

Role of Electronic versus Atomic Relaxations in Stokes Shifts at Defects in Solids

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Redshifts of luminescence relative to optical absorption bands (Stokes shifts) of molecules and of defects in solids are universally attributed to slow atomic relaxations on the grounds that electronic transitions are fast (Franck-Condon principle). Here we report a novel phenomenon that can occur only in the solid state: Stokes shifts caused by slow electronic relaxations. We demonstrate that the phenomenon occurs in the nonbridging oxygen defect in amorphous SiO₂. We predict that another defect (OH group), which can exist in either crystalline or amorphous SiO₂, has a similar Stokes shift, but it arises from a mix of lattice and electronic relaxations with manifest differences in the two phases.

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Differences between the spectral positions of optical absorption (OA) and ensuing photoluminescence (PL) bands are known as Stokes shifts [1]. According to the Franck-Condon (FC) principle, electronic excitations occur on a much faster time scale than atomic relaxations. Thus, the Stokes shifts exhibited by the optical spectra of molecules and defects in semiconductors and insulators are generally attributed to slow lattice relaxations that occur after optical excitation but prior to luminescence and are termed FC shifts [2].

In this Letter, we demonstrate that, in solids, slow electronic relaxations can also be responsible for a Stokes shift. The absorption band may arise predominantly from states significantly below the top of the valence band. The resulting deep hole may then relax to the top of the valence bands by a slow, nonradiative process mediated by the sequential emission of phonons. The final luminescence line exhibits a Stokes shift. Clearly, the phenomenon can occur only in a solid where the sequential emission of phonons is possible but not in a molecule where the energy levels do not form a continuum. We show two defects in SiO₂ as examples, where in one case the Stokes shift is entirely due to slow electronic relaxations while in the other defect electronic and atomic relaxations occur simultaneously. The intriguing feature of these defects is that they may have the same Stokes shift and optical signature in spite of the different relaxation mechanisms involved.

We first consider a defect whose experimental signature is an OA band centered at 4.8 eV and ensuing PL band at 1.9 eV [3–5], appearing to be a classic example of a system with a large FC shift. These optical bands are commonly observed in high-OH containing, irradiated *a*-SiO₂. Both OA and PL bands intensify with increasing OH content and radiation (UV, x-ray, γ , or neutron) dose [6].

The defect responsible for the above OA and PL bands is invariably identified (e.g., by EPR measurements [3] and cluster calculations [7]) as a neutral nonbridging

oxygen (NBO), i.e., an oxygen atom bonded to only one Si with an unpaired electron on its nonbonding $2p$ orbital [3–5]. Our first result is that a NBO has only a shallow level at 0.3 eV above the valence-band edge (E_v), raising doubts about the proper identification of the defect. However, by calculating transition energies as differences in total energies, we show that the OA band is indeed centered at ~ 4.8 eV, as observed, resulting from a large Hubbard U and preferential excitations from states around the main peak of the valence-band density of states (DOS) at ~ 3 eV below E_v . Virtually no lattice relaxation occurs after absorption so that the FC shift is essentially zero. However, the deep hole can bubble up to the top of the valence band slowly and nonradiatively. The calculated luminescence energy for a transition to the top of the valence band is 1.8 eV, in excellent agreement with observations [4,5]. Thus, the NBO provides an excellent illustration of an “electronic FC shift,” i.e., a Stokes shift caused by slow electronic relaxations. In addition, we show that the NBO meets all the requirements to be identified as the defect responsible for the 1.9-eV luminescence.

In parallel to the calculations discussed above, we pursued alternative candidates for the observed 1.9-eV luminescence line and found a surprising coincidence. The optical cycle for interstitial OH groups in amorphous SiO₂ has virtually identical transition energies, i.e., ~ 4.8 eV and ~ 1.9 eV if it resides in the biggest voids of the oxide where it has the lowest energy. In this case, however, the optical excitations are followed by substantial atomic relaxations, in addition to the slow electronic relaxations (the interstitial OH is initially weakly bonded to the network, but a change of charge state causes it to form a tighter bond). Thus, the Stokes shift of an interstitial OH is caused by a mix of slow atomic and slow electronic relaxations. Placing the OH group into voids of different sizes reveals that, although the defect can be excited by 4.7–5.0 eV in all cases, the PL energy decreases monotonically with

void size (in small voids and in α quartz the PL energy is 0.7–0.8 eV).

The present calculations are based on density functional theory, the generalized gradient approximation for the exchange-correlation energy, ultrasoft pseudopotentials, supercells, and plane waves [8,9]. The pseudopotentials were thoroughly tested in earlier work on a variety of Si-O-H systems [10,11]. As in that work, the energy cutoff for the basis set was 24 Ry, and integrations over the Brillouin zone were done using the Monkhorst-Pack scheme with one special k point in the relevant irreducible wedge [12].

The calculations were performed for 72-atom α quartz and 72-atom amorphous SiO_2 supercells. The amorphous structures were generated by using the Monte Carlo bond-switching method [13] and relaxed until the total energy was minimized (the force on each atom is smaller than a tolerance, namely, 0.1 eV/Å). The size of supercells (~ 10 Å) is big enough to neglect the interaction of a defect with its periodic images. The electronic transition energies were calculated by comparing the total energies of the ground and excited states of the system where the excited states were created by manually fixing the band occupancy numbers. We have also calculated the optical matrix elements for transitions from different valence levels to the partially occupied defect level in the gap to evaluate the absorption coefficient.

Absorption and photoluminescence transitions involving nonbridging oxygen in amorphous SiO_2 .—We find that, in its ground state, the neutral NBO has a partially occupied level slightly above the valence-band edge [Fig. 1(a)]. It is essentially a nonbonding oxygen $2p$ state and naturally lies very close to E_v , which is made up of similar orbitals [14]. As a result, optical excitation of the NBO from the valence-band edge is suppressed, suggesting that the dominant initial states lie deeper in the valence bands. This result is consistent with the fact that

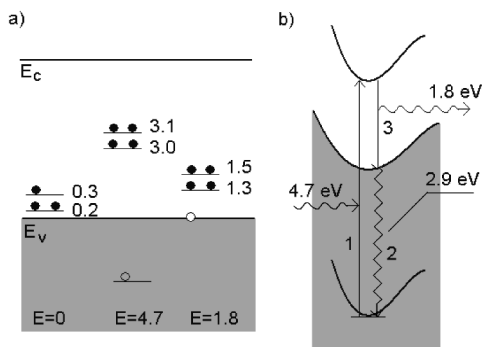


FIG. 1. (a) One-electron energy levels of the NBO defect prior to the excitation, relaxation, and luminescence processes, respectively. Corresponding total energies are listed below the level diagrams. (b) Total energy diagram as a function of a generalized coordinate. Absorption (1), luminescence (3), and slow electronic relaxation (2) processes are shown with their respective transition energies.

the OA spectrum is a broad band [15]. The calculated absorption spectrum has a maximum value for transitions coming from ~ 3 eV below E_v (Fig. 2). This peak approximately coincides with the maximum of the calculated valence-band DOS. Thus, we considered excitation from a state 3 eV below E_v into the half-empty state in the gap [Fig. 1(b), step 1]. By comparing total energies of the initial and final states, we obtained an excitation energy of 4.7 eV, in excellent agreement with the position of the peak in the observed OA spectrum (4.8 eV) [6]. The large excitation energy arises in part from a large Hubbard U that raises the one-electron energy levels by ~ 3 eV as shown in Fig. 1(a). It is clear that differences of one-electron energy levels cannot account for the excitation energy.

In the tight-binding picture of SiO_2 , the upper part of the valence band, including the deep hole state that is created by excitation, has primarily Si sp^3 and O $2p_y$ character. The orientation of the participating O $2p_y$ states is such that they are weakly interacting with the Si sp^3 orbitals (they lie in the Si-O-Si plane perpendicular to the Si-Si line) [14]. The system can lower its energy in different ways. Electrons from higher-energy states can annihilate the hole by emitting photons. This process, however, would result in additional discrete PL lines that have not been observed. Auger processes cannot be ruled out, but the simultaneous requirement for energy and momentum conservation makes them less favorable than phonon-assisted recombination processes as in the case of p - vs n -type Si [16]. The most likely process is what we refer to as a slow, nonradiative electronic relaxation [Fig. 1(b), step 2], namely, the slow bubbling up of the hole to the valence-band edge mediated by a cascade of one-phonon electronic transitions. This sequence of phonon emissions requires a continuum of energy levels to be present so that the hole can literally “bubble up” one-phonon at a time. There is virtually no atomic motion during this process, so that the electronic relaxation is solely responsible for the observed Stokes shift of the NBO defect (2.9 eV).

Clearly, once the hole is at the top of the valence band, the NBO energy levels are again shifted [Fig. 1(a)], albeit by a lesser extent since the NBO atom remains negatively

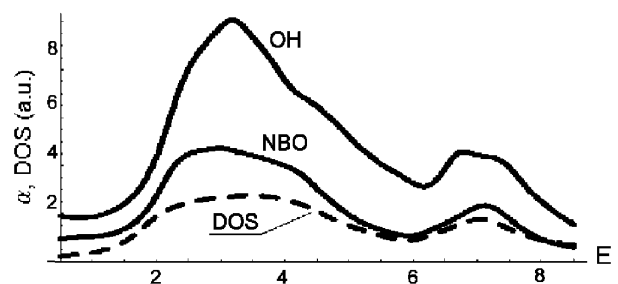


FIG. 2. Optical absorption coefficient $\alpha(\omega)$ from valence states to the NBO and OH defect levels and the density of states (DOS).

charged. This shift is a result of the change in the local potential around the NBO atom following the electronic relaxation process.

In the final photoluminescence process [Fig. 1(b), step 3], the hole at E_v is filled by the electron excited to the NBO in the first step, and we are back to the initial state. The calculated energy for this transition is 1.8 eV, again in excellent agreement with the measured 1.9 eV [4].

OH-related optical processes in SiO₂.—Neutral OH groups are easily introduced in *a*-SiO₂, e.g., by the UV photodissociation of water molecules [17], x-ray or neutron radiation breaking up either water molecules or silanol groups (Si-OH), or by the reaction of water molecules with NBO centers or peroxy radicals [18]. Since interstitial OH is very reactive and diffuses easily in the voids of the SiO₂ network, it is hard to observe directly by EPR measurements unless the water content of the oxide is very high [18]. In crystalline SiO₂, OH groups are mainly attached to group III impurities (e.g., Al atoms) that incorporate into the crystal lattice during the manufacturing process [19] and may be released and attached to Si atoms the same way as in *a*-SiO₂.

We have considered interstitial OH as an alternative candidate for the 4.8-eV OA and 1.9-eV PL bands. Using total energy calculations, we found that in equilibrium the negative (oxygen) end of the OH dipole weakly interacts with the somewhat positively charged network Si atoms. In the ground state, the OH group has a partially occupied level ~ 1.3 eV above E_v . It is again a nonbonding oxygen 2*p* state centered on the O atom of the OH molecule. Following the same reasoning as in the case of the NBO defect, we consider excitations from a valence level corresponding to the maximum of the absorption coefficient (Fig. 2) into the half-empty state in the gap. By comparing total energies, we find an excitation energy of 5.0 eV that again arises in part from a large Hubbard U [Fig. 3(a), step 1].

The second (relaxational) stage of the OH cycle consists of two parts: (i) a redistribution of electron density in the nearest Si-O-Si bonds [Fig. 3(a), step 2b] and (ii) an atomic relaxation reducing the Si-O distance from 2.34 to 1.87 Å [Fig. 3(a), step 2a]. The first part is a slow, non-radiative electronic relaxation process just as in the case of the NBO, in which the hole bubbles up to the top of the valence band reducing the total energy by 1.7 eV. Simultaneously, an atomic relaxation process is taking place, in which the OH molecule moves closer to the network Si atom. This atomic motion is caused by a Coulomb interaction between the excited (and thus negatively charged) OH molecule and the network accommodating the hole. In this process, a new defect is formed: a fivefold coordinated Si atom with a negatively charged OH group attached to it. The atomic relaxation and the forming of a strong bond between the OH and the network reduces the energy by a further 1.4 eV. Since these two processes are both nonradiative, they can be grouped together as the second step in the OH-related OA/PL cycle.

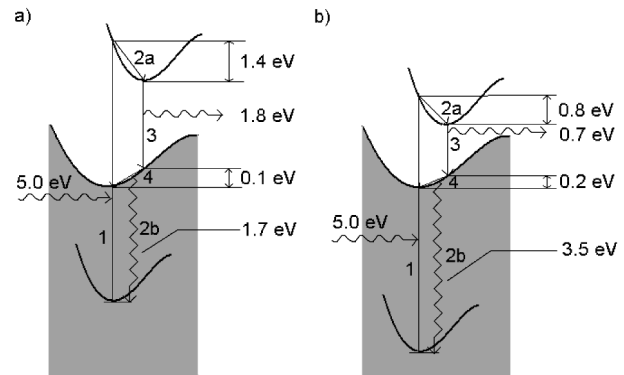


FIG. 3. Total energy diagram as a function of a generalized coordinate illustrating the combined “atomic” and “electronic” FC shift in (a) *a*-SiO₂ with the OH in a large void and (b) α quartz.

The luminescence stage of the OH cycle consists of a deexcitation of an electron from the 2*p* orbital in the OH group to the top of the valence band by the emission of a 1.8-eV photon [red PL, Fig. 3(a), step 3]. This luminescence transition leaves a neutral OH behind, but still closer to the Si atom than its equilibrium position. Therefore a subsequent atomic relaxation has to occur to finish the OA/PL cycle [Fig. 3(a), step 4]. Since there is only weak interaction between a neutral OH molecule and the amorphous network, the energy released in this relaxation process is only 0.1 eV.

Since OH groups may experience different electronic environments at different positions in the amorphous oxide, we have calculated the respective transition energies in three voids of decreasing sizes and in α quartz (Table I). The data presented above are representative of the bigger voids of *a*-SiO₂ that are ~ 6 Å in diameter. These are the voids where interstitial water molecules are most likely to reside [11]. In small voids, the OH molecule is “squeezed” close to network Si atoms, which leads to a greater overlap of the wave functions of the oxygen 2*p* states in the OH molecule and those of the network resulting in a smaller charge separation between the OH molecule and the amorphous network upon excitation by UV light. The smaller charge separation causes smaller Hubbard U shifts in the one-electron levels that in turn lead to lower PL energies. Thus, luminescence from OH in *a*-SiO₂ is predicted to be dominant at 1.8 eV with a low-energy shoulder to about 0.8 eV, which is different from the rather sharp line in the case of the NBO.

In general, as the void in which the OH resides decreases in size, the luminescence and atomic relaxation energies are lower, whereas the electronic relaxations provide higher-energy gains (Table I). The reason for smaller atomic relaxation energies lies in the smaller displacement of the OH molecule (0.5 Å in large voids vs 0.18 Å in quartz). The larger energy gain from slow electronic relaxations in smaller voids is apparently related to different hole relaxation energies. This relaxation

TABLE I. Variations in Si-O distance (in Å), relaxation, and PL energies (eV) in voids of different diameters (Å).

Void diameter	Si-O distance before–after relaxation	Electronic relaxation energy	Atomic relaxation energy	PL energy
~6.0	2.34–1.87	1.7	1.4	1.8
~5.0	2.20–1.77	2.1	1.4	1.4
~3.5	2.07–1.71	3.1	0.9	0.8
~3.5 (quartz)	1.87–1.69	3.5	0.8	0.7

energy is dependent on the proximity of a negatively charged OH group that is again determined by the size of the voids.

In α quartz, which has smaller voids and a more rigid structure than the amorphous material, the behavior observed for smaller voids in α -SiO₂ is further accentuated (Table I). The main difference from the amorphous phase is that the PL band comprises of a sharp line in the infrared region (0.7 eV). This line, however, has not been detected thus far probably because of low concentration of interstitial OH groups in crystalline quartz.

Comparison of NBO and OH defects.—We now examine the experimental observations that have been used to identify the NBO as the defect responsible for the 4.8-eV OA and 1.9-eV PL bands and inquire whether they are also consistent with OH being the defect in question.

A characteristic phonon sideband of the zero-phonon line of the 1.9-eV PL band at 890 cm⁻¹ was suggested to be due to Si-O stretching vibrations in the NBO defect [4]. We calculated the relevant Si-O stretching modes for both the NBO and 5Si-OH⁻ defects and found 940 ± 100 cm⁻¹ and 800 ± 100 cm⁻¹, respectively. Clearly, the observed sideband cannot distinguish between the two defects.

The polarization degree of the PL is another observation invoked in support of interpreting the 1.9-eV PL as arising from a NBO. The PL degree can be related to the angle between the absorption and emission dipole momenta [20]. We performed an analysis similar to that in Ref. [5] and again found that no distinction can be made between the two defects.

The reported disappearing of the PL below ~110 K [5] is also consistent with the OH-related mechanism: We have found that the binding energy of a neutral OH group is 0.2–0.3 eV when it is weakly attracted to network Si atoms. Once this weak dipole interaction is overcome by thermal excitations, the OH group becomes “free” and will not participate in any electronic transitions because of the insufficient overlap of the wave functions of the OH levels with those of the SiO₂ network.

In summary, we have shown that the large Stokes shift of the NBO defect in α -SiO₂ is entirely due to slow nonradiative electronic relaxations. Another defect (OH group) exhibits a similar Stokes shift that consists of a

mix of lattice and electronic relaxations resulting in site-dependent luminescence energies ranging from 1.8 to 0.7 eV. Since interstitial OH resides preferentially in large rings in the α -SiO₂ network where the PL is at ~1.8 eV, the OA/PL data and accompanying experiments cannot be unambiguously attributed to either NBO or OH. Additional experiments in both α -SiO₂ and α quartz are needed to resolve the issue.

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