way is forced into the interstitial region. The underlying chemical origin of the differences is revealed by an analysis of the electronic impurity levels, and the results clarify previous experimental data.

Silica glass is becoming an increasingly important material for application in optical communication systems. The fundamental basis for creating advanced optical components is the ability to engineer the optical properties of the glass by doping with various impurity elements. P doping has been used extensively to modify the elastic properties and refractive index of silica glasses, and it has been shown that implantation of P ions can significantly enhance the nonlinear parts of the optical susceptibility.¹ Both Al and P doping have been found to enhance the solubility of rare-earth ions in silica (which is essentially zero in the absence of such codoping), and this effect is of great practical importance in the fabrication of, e.g., light-amplifying optical devices.

A number of experimental investigations have been performed in order to clarify the properties of Al and P impurities in both crystalline and amorphous silica,¹⁻¹¹ but most of the results obtained are of a qualitative nature. The purpose of the present paper is to complement the experimental information by a theoretical study of the local chemistry governing the behavior of dilute Al or P impurities in a silica environment. In real, disordered, silica glass, local chemical order is preserved to a large extent, while the long-range disorder is brought about by small variations in bond angles and lengths.¹² Therefore, it is reasonable to expect that the local structure around an impurity in silica glass will resemble that in a regular crystal, and in the present paper we shall study the incorporation of isolated Al, P atoms in crystalline α -quartz. Results are presented for two distinct cases: "implanted" impurities, which are not accompanied by additional oxygen atoms, and impurities that substitute for a Si atom in the lattice. The former configuration would result from ion implantation of impurities, while the latter is one of several possible results of impurity incorporation during the process of silica growth.

Our study is based on density-functional theory (DFT),¹³⁻¹⁵ which is the most accurate method for structural calculations capable of treating extended systems with large unit cells. To our knowledge, the study by Continenza and Di Pomponio using an all-electron method but without structural optimization, is the only previous theoretical study of

Al/P impurities in silica based on DFT methods.¹⁶ The phase diagram of quartz, on the other hand, has recently been investigated by several authors,¹⁷⁻¹⁹ using both the simple local-density approximation^{14,20} as well as the more advanced generalized gradient approximation²¹ (GGA) to the exchange-correlation energy. It has been found that the two approximations give comparable errors in the equilibrium structure parameters, while the magnitude of energy differences between various crystal structures (and hence the phase diagram) are much better described by GGA. Therefore, we have chosen to use the Perdew-Wang 91 (PW91) GGA energy functional²² throughout the present paper. The Kohn-Sham equations are solved using Vanderbilt ultrasoft pseudopotentials,^{23,24} and a plane-wave expansion with an energy cutoff of 25 Ry. Brillouin zone (BZ) integrations were done by special point sampling. For calculations within a single α -quartz unit cell, a mesh of 12 \mathbf{k} points in the full zone was used. Calculations were also done in a supercell consisting of six elementary unit cells. For these geometries, structural relaxations were carried out using a single \mathbf{k} point in the center of the BZ. Subsequent checks confirmed that total energies and forces were well converged with respect to \mathbf{k} points also in this case. Spin polarization was taken into account in the large cell, but was not found to have decisive influence on the structural parameters. Ionic coordinates were optimized until the length of the total force vector was less than 0.15 eV/Å (in the small cell, a criterion of 0.05 eV/Å was used).

As a preparation for the investigations of impurity configurations the equilibrium structure of pure α -quartz was determined. The crystal structure of α -quartz is hexagonal, with a basis cell consisting of three formula units. We determined the lattice constant to be 5.03 Å (at $c/a = 1.11$), which is larger than both the experimental value²⁵ (4.92 Å, $c/a = 1.10$) and the value found by Hamann¹⁷ (4.97 Å, $c/a = 1.11$) but more consistent with another recent study using ultrasoft pseudopotentials.^{19,26}

The substitutional Al and P impurities were initially put in place of an α -quartz Si atom in the supercell, whereafter the structure was allowed to relax. Subsequently, it was checked

TABLE I. Structural parameters for substitutional Al and P impurities in quartz. Indices (1) and (2) refer to short and long (Al,P)-O bonds, respectively. The O-(Al,P)-O angles are between the two short (1) and long (2) bonds to the impurity atom.

	SiO ₂	SiO ₂ :AlO ₂	SiO ₂ :PO ₂		
Si-O(1)	1.625 Å	Al-O(1)	1.720 Å	P-O(1)	1.626 Å
Si-O(2)	1.628 Å	Al-O(2)	1.722 Å	P-O(2)	1.677 Å
Si-O-Si(1)	149°	Al-O-Si(1)	147°	P-O-Si(1)	158°
Si-O-Si(2)	149°	Al-O-Si(2)	147°	P-O-Si(2)	143°
O-Si-O(1)	109°	O-Al-O(1)	110°	O-P-O(1)	102°
O-Si-O(2)	109°	O-Al-O(2)	110°	O-P-O(2)	153°

that the system was stable against distortions. The results are summarized in Table I. It can be seen that both ions have stable fourfold coordinated configurations. The Al-O bond length is expanded compared to that of α -quartz, but all four O neighbors have (nearly) the same distance to the Al atom, and the bond angles are similar to the ones found in pure quartz. The structure around the P impurity, on the other hand, is markedly altered, with two of the O neighbors displaced ~ 0.05 Å outward, and with significantly perturbed bond angles.

The density of states (DOS) of quartz with a substitutional Al impurity is shown in Fig. 1(a), and correlates well with the results of Continenza and Di Pomponio.¹⁶ As discussed by these authors, the uppermost valence bands can be ascribed to nonbonding oxygen states, while the states appearing below ~ -4 eV are bonding states and the Al-O states appear higher than the Si-O states. It has commonly been assumed that the hole arising from the reduced valency of Al compared to Si would localize on a particular O atom and result in structural relaxations breaking the symmetry of the quartz crystal. However, we find that the hole is distributed evenly over the four oxygen neighbors, and that no significant distortion of the tetrahedral symmetry occurs. This is probably because the hole resides in the nonbonding O bands, whereas the equilibrium structure is controlled by the Al-O bonding states.

Figure 1(b) shows the DOS of the crystal with a substitutional P impurity. In contrast to the case of Al substitution, the P impurity introduces defect states in the insulating gap. This effect is readily understood in a tight-binding picture, using the fact that the position of the $3p$ level in P is lower than in Si, whereas the position of the Al $3p$ level is higher than in Si. While the Al-O antibonding state would be buried in the Si-O antibonding bands, the corresponding P-O state falls below and forms a localized state. The extra electron from the P impurity goes into this state that is mostly located on the P atom and the two O atoms with elongated P-O bonds. The increased bond length reduces the hybridization and thus pulls the antibonding state towards lower energies, which appears to be favorable.

To investigate the atomic structure around implanted impurity atoms a preliminary investigation was carried out within the elementary unit cell of quartz, introducing an impurity atom without modifying the stoichiometric silica network. A mesh of 14 initial impurity positions in the irreducible part of the Wigner-Seitz cell was investigated. Already in these calculations it became clear that Al and P impurities

behave in quite distinct manners. The Al impurities showed in all cases a strong tendency to oxidize and ended up as being threefold or fourfold coordinated to O in the relaxed configurations. This caused strong modifications of the lattice geometry, and several Si-O bonds were broken. Therefore, a second set of calculations were carried out in which Al was placed substitutionally in the quartz lattice while the various interstitial positions were taken up by a Si atom. It was found that this initial geometry led to the lowest total energy values. The P impurities were found to behave differently, forming only a single P-O bond, and in addition replacing a Si-O bond with a P-Si bond.

In the supercell, initial configurations were constructed either by introducing the impurity (or the interstitial Si atom in the case where an Al atom was placed in a Si-substituting position from the outset) in the pure quartz structure at one of the positions, which had led to a low-energy relaxed structure in the unit cell, or by joining a single impurity-containing unit cell with a relaxed structure to a pure-quartz surrounding. Similar results were obtained in both cases. The relaxed structure around the P impurity, shown in Fig. 2(b), is similar to the one found with the unit cell. One Si-O bond is broken and replaced by a P-O bond, and the oxygen-deficient Si atom is attracted to the P impurity, indicating that a P-Si bond is formed. The length of this bond is comparable to the bond length in elemental Si (2.35 Å). The most favorable configuration for the Al impurity is shown in Fig. 2(c). In this structure, all Si atoms except one are fourfold coordinated. The Si atom that in this way, has “gone interstitial,” has two bonds to oxygen atoms also bonded to the Al impurity, but with bond lengths considerably larger than the value in pure quartz. The (threefold coordinated) O atoms bonded to the “interstitial” Si are at the same time the ones with the longest (i.e., weakest) bonds to Al.

The marked difference in behavior between Al and P implants is most easily understood by considering the electronegativities of the elements involved, which on the Pauling scale, are 1.61, 1.90, 2.19, and 3.44 for Al, Si, P, and O, respectively. Thus, while it is always favorable to transfer electrons to O from one of the other species, the gain is largest for transfer from Al atoms, which explains why Al tends to go into a substitutional position in a quartz environment even if it involves the breaking of Si-O bonds. For a P impurity, on the other hand, it would be more favorable to stay interstitial as an electron localized on an interstitial P atom would have a lower energy than an electron localized on Si. The replacement of a Si-O bond with P-O and P-Si bonds probably occurs because the total number of bonds is increased and the residual electron on the Si atom can still be transferred to P to the extent that this is favorable.

The DOS of the structures with implanted impurities is shown in Figs. 1(c) for (Al) and 1(d) for (P). In both cases, there are three excess electrons that occupy two impurity levels (the P levels are exchange split) residing in the gap between the α -quartz nonbonding O and antibonding Si-O states. The gap states are, however, of a different nature in the two cases. For the structure with an implanted P impurity, the (exchange split) state at the Fermi level has the most weight on the P atom with some hybridization to the nearest-neighbor O atom, while the second impurity state below is of mixed P-O-Si character (the exchange splitting of this level

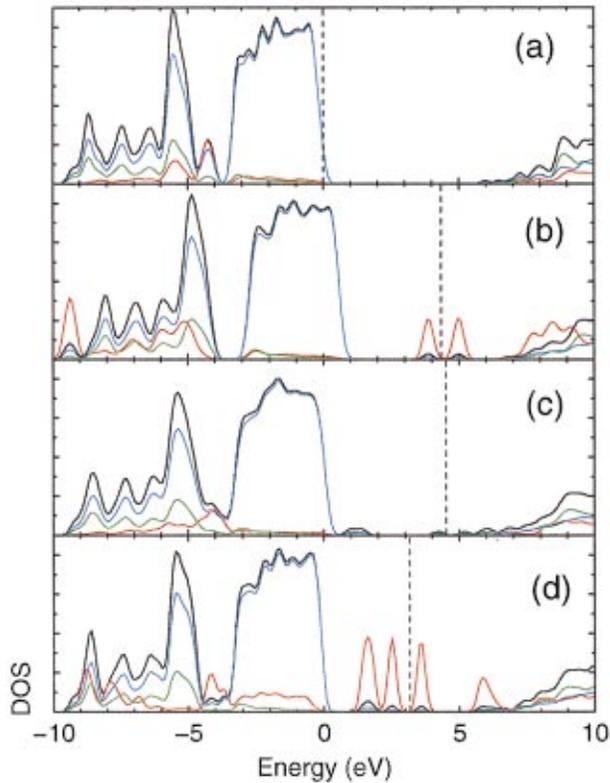


FIG. 1. (Color) Projected DOS for the four different impurity-containing quartz crystals: Substitutional Al (a), substitutional P (b), implanted Al (c), and implanted P (d). Black lines give the total DOS, red lines the projection on the impurity (scaled by a factor of 18 to facilitate comparison), green lines the Si projection, and blue lines the O projection. The curves were obtained by sampling 8 \mathbf{k} points in the BZ with a Gaussian broadening of 0.25 eV, and have been aligned so that the O 2s band is centered around -19.25 eV in all cases. Dashed lines indicate the position of the Fermi levels.

is ~ 0.25 eV and is masked in the figure due to the Gaussian broadening). For the Al-implanted structure, on the other hand, the two gap states have no significant weight on the Al atom, but rather on the Si atom, which has gone interstitial and, less pronounced, on the two nearest O atoms.

Experimental investigations of doped silica in which dopants were introduced during the growth process have revealed that the substitutional Al impurity studied in this work is the dominant form of Al appearing at low concentrations. The Al-O bond length found by us (~ 1.72 Å) agrees reasonably with the values of 1.74–1.77 Å found by extended x-ray-absorption fine structure in various $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses with tetrahedrally coordinated Al atoms. The anisotropies in the hyperfine matrices extracted from electron spin resonance (ESR) data have been interpreted as indicating that significant departures from tetrahedral symmetry around Al occur.²⁷ We are currently working to extract an ESR spectrum from our calculations to facilitate a more direct comparison with the available experimental data for these impurities.

The ^{31}P nuclear magnetic resonance signal observed from as-grown P-doped silica samples has been ascribed by Douglass and co-workers⁷ to a configuration in which the P atom is connected to three bridging O atoms via the usual bonding states, and a fourth nonbridging O via a double

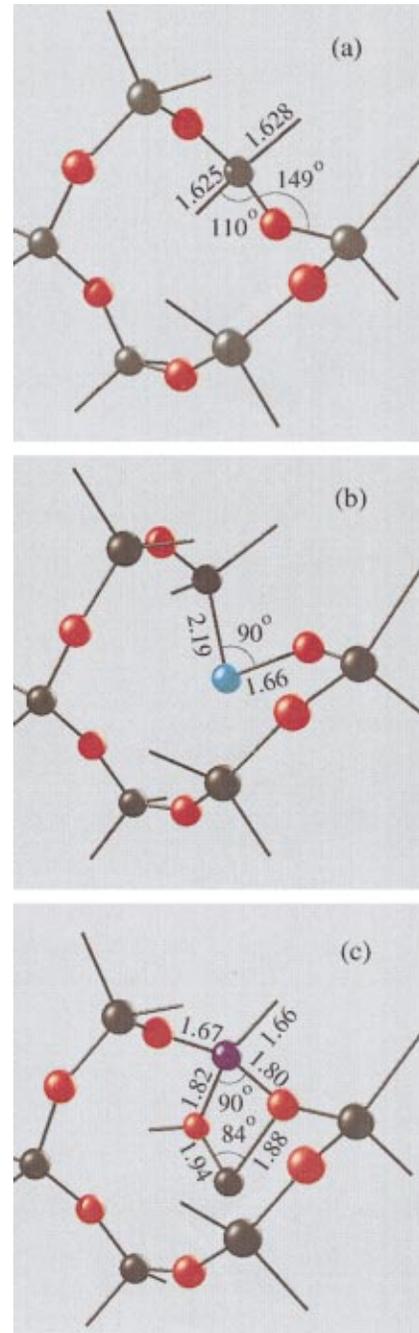


FIG. 2. (Color) The shortest closed path in the α -quartz structure is a six-membered ring, shown in (a). Black atoms are Si, while red atoms are O. In (b) and (c) the modifications of the ring structure upon P (b) and Al (c) implantations are shown. Bond lengths are given in angstroms.

bond. This interpretation is supported by results from Raman spectroscopy indicating the presence of P-O double bonds.²⁸ To incorporate such a configuration in the silica network would require a complicated modification of the α -quartz structure. The substitutional impurity configuration studied in the present work has been observed experimentally as a radiation-induced defect. ESR studies of this structure confirm that the uncompensated spin that gives rise to the ESR signal is primarily located in the direction of the long P-O bonds, as found in our calculation. However, no quantitative

results for the bond lengths have, to our knowledge, been obtained.

For the implanted impurities, experimental results show that Al and P impurities do behave in quite distinct manners, as suggested by our calculations. For Al-implanted silica glass, it has been found^{8,11} that the implanted Al atoms are O coordinated for all implantation doses, and that this behavior persists during heat treatments, with no signs of cluster formation. For large implantation doses, Si-Si bonds were seen to form, presumably arising from bonding between the Si atoms that are pushed into the interstitial region. Implanted P impurities on the other hand, only appeared to form P-O bonds at low implantation doses, while at higher concentrations, colloids of P atoms were observed, and only P-P bonds could be discerned in x-ray photoelectron spectroscopy.^{1,29} This result is consistent with our calculations, as the presence of localized electrons on the interstitial P atoms implies that energy may be gained by P-P hybridization.

In conclusion, we have clarified the chemical nature of substitutional and implanted Al and P impurities in α -quartz. Al and P were both found to have stable substitutional configurations, but with some differences in the local structure. While the extra electron in the PO_4 unit is mainly located in

two of the bonds that are ~ 0.05 Å longer than the other two, the hole present in the AlO_4 unit is evenly distributed over the four bonds, and the difference between short and long bond lengths is comparable to that in pure quartz. The implanted impurities are shown to behave in quite distinct manners. While Al tends to substitute for a Si atom, P prefers to stay interstitial although a single P-O bond is formed. This is in accord with experimental investigations^{1,8}, which show that Al implanted in silica is always coordinated to O atoms and does not form clusters, while P tends to form colloids for sufficiently high implantation doses. An analysis of the electronic structure of the various impurity configurations shows that the different behaviors can be understood from simple tight-binding arguments taking into account the relative positions of the sp -levels in Al, Si, and P.

We thank Lars B. Hansen and the Center for Atomic-Scale Materials Physics (CAMP) for valuable guidance on the use of their plane-wave band-structure program. Stimulating discussions with M. R. Poulsen, M. Kristensen, M. Brandbyge, and A. P. Jauho are gratefully acknowledged. The use of Danish national computer resources was supported by the Danish Research Council.

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