PHYSICAL REVIEW B, VOLUME 63, 054102

Theoretical description of hole localization in a quartz Al center: The importance of exact electron exchange

Gianfranco Pacchioni,* Fabiano Frigoli, and Davide Ricci
Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Istituto Nazionale per la Fisica della Materia,
via R. Cozzi 53, 20125 Milano, Italy

John A. Weil
Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon SK, Canada S7N 5C9

(Received 30 August 2000; published 27 December 2000)

The ''classical'' model of the $[\mathrm{AlO}_4]^0$ defect center in irradiated quartz, an Al impurity having replaced a four-coordinated Si atom, is that a hole forms in a nonbonding orbital of an oxygen atom, with consequent asymmetric relaxation along that particular Al-O direction. This model has been proposed years ago, based on the analysis of the electron-paramagnetic-resonance spectra of Al-containing crystalline SiO_2 and analysis of Hartree-Fock cluster model calculations. Three recent theoretical studies based on first-principle density-functional theory (DFT) and band-structure plane-wave calculations proposed an alternative model where the hole is completely delocalized over four oxygen neighbors to the Al impurity, at 0 K. Using cluster models containing as many as 104 Si and O atoms and various theoretical approaches, we show that the delocalized picture is an artifact of the DFT approach and that a fully localized hole is obtained when an exact treatment of the exchange term is used. The validity of this conclusion is based on the direct comparison of computed and measured quantities such as the ^{17}O hyperfine and ^{27}Al, ^{29}Si superhyperfine coupling parameters, the ^{27}Al nuclear quadrupole effect, and the derivable local distortion around the defect. This work shows that great care is needed when DFT is used to describe localized holes in insulators.

DOI: 10.1103/PhysRevB.63.054102 PACS number(s): 61.72.Bb, 61.72.Ji, 31.15.Ar, 42.70.Ce

I. INTRODUCTION

Al-doped SiO_2 has been studied in great detail, both theoretically and experimentally in the past four decades.[1–14] Early experimental studies based on electron-paramagnetic-resonance (EPR) spectroscopy have shown that the defect center corresponding to an Al atom substituting for a four-coordinated Si atom in the lattice, the neutral $[\mathrm{AlO}_4]^0$ center, contains a hole trapped in a nonbonding $2p$ orbital of an O atom adjacent to Al.[1–3,6] The existence of a fully localized hole at sufficiently low temperatures has been shown by the accurate analysis of the EPR spectrum and in particular by the determination of the hyperfine coupling constants with the ^{27}Al, ^{29}Si, and ^{17}O nuclides.[6] Above room temperature, the hole jumps rapidly among all four adjacent O atoms. Cluster calculations performed at the Hartree-Fock level have then confirmed the model proposed based on the experimental data, showing the occurrence of the hole localization at 0 K and the elongation of the corresponding Al-O bond.[9,10,12,13]

This ''classical'' model has recently been challenged by three theoretical papers based on advanced first-principle approaches.[15,16,17] These studies were based on supercell calculations with proper inclusion of boundary conditions and density-functional theory (DFT). They all concluded that the hole in the $[\mathrm{AlO}_4]^0$ defect is completely delocalized over the four O neighbors[15–17] ''in contrast to the phenomenological model results'' reported previously.[16]

Paramagnetic centers in pure and doped SiO_2 play a major role in determining the electrical properties of the material and are of paramount importance for the elucidation of several processes occurring in silicate glasses.[18] Their importance is also connected to the proven possibility for use of the highly sensitive EPR spectroscopy in combination with other techniques (such as optical absorption and photoluminescence measurements) to identify the structure of point defects.[19] The theoretical description of these centers is of great help for the correct assignment of an observed spectral feature to a given structural defect.[20] Therefore the contradictory results reported in the literature about the nature of holes associated to Al impurities in crystalline SiO_2 open questions which go beyond the simple scientific controversy, and make the elucidation of the reasons for the different answers given by the various theoretical methods of highest priority.

In this study we have examined the electronic structure and spin distribution in the $[\mathrm{AlO}_4]^0$ center using cluster models of various sizes, as well as various first-principle theoretical methods. These range from unrestricted Hartree-Fock (UHF) with exact treatment of the electron exchange but neglect of electron correlation, to more sophisticated approaches where the exchange and correlation terms are described in various ways. In particular, we explicitly included correlation effects using second-order Møller-Plesset perturbation theory (MP2). We compared these results with those of DFT calculations or of hybrid methods where the HF exchange is mixed in with the DF exchange or where the exchange is treated at the HF level and only correlation is included through a self-consistent DF treatment. The validity of our theoretical results has been checked by comparing the hyperfine coupling parameters computed at various levels of theory with the corresponding experimental quantities. Herein, we present a very complete theoretical

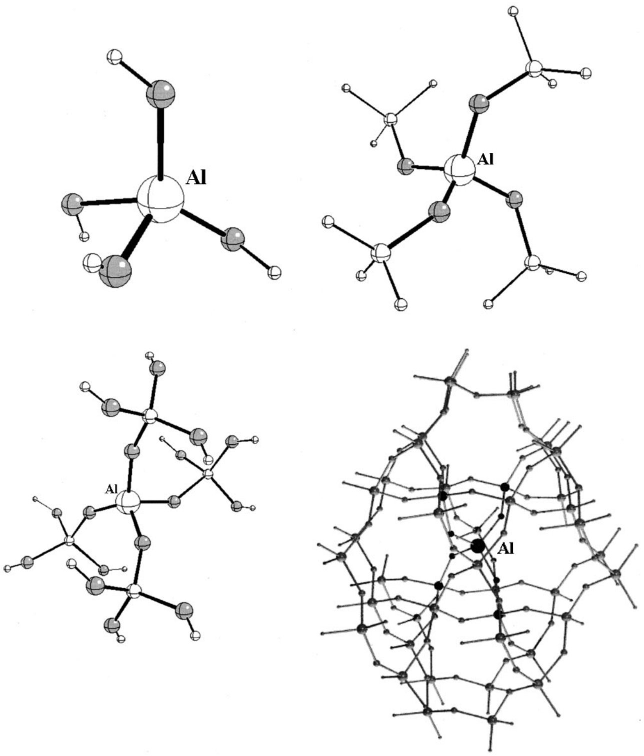

FIG. 1. Cluster models used to represent the $[AlO_4]^0$ center in α-quartz: $Al(OH)_4$, $Al(OSiH_3)_4$, $Al[OSi(OH)_3]_4$, and $AlO_{60}Si_{44}H_{60}$. In the last of these, the Si atoms occur as 6 with no bonds to H (as is true also for Al), 14 with one such bond, and 23 with two; the black atoms are treated with a first-principle Hamiltonian, the rest with a semiempirical Hamiltonian (see text).

analysis of the hyperfine and superhyperfine coupling parameters of the $[AlO_4]^0$ defect center. The results show the inadequacy of the DF method without self-interaction correction in describing the hole localization in the $[AlO_4]^0$ center.

II. COMPUTATIONAL METHOD

The calculations have been performed within the cluster model approach. The cluster dangling bonds have been saturated with H atoms, and the positions of the cluster atoms were initially fixed to those of α-quartz at 94 K.[21] The fixed H atoms provide a simple representation of the mechanical embedding of the center within the solid α-quartz matrix. The atoms were fixed at a distance of 0.98 and 1.48 Å from the respective O and Si atoms along the O-Si directions of α-quartz. The positions of the Al, Si, and O atoms in the electrically neutral cluster were then fully optimized. This approach has been successfully adopted previously for the study of the ground state and some excited states of point defects in SiO_2[22–29] and Si_3N_4.[30,31] Note that in pure α-quartz, each Si cation is surrounded by O anions, with two bond distances: $Si\text{-}O_{1,2}=1.6101$ Å and $Si\text{-}O_{3,4}=1.6145$ Å, at 94 K;[21] there is C_2 local symmetry at the cation.

The clusters used to model the $[AlO_4]^0$ center are: $Al(OH)_4$, $Al(OSiH_3)_4$, $Al[OSi(OH)_3]_4$, and $AlO_{60}Si_{44}H_{60}$, as seen in Fig. 1. This latter structure has been computed with the help of a mixed *ab initio* semiempirical approach (see below). These clusters are terminated by either O-H or Si-H groups; however, in our experience, this kind of ''chemical distinction'' does not reflect in a different electronic structure of the defect. The $Al(OH)_4$ cluster has been used in previous HF calculations,[9,10,12,13] and yielded results very similar to those obtained with larger clusters, and hence will not be discussed in detail herein.

The cluster wave functions were constructed using the following Gaussian-type atomic orbitals all-electron basis sets: $6\text{-}31{+}{+}G^*$ on Al,[32] $6\text{-}31G^*$ on Si,[32] EPR-II (Ref. 33) on the four O atoms nearest neighbors to the Al impurity, and $6\text{-}31G$ (Ref. 34) on the other O atoms and on the terminating H atoms. The EPR-II basis set has been specifically designed to accurately compute hyperfine coupling (HFC) ''constants'' for O atoms.[33] Geometrical optimizations were performed by computing analytical gradients of the total energy.

Unrestricted HF (UHF) calculations were performed as a reference. In HF theory, the energy has the form

$$E_{\mathrm{HF}}=E_{\mathrm{NUCL}}+\langle hP\rangle+\tfrac{1}{2}\langle PJ(P)\rangle-\tfrac{1}{2}\langle PK(P)\rangle, \tag{1}$$

where E_{NUCL} is the nuclear repulsion energy, P is the density matrix, $\langle hP\rangle$ is the one-electron energy including kinetic and potential energy terms, $\frac{1}{2}\langle PJ(P)\rangle$ is the classical Coulomb repulsion term and $-\frac{1}{2}\langle PK(P)\rangle$ is the exchange energy resulting from the quantum nature of the electrons. Notably, the HF method does not include electron correlation, and in principle this can lead to a different hole localization, or lack thereof. Correlation effects have been included in two ways. First we performed unrestricted MP2 calculations (UMP2) where electron correlation is treated by perturbation theory at the second-order level. The second group of calculations has been based on DFT. In the Kohn-Sham formulation of DFT, the exact HF exchange for a single determinant is replaced by a general expression, the exchange correlation functional, which can include both exchange and electron correlation energy terms:

$$E_{\mathrm{KS}}=E_{\mathrm{NUCL}}+\langle hP\rangle+\tfrac{1}{2}\langle PJ(P)\rangle+E_X+E_C, \tag{2}$$

where $E_X[P]$ is the exchange functional and $E_C[P]$ is the correlation functional. In HF $E_X[P]$ is given by the exchange integral $-\frac{1}{2}\langle PK(P)\rangle$ and $E_C=0$. Here we used three different approaches: one based on the DFT formalism, and two hybrid approaches where the exchange interaction is described partially or totally by the HF exchange. In the pure DFT scheme, we used the gradient-corrected exchange functional proposed by Becke,[35] combined with the nonlocal expression of the correlation functional proposed by Lee, Yang, and Parr,[36] denoted by BLYP. In one hybrid approach, B3LYP, the HF exchange was mixed in with the DF exchange while the correlation was treated as in the previous case (LYP correlation functional).[36] For the exchange treatment, we used the Becke approach[37] where three parameters were derived in order to accurately describe the thermochemistry of a set of molecules. In the last case, we used another hybrid approach where the $E_X[P]$ term was completely removed and the exchange interaction was described at the HF (UHF) level while the correlation part $E_C[P]$ made use of the LYP correlation functional described above;[36] this approach is referred to as UHF/LYP in the following. All the calculations are for open-shell structures and correspond to nearly pure spin doublet states ($\langle S^2 \rangle = 0.75 \pm 0.01$).

The effect of long-range mechanical relaxation on the local structure of the $[AlO_4]^0$ center has been studied by using the ONIOM (our own *n*-layered integrated molecular orbital and molecular mechanics) method.[38–41] The idea behind the ONIOM approach is to partition a system into two or more parts, where the most interesting part of the system is treated at a ''high'' level of theory and the rest is described by a computationally less demanding method. Here a cluster containing 1 Al, 60 O, 44 Si, and 60 terminal H atoms has been derived from α-quartz and divided into a ''core'' region in which the defect is positioned and a surrounding ''matrix.'' The core has been described at the UHF, UHF/LYP, B3LYP, and BLYP levels, while the matrix has been treated with the semiempirical medium neglect of differential overlap (MNDO) Hamiltonian.[42] For the core region we considered two sizes, AlO_4 and $Al(OSi)_4$, and we used the same basis sets as described for the $Al(OH)_4$ and $Al(OSiH_3)_4$ clusters. Applications of the ONIOM method to the study of point defects in insulators have been reported recently.[43]

The hyperfine interactions of the electron spin with the nuclear spins of the ^{17}O, ^{27}Al, ^{29}Si, nuclides have been determined. The hyperfine spin-hamiltonian for each, $H_{\mathrm{HFC}} = \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}$, is given in terms of the hyperfine matrix **A** which describes the coupling of the electron with the nuclear spin.[44] The components of **A** can be represented in matrix notation:

$$\mathbf{A} = \begin{bmatrix} A_1 & 0 & 0 \\ 0 & A_2 & 0 \\ 0 & 0 & A_3 \end{bmatrix} = a_{\mathrm{iso}} \mathbf{U} + \begin{bmatrix} B_1 & 0 & 0 \\ 0 & B_2 & 0 \\ 0 & 0 & B_3 \end{bmatrix}, \qquad (3)$$

where **U** is the unit matrix. The isotropic part a_{iso} of each coupling constant is related to the spin density at the nucleus (the Fermi contact term):

$$a_{\mathrm{iso}} = (2\mu_0/3) g_N \beta_N g_e \beta_e \langle \rho^s \rangle, \qquad (4)$$

where μ_0 is the permeability of free space, g_N and g_e are the nuclear and electronic g factors, β_N and β_e are the nuclear and Bohr magnetons, and $\langle \rho^s \rangle$ is the expectation value at the nucleus of the spin-density operator. In one-electron systems, $\langle \rho^s \rangle = |\Psi^s(0)|^2$. The anisotropic traceless contribution **B** results from the dipolar interaction. The comparison of the computed with the experimental hyperfine parameters provides an extremely useful way of associating a structural model with an observable quantity. The calculations have been performed using the GAUSSIAN-98[45] computer code.

III. RESULTS AND DISCUSSION

A. Hartree-Fock and MP2 results

The electronic structure of the $[AlO_4]^0$ center has been investigated with an $Al(OSiH_3)_4$ cluster. At the UHF level, the ground state is characterized by the presence of an unpaired electron localized in a nonbonding orbital of a bridging O atom. This is shown by the values of the spin population, Table I, as well as by spin-density plots, Fig. 2. The Al-O bond involving the hole-bearing O atom is substantially elongated with respect to normal Si-O bonds in quartz and to the other Al-O bonds of the center (Table II). In fact, the computed Al-O distance is 1.96 Å, which corresponds to an elongation of 17% compared to the other Al-O distances (experimentally the elongation was estimated to be of the order of 12%).[6] Furthermore, we found that the hole localizes preferentially on the O atom which corresponds to the longer type of Si-O bond in quartz, as was experimentally observed.[6] Also the Al-O-Si angle changes and becomes 128° for the hole-bearing oxygen ion, 12° smaller than in the corresponding cluster model of nondefective quartz. The structural deformation is consistent with that found in previous cluster calculations[9,12,13] and with that estimated from EPR.[6] The computed principal values (A_1, A_2, and A_3) of the matrix $\mathbf{A}(^{17}O)$ are 11.5, 13.6, and -128.6 G, respectively. The corresponding experimental values, 15.3, 17.9, and -111.0 G,[5,6] are close to the UHF ones; the small difference is entirely due to the a_{iso} value, -34.9 G in the calculation and -26.0 G in the experiment, while the dipolar interaction is reproduced with very high accuracy. The reproduction of an observable quantity such as the hyperfine coupling parameters provides a strong validation of the model of a fully localized hole. This result is in line with previously reported UHF results for cluster models of the $[AlO_4]^0$ center[9,12,13] and confirms the picture originally proposed for the paramagnetic Al impurity center in quartz. The analysis of the spin population shows that the unpaired electron has 2.2% of $2s$ and 97.8% of $2p$ character, in qualitative agreement with the estimates of Nuttall and Weil[5,6] (For a discussion, see also Ref. 9). In principle, however, the absence of electron correlation effects casts some doubts on the validity of this conclusion. In fact, electron correlation could lead to a more pronounced delocalization of the hole, so that the above-cited agreement could be fortuitous. To this end, we have performed UMP2 calculations where correlation effects are explicitly taken into account. Starting from the structure of α-quartz with presence of an Al impurity ion, and reoptimizing the structure, we find an elongation of the Al-O bond and localization of the unpaired electron similar to the UHF solution. The spin-population analysis shows that the hole is completely localized; the value of the spin population on the other O atoms around the Al impurity is 0.01 at most (Table I). Also in this case we have determined the HFC parameters for ^{17}O; the resulting principal values (11.4, 13.6, and -128.8 G) are virtually identical to those obtained at the UHF level.

The analysis herein of the hyperfine interaction has not been restricted to the ^{17}O nucleus. In Table I we also report the **A** matrix for the coupling with the ^{27}Al and ^{29}Si nuclei of the two atoms nearest neighbor to the hole-bearing O atom. The results are compared with the values measured by Nuttall and Weil for Al-containing quartz.[5,6] The agreement between theory and experiment is almost quantitative for Al, while for Si the a_{iso} is somewhat overestimated. The general picture, however, is quite consistent with the experimental spectrum. Also, the UHF and UMP2 results are virtually identical. Thus no significant differences in the description of

TABLE I. Spin distribution and hyperfine coupling parameters for the ground state of the $[\mathrm{AlO_4}]^0$ center, as computed with the $\mathrm{Al(OSiH_3)_4}$ model.

Spin population	UHF	UHF/LYP	UMP2	B3LYP	BLYP	Expt. (Refs. 5 and 6)
O_4	1.04	1.02	1.04	0.29	0.24	
$O_{1,2,3}$	<0.01	<0.01	<0.01	0.21-0.29	0.23-0.24	
			^{17}O hyperfine matrix G^a			
A_1	11.5	11.2	11.4	8.5/6.9	7.6/8.5	15.3
A_2	13.6	12.5	13.6	8.7/6.9	7.7/8.6	17.9
A_3	−128.6	−130.4	−128.8	−33.9/−24.0	−26.3/−23.7	−111.0
a_{iso}	−34.5	−35.6	−34.6	−5.6/−3.4	−3.0/−2.2	−26.0
B_1	46.1	46.8	46.0	14.1/10.3	11.6/10.7	41.2
B_2	48.1	48.1	48.2	14.3/10.3	11.7/10.8	43.8
B_3	−94.1	−94.8	−94.2	−28.3/−20.6	−23.3/−21.5	−85.0
			^{27}Al hyperfine matrix, G			
A_1	−5.1	−4.5	−5.3	−10.7	−8.7	−6.1
A_2	−5.0	−4.5	−5.3	−10.8	−8.8	−6.2
A_3	−4.1	−3.4	−4.4	−10.2	−8.5	−5.0
a_{iso}	−4.8	−4.1	−5.0	−10.6	−8.7	−5.8
B_1	−0.3	−0.4	−0.3	−0.1	0.0	−0.3
B_2	−0.3	−0.4	−0.3	−0.2	−0.1	−0.4
B_3	0.6	0.8	0.6	0.3	0.2	0.7
			^{29}Si hyperfine matrix G^a			
A_1	17.4	14.2	17.5	6.0/4.7	4.6/4.5	11.4
A_2	17.8	15.4	17.9	6.2/4.8	4.7/4.7	11.6
A_3	15.5	13.0	15.6	5.9/4.6	4.5/4.2	10.8
a_{iso}	16.9	14.2	17.0	6.0/4.7	4.5/4.5	11.3
B_1	0.5	0.0	0.5	0.0/0.0	0.0/0.0	0.1
B_2	0.9	1.2	0.9	0.2/0.1	0.1/0.3	0.3
B_3	−1.4	−1.2	−1.4	−0.1/−0.1	−0.1/−0.3	−0.5

[a] Two sets of values, separated by a slash, are given for the pairs of O atoms bearing the hole (or for the neighboring nuclei) when the hole is computed to be present on both such anions.

the electronic structure of the $[\mathrm{AlO_4}]^0$ center are found after inclusion of correlation effects at the UMP2 level, in this case.

We also computed the electric-field-gradient (EFG) tensor **E** evaluatable at any nucleus selected as provided by the GAUSSIAN-98 code. For ^{27}Al, the principal values calculated with the cluster $\mathrm{Al(OSiH_3)_4}$ are −0.669 553, 0.261 613, 0.407 940 a.u., while the principal values of nuclear quadrupole tensor **P** measured by EPR, using spin Hamiltonian $H_{nq}=\mathbf{I}\cdot\mathbf{P}\cdot\mathbf{I}$,[44] are 0.037 56, −0.015 33, −0.022 23 mT.[6] The relation between tensors **P** and **E** is

$$\mathbf{P}=\{-e^2Q/[I(I-1)4\pi\varepsilon_0 g_e\beta_e r_B^3]\}\mathbf{E}, \tag{5}$$

where ε_0 is the permittivity of free space and r_B is the Bohr radius. We can adjust the first member of the measured set, normalizing with the factor −17.8262 a.u./mT, to equal the first of the computed set, yielding the set −0.669 553, 0.273 28, 0.396 28 a.u., which agrees nicely with the computed set. Furthermore, the value of the nuclear quadrupole parameter Q for ^{27}Al obtained thereby is +0.134 barns, to be compared with the literature value +0.150(6) barns.[46] Thus, with this physical property too, we see that the computed fixed-hole model simulates the experimental results very well.

These results have been obtained with a cluster model of medium size, i.e., one which includes the first and second neighbors to the defect Al atom. The model electronic structure of the $[\mathrm{AlO_4}]^0$ center is very similar if one uses the minimal model $\mathrm{Al(OH)_4}$, a model employed in previous calculations.[9,10,12,13] Going from the minimal to the medium-sized cluster, we do not find any qualitative difference in the description of the hole localization or of the structural deformation (Table II). Minor differences in the observable quantities are primarily due to the presence of O-H replacing O-Si bonds around the impurity. For instance, with the $\mathrm{Al(OH)_4}$ cluster, the HFC values show a slightly larger deviation from experiment than with $\mathrm{Al(OSiH_3)_4}$, but these differences do not change the conclusions. The similar responses of the $\mathrm{Al(OH)_4}$ and $\mathrm{Al(OSiH_3)_4}$ clusters is one piece of evidence for the highly localized nature of the defect.

To further bolster this conclusion, and in particular to prove beyond any doubt that the asymmetric relaxation and

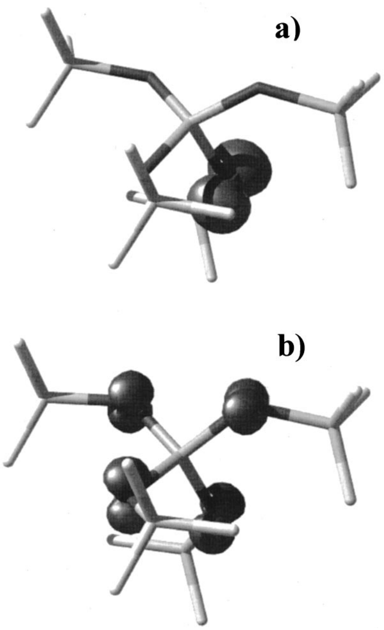

FIG. 2. Spin-density plots depicting $Al(OSiH_3)_4$, computed at: (a) the UHF level (yielding the hole localized on a single oxygen atom), and (b) the DFT/BLYP level (yielding the hole spread over four oxygens).

spin localization are not artifacts of the relatively small clusters used, we have considered two larger models: $Al[OSi(OH)_3]_4$, where the next shell of 12 O third neighbors to the Al impurity is included, and $AlO_{60}Si_{44}H_{60}$, shown in Fig. 1. In this latter case we used the ONIOM technique described above. The results, Table II, fully confirm the conclusions obtained with the smaller clusters. In particular, the asymmetric distortion is also observed here with one Al-O bond distance (1.92 Å), which is 14% longer than the other ones (the elongation estimated from EPR is 12%).[6] Even a more quantitative analysis of the spin distribution and HFC values does not show significant deviations as one goes from the minimal $Al(OH)_4$ to larger models. Thus we can conclude that the hole localization and the corresponding asymmetrical distortion are features which do not vary with the cluster size.

The solution yielding the hole fully localized is not the only minimum on the potential-energy surface of the $[AlO_4]^0$ center. It has been discussed in the literature that a thermally excited state of this center can be observed by EPR,[47] which is ca. 42 meV above the ground state, and which contains the hole on the other type (short-bond) of oxygen atom. Self-consistent field molecular orbital modeling of this state also has been accomplished,[9] and agrees well with the experimental findings. With the $Al(OSiH_3)_4$ cluster and a UHF wave function, we found that the excited state with the hole localized on the short-bond O atom lies 79 meV above the ground state. While this is extremely close to the energy separation deduced from experiment, one has to be cautious in attributing too much importance to this result, given the small energy at stake and the lack of periodic boundary conditions in our approach.

We have found still another state, one in which the hole is delocalized over two O atoms, Table III. This structure is characterized by two elongated Al-O bonds, but the whole deformation is smaller than for that of the fully localized hole. The second minimum is 1.60 eV higher in energy than the fully localized hole (UHF). No attempt was made to calculate the barrier which separates the two minima. Here the hole is distributed over two O atoms of the short-bond type. Not surprisingly, the modeled hyperfine structure of an unpaired electron delocalized over two O atoms is substantially different from that of the single hole-bearing O atom. This is clear from inspection of the ^{17}O HFC, and in particular of the dipolar part (Table III). The computed **A** for the ^{27}Al nucleus differs substantially from the experimentally observed matrix. The existence of a local minimum where the hole is delocalized over two O atoms is not inconsistent with reality, as it has been observed by 10 GHz EPR that at temperatures >100 K the hole hops from one O atom to another at a rate which is fast relative to the inverse EPR time scale at this frequency.[7,48]

B. Density-functional theory results

Three recent papers based on a DFT supercell band structure approach come to the conclusion that the spin density in the electronic ground state of $[AlO_4]^0$ at 0 K is evenly distributed over the four oxygens nearest neighbors to Al.[15–17] This conclusion contrasts with the results described above showing the presence of a localized hole. Several explanations can in principle be proposed to explain the discrepancy: (i) the inadequacy of the HF approach, due to the lack of correlation effects; (ii) a failure of the cluster model (a possibility which is indeed mentioned in one of these papers);[16] (iii) an incorrect interpretation of the EPR spectra; (iv) inadequacy of DFT. We have shown already that HF and correlated calculations give the same results, so that hypothesis (i) can be discarded. Clearly, to establish which of the remaining possible reasons is the correct one has an importance which goes beyond the simple question of the electronic structure of the $[AlO_4]^0$ impurity center. Therefore the electronic structure of the $[AlO_4]^0$ system has been recalculated using the DFT approach and the same cluster models.

We consider first the purely DFT BLYP approach with the medium-sized cluster $Al(OSiH_3)_4$. Starting the optimization from the structure of α-quartz, we found an energy minimum where the hole is completely delocalized over four O atoms, Fig. 2, in full agreement with the results obtained in supercell DFT studies where periodic boundary conditions are properly included.[15–17] The Al-O bond distances computed with the cluster model are all very similar, 1.75 ± 0.01 Å, and only slightly longer than those reported in other gradient-corrected DF calculations, 1.72 Å.[17] We repeated the optimization starting from the UHF minimum structure (fully localized hole) but the calculation converges to the same delocalized minimum found before. The calculations have been repeated for the whole series of clusters of increasing size, and the hole delocalization is always found. Actually, when we consider the $Al(OSiH_3)_4$ cluster at the DFT/BLYP level we found a tendency to partially delocalize the hole even on the next shell of O atoms, Table II. Low-

TABLE II. Structural parameters and spin distribution of the ground state of the $[AlO_4]^0$ center as computed with cluster models of various size and by different methods.[a]

Cluster	Property	UHF	UHF/LYP	B3LYP	BLYP
$Al(OH)_4$	$Al\text{-}O_4$ (Å)	2.10	2.01	1.77	1.78
	$Al\text{-}O_{1,2,3}$ (Å)	1.70	1.68	1.77	1.79
	spin O_4	1.07	1.05	0.29	0.28
	spin $O_{1,2,3}$	<0.01	<0.01	0.28-0.29	0.27
$Al(OSiH_3)_4$	$Al\text{-}O_4$ (Å)	1.96	1.94	1.75	1.76
	$Al\text{-}O_{1,2,3}$ (Å)	1.68	1.67	1.72	1.74
	spin O_4	1.04	1.01	0.29	0.25
	spin $O_{1,2,3}$	<0.01	<0.01	0.21-0.29	0.23-0.24
$Al[OSi(OH_3)]_4$	$Al\text{-}O_4$ (Å)	1.98	1.96	1.76	1.78
	$Al\text{-}O_{1,2,3}$ (Å)	1.70	1.68	1.75	1.77
	spin O_4	1.04	1.03	0.23	0.16
	spin $O_{1,2,3}$	<0.01	<0.01	0.20-0.22	0.13-0.17
$AlO_{60}Si_{44}H_{60}$[core-AlO_4]	$Al\text{-}O_4$ (Å)	1.91		1.76	1.76
	$Al\text{-}O_{1,2,3}$ (Å)	1.67		1.70	1.72
	spin O_4	1.07		0.44	0.36
	spin $O_{1,2,3}$	<0.01		0.15-0.35	0.28-0.23
$AlO_{60}Si_{44}H_{60}$[core-$Al(OSi)_4$]	$Al\text{-}O_4$ (Å)	1.92		[b]	1.76
	$Al\text{-}O_{1,2,3}$ (Å)	1.68			1.75
	spin O_4	1.04			0.27
	spin $O_{1,2,3}$	<0.01			0.21-0.25

[a] The oxygen-atom labels are consistent with those of Ref. 6 (see Fig. 1 therein). The choice of O_4 rather than O_3 as being hole-bearing is arbitrary.

[b] Convergence was not reached for this calculation; see text.

lying states of this kind have been found also in Ref. 16. Thus local cluster models and periodic supercell calculations give the same answer. Not surprisingly, the HFC values for a system where the hole is delocalized are completely different from those obtained for the fully localized case, and are in gross disagreement with the experimental values (Table I).

We have repeated the calculations using the B3LYP approach where the HF exchange is partially mixed in with the DFT exchange. The results are similar to, although not exactly identical with, those obtained with the BLYP method. In fact at the B3LYP level we found two states very close in energy, one corresponding to a complete delocalization of the hole over all four O atoms, and the other where the hole is distributed over only two O atoms. In the first case, the spin population on two O atoms is 0.29 and on the other two it is 0.21 and the four Al-O distances are similar, 1.77 Å (Table II). This state is slightly higher (0.05–0.15 eV, depending on the cluster used) in energy than a state with the hole distributed over two O atoms. This suggests that the use of a mixed HF-DFT exchange leads to a more pronounced tendency towards a partial localization. The HFC values (fully delocalized case) remain very far from the experimental ones. These results have been checked against cluster size by computing the structure of the $[AlO_4]^0$ center with the $[Al(OSi(OH)_3)]_4$ and $AlO_{60}Si_{44}H_{60}$ clusters. As for the UHF calculations, also at the B3LYP level no significant change is found as function of cluster size. The only difference is that, by increasing the dimensions of the model, more conformational minima appear, leading to a more difficult convergence of the geometry optimization. This is true in particular for the $AlO_{60}Si_{44}H_{60}$ cluster where two different Hamiltonians are used, the DFT one for the core and the MNDO one for the matrix. Since the MNDO method is a simplified HF approach, and because of the implementation of the ONIOM technique which requires the calculation of the ‘‘core’’ part at both levels of theory, MNDO and DFT, we are in the

TABLE III. Spin distribution, ^{17}O hyperfine coupling parameters in G, and energy for the excited state of the $[AlO_4]^0$ center bearing the hole on two O atoms, as computed with the $Al(OSiH_3)_4$ model.

Spin population	UHF[a]	UHF/LYP[a]
$O_{1,2}$	0.57	0.55
$O_{3,4}$	<0.01	<0.01
$A_1(O)$	-10.0	-4.0
$A_2(O)$	-9.2	-3.2
$A_3(O)$	-97.5	-90.2
$a_{iso}(O)$	-38.9	-32.5
$B_1(O)$	28.9	28.5
$B_2(O)$	29.7	29.3
$B_3(O)$	-58.8	-58.7
ΔE (eV)[b]	-1.60	-1.67

[a] Values averaged for the two slightly nonequivalent O atoms bearing the hole are reported.

[b] Energy difference with respect to the ground state having a fully localized hole.

presence of an opposite tendency: the MNDO Hamiltonian tends to localize the hole, the DFT one tends to delocalize it, and the result is an oscillatory behavior in one of the calculations for which convergence in the optimization has not been achieved (Table II).

At this point, we considered a second hybrid approach where the exchange is treated exactly (HF exchange), and correlation is treated with the LYP functional, see UHF/LYP in Table I. The method has been applied only to the $Al(OH)_4$, $Al(OSiH_3)_4$, and $Al[OSi(OH)_3]_4$ models, Table II. In the ground state, the hole is found to be fully localized and the results are extremely close to those obtained at the UMP2 level. The computed HFC values are virtually the same as in UMP2 and in close agreement with the experiment. We also found a second minimum, with the hole distributed over two O atoms (Table III), at an energy of 1.67 eV above the ground state (1.60 eV in UHF). This result shows unambiguously the importance of the exact exchange for the description of a localized hole in $[AlO_4]^0$. The failure of the DFT method in this case is probably due to the afore-mentioned problem: the self-interaction correction.[49] The HF energy contains no self-interaction contributions because the self-interaction part of the Coulomb energy cancels that of the exchange part. This requirement cannot be satisfied in DFT without special efforts. Because of the self-interaction, in DFT the unpaired electron tends to delocalize over many atoms to reduce the Coulomb repulsion.

IV. CONCLUSIONS

The first model structure of an $[AlO_4]^0$ center in α-quartz was proposed almost 50 years ago by O'Brien.[2,3] It consists of ''an unpaired electron in a localized orbital on one of the four nearest O atoms.'' This model was refined by Nuttall and Weil in 1981.[6] In a careful analysis of the relevant EPR spectrum of Al-doped quartz at 35 K, they determined the hyperfine coupling parameters for ^{27}Al, ^{29}Si, and ^{17}O, despite the very low natural abundance (0.037%) of the oxygen isotope.[6] The spin-Hamiltonian parameters that they derived confirmed the original assignment of the signal to an Al atom substituting for a four-coordinated Si cation with an unpaired electron located in a nonbonding O orbital.[6] Furthermore, they established that the trapping oxygen is of the type which would have a ''long'' bond in quartz, relative to Si(Al).[6] These experimental findings have then been corroborated by four *ab initio* studies based on small-cluster models and *ab initio* Hartree-Fock wave functions.[9,10,12,13] In all these studies a full localization of the hole has been observed, consistent with the O'Brien model.[2,3]

The picture of a fully localized hole in $[AlO_4]^0$ centers has been brought into question by three recent band-structure calculations performed at the DFT level.[15–17] In particular, the last of these studies[17] (which includes gradient corrections) represents a considerable improvement in the level of theory compared to the previous *ab initio* cluster calculations. In fact, gradient-corrected DFT combined with a supercell approach where periodic boundary conditions are included is generally considered to provide very accurate answers for solid-state problems. From these three studies, a completely different picture emerged. In fact, it is found that the hole in $[AlO_4]^0$ is completely delocalized over four O atoms.[15–17] It is somewhat surprising that in two of these studies[15,17] the previous literature on the subject has been ignored and that no attempt was made to compare the new with the old results. In the work of Magagnini *et al.*,[16] on the other hand, this comparison was done and the ''classical'' model was discarded as a ''phenomenological'' one in favor of the new model of a delocalized hole. It is also surprising that these conclusions have been reached without computing any physical observable, but were simply based on theoretical arguments.

In the present work, we have shown that the two different physical pictures emerging from cluster HF and from supercell DF calculations have nothing to do with the model used (cluster or supercell) but rather are due to the nonexact treatment of exchange in DFT and to the well-known problem of the self-interaction correction. Correlation effects, explicitly included in a post-HF approach through perturbation theory, do not change the picture obtained at the HF level of a fully localized hole. On the other hand, the use of the DF exchange, even when mixed with the HF exchange in a hybrid HF/DFT approach, leads to the incorrect picture of a delocalized hole. The inadequacy of the delocalized model is shown by the direct comparison of the hyperfine matrix, a physical observable. In some of the previous *ab initio* studies, the isotropic part of the hyperfine interaction was computed.[13] Here we have reported a theoretical analysis of the dipolar parameters. The agreement between the computed and measured values is almost quantitative for the ''classical'' model, while it is very poor for the ''delocalized'' model. It is worth mentioning that the ''classical'' picture is consistent also with dielectric relaxation and acoustic-loss experiments[50–52] suggesting that the Al center hole can jump between different O atoms under an applied electric field, a fact which is not easy to reconcile with the ''delocalized'' description.

In conclusion, we have shown that the ''classical'' model of an Al impurity center in SiO_2 is correctly described by high quality first-principle calculations, provided that a proper treatment of the exchange is done. Specifically, care is necessary in the use of DFT for the study of localized holes in insulators. We note that no excitonic or vibronic effects were invoked in our modeling.

ACKNOWLEDGMENT

This work has been supported in part by the Italian INFM through a PAIS project.

---

*Email address: gianfranco.pacchioni@mater.unimib.it

[1] J. H. E. Griffiths, J. Owen, and I. M. Ward, Nature (London) **173**, 439 (1954).

[2] M. C. M. O'Brien and M. H. L. Pryce, in *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 88.

[3] M. C. M. O'Brien, Proc. R. Soc. London, Ser. A **231**, 404 (1955).

[4] A. L. Taylor and G. W. Farnell, Can. J. Phys. **42**, 595 (1964).

[5] R. H. D. Nuttall and J. A. Weil, Solid State Commun. **35**, 789

(1980).

[6] R. H. D. Nuttall and J. A. Weil, Can. J. Phys. **59**, 1696 (1981).

[7] R. Schnadt and A. Räuber, Solid State Commun. **9**, 159 (1971).

[8] O. F. Schirmer, Solid State Commun. **18**, 1349 (1976).

[9] M. J. Mombourquette, J. A. Weil, and P. G. Mezey, Can. J. Phys. **62**, 21 (1984).

[10] M. J. Mombourquette and J. A. Weil, Can. J. Phys. **63**, 1282 (1985).

[11] F. J. Adrian, A. N. Jette, and J. M. Spaeth, Phys. Rev. B **31**, 3923 (1985).

[12] P. S. Rao, R. J. McEachern, and J. A. Weil, J. Comput. Chem. **12**, 254 (1991).

[13] F. Sim, C. R. A. Catlow, M. Dupuis, and J. D. Watts, J. Chem. Phys. **95**, 4215 (1991).

[14] M. Martini, A. Paleari, G. Spinolo, and A. Vedda, Phys. Rev. B **52**, 138 (1995).

[15] A. Continenza and A. Di Pomponio, Phys. Rev. B **54**, 13 687 (1996).

[16] M. Magagnini, P. Giannozzi, and A. Dal Corso, Phys. Rev. B **61**, 2621 (2000).

[17] J. Laegsgaard and K. Stokbro, Phys. Rev. B **61**, 12 590 (2000).

[18] D. L. Griscom, J. Non-Cryst. Solids **73**, 51 (1985).

[19] L. Skuja, J. Non-Cryst. Solids **239**, 16 (1998).

[20] G. Pacchioni, in *Defects in SiO_2 and Related Dielectrics: Science and Technology*, edited by G. Pacchioni, L. Skuja, and D. L. Griscom, *NATO Advanced Study Institute*, Series C (Kluwer, Dordrecht, 2000), p. 161.

[21] Y. Le Page, L. D. Calvert, and E. J. Gabe, J. Phys. Chem. Solids **41**, 721 (1980).

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

[23] G. Pacchioni and G. Ieranò, J. Non-Cryst. Solids **216**, 1 (1997).

[24] G. Pacchioni and G. Ieranò, Phys. Rev. Lett. **79**, 753 (1997).

[25] G. Pacchioni and G. Ieranò, Phys. Rev. B **57**, 818 (1998).

[26] G. Pacchioni, G. Ieranò, and A. M. Marquez, Phys. Rev. Lett. **81**, 377 (1998).

[27] G. Pacchioni and R. Ferrario, Phys. Rev. B **58**, 6090 (1998).

[28] G. Pacchioni and M. Vitiello, Phys. Rev. B **58**, 7745 (1998).

[29] G. Pacchioni and A. Basile, Phys. Rev. B **60**, 9990 (1999).

[30] G. Pacchioni and D. Erbetta, Phys. Rev. B **60**, 12 617 (1999).

[31] G. Pacchioni and D. Erbetta, Phys. Rev. B **61**, 15 005 (2000).

[32] R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971).

[33] V. Barone, in *Recent Advances in Density Functional Methods, Part I*, edited by D. P. Chong (World Scientific, Singapore, 1996).

[34] H. Tatewaki and S. Huzinaga, J. Chem. Phys. **71**, 4339 (1979).

[35] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[36] C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[37] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[38] F. Maseras and K. Morokuma, J. Comput. Chem. **16**, 1170 (1995).

[39] S. Humbel, S. Sieber, and K. Morokuma, J. Chem. Phys. **105**, 1959 (1996).

[40] M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber, and K. Morokuma, J. Phys. Chem. **100**, 19 357 (1996).

[41] S. Dapprich, I. Komaromi, K. Suzie Byun, K. Morokuma, and M. J. Frisch, J. Mol. Struct.: THEOCHEM **461–462**, 1 (1999).

[42] M. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977).

[43] D. Erbetta, D. Ricci, and G. Pacchioni, J. Chem. Phys. (to be published).

[44] J. A. Weil, J. R. Bolton, and J. E. Wertz, *Electron Paramagnetic Resonance* (John Wiley & Sons, New York, 1994).

[45] GAUSSIAN 98, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheesman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chem, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Repogle, and J. A. Pople (Gaussian Inc., Pittsburgh, PA, 1998).

[46] P. Raghavan, At. Data Nucl. Data Tables **42**, 189 (1989).

[47] R. Schnadt and J. Schneider, Phys. Kondens. Mater. **11**, 19 (1970).

[48] M. Saint-Paul and R. Nava, Ferroelectrics **51**, 193 (1984).

[49] R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford Science Publications, Oxford, 1989).

[50] A. L. Taylor and G. W. Farnell, Can. J. Phys. **42**, 595 (1964).

[51] J. J. Martin, J. Appl. Phys. **56**, 2536 (1984).

[52] A. B. Brik, A. L. Larikov, and I. V. Matyash, Pis'ma Zh. Eksp. Teor. Fiz. **57**, 179 (1993) [JETP Lett. **57**, 185 (1993)].