Density functional theory investigation of native defects in SiO_2: Self-doping and contribution to ionic conductivity

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We present here a theoretical study of the effect of self-doping and the contribution of native defects to the ionic conductivity of α-quartz. A thorough first principles study of native defects in quartz, comprising silicon and oxygen defects in several charge states, is presented. On the basis of this comprehensive study of defect energetics, we can evaluate the equilibrium concentrations of defects at a given temperature, including the effect of doping of the material coming from its native defects. Moreover, in open conditions, oxygen partial pressure has an influence on the concentrations and self-doping of the material. Our results show that oxygen interstitial is the native defect of highest concentration at equilibrium and that charge compensation occurs between negative oxygen interstitials and holes in the valence band. Moreover, we find that in pure quartz neutral defects are dominant at low temperature and relatively high partial oxygen pressures, but for low enough oxygen pressures and sufficiently high temperatures, negative interstitials are expected to play a significant role in diffusion. The concentrations of the latter are low enough that their contribution to ionic conductivity is negligible, but their sensitivity to the Fermi level is high; thus, if for some reason (e.g., impurities) the Fermi level is raised, the intrinsic contribution to ionic conductivity will become important.

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I. INTRODUCTION

Quartz and silica are very important as prototypical crystalline and amorphous oxides; the comprehension of a variety of physical properties of these materials, electrical, mechanical, piezoelectric, optical, is important in several domains, from a technological as well as a conceptual point of view. Several properties of quartz and of oxides in general depend crucially on point defects and their concentration. Defect thermodynamics allows the prediction of the equilibrium concentration of defects on the basis of free enthalpies of formation. However, in insulators charge compensation effects need to be taken into account, which complicates the picture, because concentrations of defects become mutually dependent. In highly ionic insulators the assumption of formal charges for cation and anion defects and their mutual compensation has been almost traditional,[1] but in binary oxides it is certainly not justified.[2] In this paper we devise, by applying it to the major case of quartz, a general procedure able to describe charge compensation and self-doping in an insulator and thus to obtain equilibrium concentrations of defects and their contributions to diffusion and ionic conductivity.

Quartz and silica are insulators with a large band gap (9 eV); the very low conductivity that one can measure is considered to be ionic in character,[3] as the activation energy for electron/hole conductivity is expected to be higher. This ionic conductivity has been generally attributed to Na impurities [3–6] which are supposed to form complexes with Al (or other trivalent impurities like B); the latter have low mobility, but the former are highly mobile, provided they become unassociated with Al atoms by overcoming an energy barrier.

As far as we know, the native (or intrinsic) contribution to ionic conductivity has been neglected.

The present study of native defects in α-quartz is aimed at giving a solid basis to theories of ionic conductivity based on the isolated point defects model; in particular we evaluate the contribution due to native defects. In an insulator the concentration of defects in several charge states and the position of the Fermi level are determined together by imposing the neutrality of the system. This corresponds to minimizing the canonical partition function which should contain, in principle, all possible defects. In reality this rule has been frequently applied, but seldom with a large database of defects: we found two works that have given a true first-principles estimation of self-doping of a solid, one[7] for $CuInSe_2$ and the other[8] for GaSb. In the case of quartz it has already been pointed out that negative interstitials could be responsible for p-doping conditions in quartz under irradiation,[9] but no assessment was made about normal quartz in equilibrium conditions; and in any case, only oxygen defects were taken into account. At variance with semiconductors, in a large band gap material electron or hole concentrations can be too small to compensate charge imbalance due to charged defects; so that charge neutrality is in effect a constraint for the relative concentrations of all carriers (both ionic and electronic). Here we take into account oxygen and silicon defects in several charge states and calculate defect concentrations and the Fermi level as a function of temperature and oxygen partial pressure.

The paper is organized as follows: in Sec. I we describe the relation between concentrations and the Fermi level; in Sec. II we give the technical details about density functional theory (DFT) calculations, their accuracy, and the quality of our model for quartz; in Sec. III the results of our defect calculations (structures and energetics) are presented; finally, in Sec. IV, we discuss the implications for ionic conductivity.

II. CHARGED DEFECTS, CONCENTRATIONS, AND SELF-DOPING

Defects, in insulators, are present in several charged states. Equilibrium concentrations of isolated defects are ex-

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ponentials of formation free energies, which depend on the chemical potentials of the system under study, as discussed in Ref. 10. Consider a solid in equilibrium with gaseous oxygen, the chemical potential μ_O is one-half of the free energy of an oxygen molecule F_{O_2}. Each defect (i.e., each set of nuclear positions) can appear in several charge states, which means that a number of electrons has been transferred to/from a reservoir of chemical potential μ_e, that is, the Fermi level. In fact, formation energies for charged defects depend on μ_e; let us write the formation free energy for a defect obtained by adding/removing n_O oxygen atoms and n_{Si} silicon atoms, and having excess charge Q:

$$F_f^{n_O,n_{Si},Q} = F^*_{quartz+n_O+n_{Si}+Q} - F_{quartz} - n_O\mu_O - n_{Si}\mu_{Si} + Q\mu_e, \tag{1}$$

where n_O and n_{Si} can be positive (interstitial case) or negative (vacancy case); the last term has the similar meaning of adding/removing electrons, except for the sign: in fact, due to the usual sign convention for the charge, adding charges means subtracting electrons. As we consider equilibrium with gaseous oxygen, the silicon chemical potential is bound to be $\mu_{Si}=\mu_{SiO_2}-2\mu_O$, where μ_{SiO_2} is the free energy per formula unit of quartz in our calculations. In the calculations presented in this paper, we have neglected the vibrational contributions to free energies, which, even if not completely negligible,[10] are not essential for the conclusions of the present paper. Furthermore, an estimation of the specific effect due to vibrational entropies of all the defects would be well beyond the scope of the present paper.

The electron chemical potential is nothing else than the Fermi level of the crystal itself, which acts as an electron/hole reservoir. Since the system and the reservoir are the same, the Fermi level is influenced by the concentration of defects which alters the density of states, especially by localized levels located in the gap.

We neglect here the defect formed by an oxygen molecule sitting in interstitial voids inside the network of SiO_2; this is justified by the fact that we consider oxygen partial pressures low enough for these species to be penalized by their formation entropy, with respect to single interstitial atoms. We also neglect the exchange of charges with the oxygen gas, as the interface reference potential between the solid and the gas turns out to be very close to the solid bulk potential.

We can now write the equation imposing the conservation of the number of electrons in our closed system:

$$p_v(T,\mu_e) + \sum_j Q_j c_j(T,\mu_e) - n_c(T,\mu_e) = 0, \tag{2}$$

where n_c and p_v are the number of electrons in the conduction band and the number of holes in the valence band, respectively; c_j is the concentration of the defect labeled by j, carrying a charge Q_j; j runs, in principle, over all possible defects.

In the following we present the results obtained for the c_j's and μ_e by solving Eq. (2) at a given temperature T and oxygen partial pressure P_{O_2}. The temperature enters the equation through entropy terms and Boltzmann factors; total energies are all computed at 0 K. In the present calculation we take into account the translational entropy of the oxygen molecule—giving the P_{O_2} dependence—which is the dominating contribution of the entropy of the gas and cannot be neglected, as we discussed in Ref. 10. The concentrations of conduction electrons and valence holes, respectively, are calculated using the experimental gap by the means of a standard textbook expression based on the effective mass approximation.

III. COMPUTATIONAL DETAILS

We have performed pseudopotential DFT local density approximation (LDA) calculations using the PWSCF code;[11] most details of the calculation, pseudopotentials, plane wave cutoffs, thresholds on forces and stresses, are the same as in Ref. 10; here all results are obtained with supercells of size $2\times2\times2$ the α-quartz unitary cell (i.e., containing 72 ± 1 atoms) and Γ for Brillouin-zone sampling; we relaxed atomic positions and cell parameters, allowing also cell deformation. The relaxations led to forces/atom smaller than 10^{-4} a.u. and stresses smaller than 2 kbar; at this level of pressure we have a good approximation of formation enthalpies. For the relaxations we used either a conjugate gradient algorithm or variable-cell damped dynamics.[12] Departures from the hexagonal symmetry of quartz are not always negligibles. We can estimate them by comparing the volume of the distorted cell with that of an ideally hexagonal cell having the same a_0 and c_0. These differences range from the small departures of the negative oxygen interstitials (0.2% and 0.7%) to much larger ones for positive oxygen vacancies in the puckered configuration (as large as 5.6% for $Q=+2$). Calculation for charged defects were performed by imposing a compensating charge background, as implicitly included by PWSCF when the number of electrons does not match the nuclear pseudocharge. Furthermore, in order to compare the calculated energy for variously charged defects, corrections for periodic image interactions have to be considered. We have calculated the shift of the average potential with respect to the one of pure quartz, $\Delta\bar{V}$. The energy correction for a defect of charge Q is $Q\Delta\bar{V}$. The shift of the average potential for a defect calculation has been obtained by maximizing the overlap between the density of states of the defected crystal and that of quartz; this procedure allows to determine an optimal shift with an accuracy of 10^{-2} eV.

IV. DEFECT STRUCTURES AND ENERGETICS

In principle it is not possible to predict which defects, in which charge state, will be relevant to our study, in spite of several works on a few well known oxygen defects.[9,10,13–15] In fact, except for a preliminary paper,[16] to our knowledge, no study has been performed on quartz having an overall look over native oxygen and silicon defects, as has been done for other materials.[7,8]

Here we have taken into account oxygen and silicon vacancies and interstitials, and for every single defect we have relaxed the structures for neutral and a few charged states. Details of their structure and their formation enthalpy H_f at standard temperature and pressure are shown in Tables I and

TABLE I. Structure of native oxygen defects in quartz and their formation enthalpies at ambient temperature and pressure. V=vacancy, I=interstitial; some relevant bond lengths are shown. Oxygen atoms are black, silicons are light gray. See the text for further details.

Defect	Charge	Structure	Distance (Å)	H_f(eV)
V(O)	0		Si-Si: 2.41; Si-O: 1.63–1.65	5.58
V(O) (puck.)	0		Si-O: 1.75–1.92	8.09
V(O)	+1		Si-O: 1.65–1.83	7.46
V(O)	+2		Si-O: 1.74–1.87	7.04
V(O)	−1		Si-Si: 2.41; Si-O: 1.64–1.66	9.16
I(O)	0		O-O: 1.50; Si-O: 1.66/1.67	1.84
I(O)	−1		Si-O: 1.66–1.71/1.90	2.22
I(O)	−2		Si-O: 1.69–1.80	2.13
I(O)	+1		O-O: 1.40; Si-O: 1.73/1.74	3.97

II. The structures shown in the table are obtained by selecting atoms which have coordination anomalies (i.e., Si which are not four-coordinated with oxygens and O which are not dicoordinated with silicons) and their bonds, shown as sticks. Let us take an example, in order to clarify the meaning of the structures: the oxygen interstitial with $Q=-2$ in Table I. Here two oxygen atoms "share" the Si-O-Si bond of the silica network structure. The two silicon atoms are shown, because they became five-coordinated; the two oxygen atoms are not shown (since they have the right Si-O-Si coordination), but their position is clear, being at the ends of two bonds coming from the silicon atoms and connecting to each other. The criterion for bonding is distance; the upper thresholds are 1.6 Å for O-O bonds, 2.0 Å for Si-O bonds, and 2.5 Å for Si-Si bonds. Some of these structures, like the dimer or puckered configuration of oxygen vacancies, are well known, but others—for example, those of silicon defects—are not.

Let us make a couple of remarks. The first is that a few local bonding configurations, say oxygen dumbbells or Si-Si bonds, arise in various defects, more or less stretched according to the charges locally available. The second remark is that silicon vacancies, which have not been investigated up to now from first principles, as far as we know, have formation enthalpies which are not very high, and are lower than those of the oxygen vacancies. This is not so surprising, because forming a silicon vacancy in equilibrium with O_2, as it turns out, corresponds from the point of view of local bonding to substituting a molecular O-O bond with two peroxy bridges (like two neutral oxygen interstitials), together with a change in the topology of the SiO_2 network. The entropic part favors Si vacancies with respect to O vacancies at high oxygen pressures. For example, at ambient tempera-

TABLE II. Structure of native silicon defects in quartz and their formation enthalpies at ambient temperature and pressure. V=vacancy, I=interstitial; some relevant, bond lengths are shown. Oxygen atoms are black, silicons are light gray. See the text for further details.

Defect	Charge	Structure	Distance (Å)	H_f (eV)
V(Si)	0		O-O: 1.49/1.50; Si-O: 1.68–1.70	4.51
V(Si)	+1		O-O: 1.37/1.47; Si-O: 1.58–1.89	6.09
V(Si)	+2		O-O: 1.23/1.53; Si-O: 1.74–1.80	7.54
V(Si)	−1		O-O: 1.49; Si-O: 1.59–1.69	5.33
I(Si)	0		Si-Si: 2.34; Si-O: 1.64–1.72	13.78
I(Si)	+1		Si-Si: 2.37; Si-O: 1.61–1.88	13.37
I(Si)	−1		Si-Si: 2.27;Si-O: 1.65–1.72	16.37

ture, the partial pressure above which silicon vacancies are more abundant than oxygen ones is around 10^{-4} atm. The situation of course is different if quartz is in equilibrium with bulk silicon: in that case the formation enthalpy for a neutral Si vacancy is much higher: 13.74 eV.

Our first remark suggests that some of the bonding configurations shown here could be interpreted in terms of tight binding energy parameters, analogous to those used in the past for valence alternation pair concepts.[17] For instance the silicon interstitial with $Q=+1$ is stabilized by forming a three-coordinated oxygen, which allows it to gain, in the language of Ref. 17, the correlation energy of one on-site oxygen lone pair. A similar case occurs in the positively charged silicon vacancies, where the configuration containing an ozonyl group is lower in energy than the one with two dumbbells (the neutral one); the ozonyl configuration is stabilized by a three-coordinated oxygen atom and, in the +1 charge state, by a five-coordinated silicon atom. A thorough interpretation of our results in these terms would require a quantitative tight binding model for defected SiO_2, which is clearly beyond the scope of this article.

By solving Eq. (2) at $T=300$ K and $P_{O_2}=1$ atm, we find that the electron chemical potential is $\mu_e=2.25$ eV. The formation enthalpies in Tables I and II are calculated using this value of μ_e.

An important remark is suggested by the values of μ_e and the formation energy of negative oxygen interstitials, which are close to each other: charge compensation in quartz, at standard temperature and pressure, takes place between holes in the valence band and negative oxygen interstitials. In Fig. 1 we show the electron chemical potential as a function of temperature for three values of P_{O_2}.

V. THEORY OF IONIC CONDUCTIVITY IN QUARTZ

Point defects contribute in an essential way to diffusion in materials, in a way that depends on their concentration and their mobility. In a previous work we considered the role of neutral oxygen defects in self-diffusion,[10] and neglected the role of charged defects which, as it turns out from the present results, are lower in concentration at standard temperature and pressure. But on lowering the oxygen pressure, the fraction of negative to neutral interstitials raises.[21] These defects have been shown to have very high mobilities,[14] and can give an important contribution to diffusion. And what is even more relevant, being charged, they contribute to ionic conductivity.

We can estimate the contribution to ionic conductivity due to native defects (labeled by j) with charge Q_j, concentrations c_j, and mobilities μ_j:

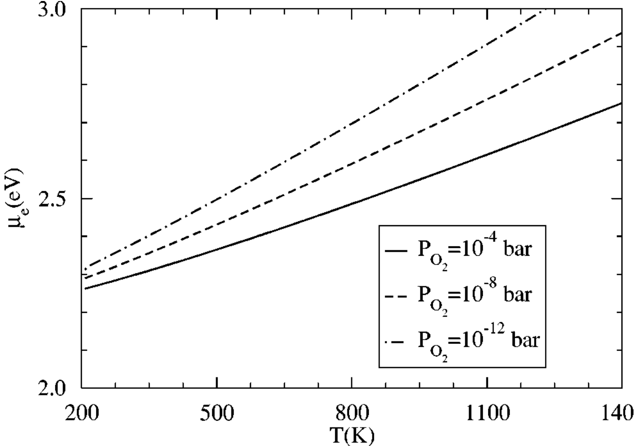

FIG. 1. Femi energy as a function of temperature in quartz for three oxygen partial pressures; the zero of energy is at the valence band top.

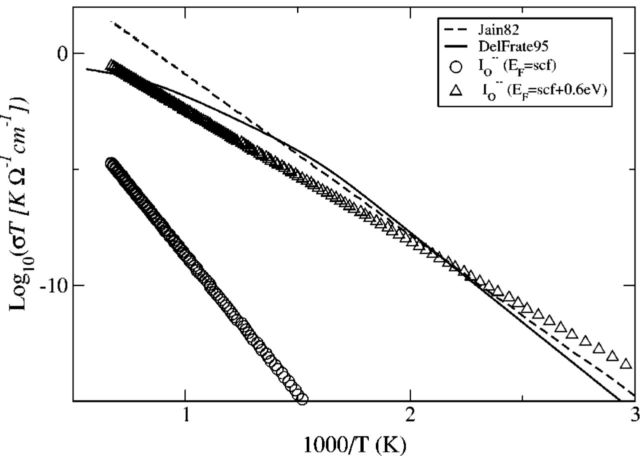

FIG. 2. Decimal logarithm of ionic conductivity times temperature in quartz: continuous and dashed lines are experimental results by Refs. 3 and 6, respectively; circles are our estimated contribution from oxygen interstitials (I^{2-}), at $P_{O_2}=10^{-8}$ atm, triangles show the contribution expected for μ_e 0.6 eV higher than the solution of Eq. (2).

$$\sigma(T) = \sum_j c_j Q e \mu_j = \sum_j c_j Q^2 e^2 d_j^2 \nu_0^j e^{-E_j^m/k_B T}. \tag{3}$$

Here the mobilities are expressed in terms of attempt frequencies ν_0, jump lengths d_j, and jump probabilities expressed as a thermal exponential of the migration energy E_j^m for each defect. As mentioned before, Jin and Chang[14] found very small migration energies for singly and doubly charged oxygen interstitials, respectively 0.27 and 0.11 eV; these figures, added to our results for formation energies, allow us to give an estimate of the contribution of intrinsic defects to ionic conductivity. This contribution, at standard temperature and pressure, is indeed negligible with respect to the measured values[3,4] in quartz as can be seen in Fig. 2, where we show the main contribution (in decimal log scale), the one due to doubly negative oxygen interstitials. The contribution of other native defects has to be excluded on the basis of their energies both of formation and migration. The latter will be the object of a forthcoming publication.

It has to be noticed that the concentration of negative oxygen interstitials is of the order 10^{-8} cm^{-3} at 1000 K, which is far lower than impurity concentrations in real samples (of the order of ppm). In fact the presence of Al and Na impurities in the samples that were used for the experiments certainly influences the position of the Fermi level. We expect that, depending on relative concentrations of Na and Al, the Fermi energy is displaced up or down with respect to our calculated equilibrium values. It is reasonable to expect that sodium abundance would raise the Fermi level, by providing weakly bound electrons. An evaluation of the effect of Al and Na concentrations on the Fermi level in quartz is certainly to be included in the future perspectives of the present work, bearing in mind that Al impurities present special problems that require one to go beyond the LDA in order to account for the observed localization of a hole in the electronic structure.[18–20] Nevertheless, it is desirable to give already an estimate of the contribution to ionic conductivity from native defects in the hypothesis of Fermi levels higher than the equilibrium one; in Fig. 2 we show this contribution for a displacement of the Fermi level of 0.6 eV, which is modest with respect to the energy gap. With such a displacement the native contribution to ionic conductivity is comparable to the measured values.

In summary, we have calculated the structure and formation enthalpy of several native defects in quartz and we have used this database to give a self-consistent theoretical estimate of the equilibrium value of the Fermi level in pure quartz, as a function of temperature and oxygen partial pressure. This allows us to conclude that (1) oxygen interstitials are the dominant native defect for a large range of temperatures and pressures and (2) charge compensation takes place between negatively charged oxygen interstitials and valence band holes.

We have then given an estimation of the contribution of oxygen interstitials to ionic conductivity; these contributions, in a hypothetical pure crystal, are negligible with respect to measured values; but in real samples the unavoidable presence of impurities, mainly alkali-metal ions and hydrogen, could have an indirect effect on ionic conductivity by enhancing the native contribution enough for it to became nonnegligible.

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[21] One could wonder if the principle of Le Châtelier is respected; the answer is yes, not only does the sum of the concentrations of oxygen interstitials lower with P_{O_2}, but also each single interstitial concentration does. Simply, the concentration of negative interstitials lowers with pressure much more slowly than the neutral or positive ones.