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Electronic structure of the interstitial lithium-associated electron trap in crystalline quartz

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A new, paramagnetic ($S = \frac{1}{2}$) defect, designated the $[SiO_4/Li]^0$ center, consisting of an interstitial lithium "atom," recently has been observed by Jani, Halliburton, and Halperin [Phys. Rev. Lett. **56**, 1392 (1986)] in irradiated α-quartz. A model for this defect has been developed utilizing *ab initio* self-consistent-field, electronic-structure calculations. In this model, the interstitial lithium nucleus lies on a crystal twofold axis passing through two adjacent silicon ions, and has a nearly neutral charge but very low spin density. The properties calculated using this model are consistent with all the available experimental information for this defect.

As-grown synthetic quartz contains a variety of "point" defects.[1-3] Interstitial alkali-metal ions, present as charge compensators for substitutional aluminum ions, are an important component of many of these defects. It is well known that by exposing a quartz crystal to ionizing radiation above 200 K, the original aluminum-alkali centers, for example $[AlO_4/Li]^0$, are converted into a mixture of aluminum-hole centers $[AlO_4]^0$, and other paramagnetic defects. The liberated alkali-metal ions move along the large c-axis channels and become trapped elsewhere in the structure.

Combined experimental and theoretical research efforts are in progress to identify those sites at which alkali-metal ions become trapped in the quartz structure following irradiation. The initial observation of one such defect has been recently reported by Jani, Halliburton, and Halperin.[4] This interstitial lithium defect is formed by double irradiation, first between 150–300 K to release the lithium ion from its associated aluminum ion, and then at 77 K to trap an electron at the lithium ion. The resulting lithium "atom" center is not thermally stable above 180 K. The c-axis EPR spectrum reported gives a hyperfine splitting of 0.9 G from a ^7Li nucleus and 404.7 G from a single ^{29}Si nucleus. From these observations, Jani *et al.* proposed a model for this defect wherein an extra electron is stabilized on a silicon ion by an adjacent interstitial lithium ion in the otherwise perfect lattice. Following the notational scheme proposed by Weil,[2] this new defect was labeled the $[SiO_4/Li]^0$ center.

The results of a theoretical investigation of this new defect in quartz are reported in the present paper. A series of electronic structure calculations for the $[SiO_4/Li]^0$ center in α-quartz has been carried out utilizing the *ab initio,* spin-unrestricted, self-consistent-field molecular orbital technique.[5,6] In this approach, clusters simulating silicon, oxygen, hydrogen, and lithium atoms are used to model the $[SiO_4/Li]^0$ defect and its immediate surroundings. These techniques have been employed with considerable success to develop and test models for a variety of aluminum-related centers,[7,8] the E_4' center,[9] and the E'' centers[10] in α-quartz. The calculations described in this paper utilized the minimal Slater-type orbital three-Gaussian (STO-3G) basis set[11] to determine the equilibrium positions of the lithium, silicon, and oxygen atoms, and subsequently an STO-6G basis set was used to calculate the charge and spin densities shown in Table I as well as other properties described in the text.

Based on the previously reported experimental results, the 19-atom neutral cluster $[Si(OH)_4/Li/Si(OH)_4]^0$ illustrated in Fig. 1 was used to simulate the $[SiO_4/Li]^0$ center. The two SiO_4 groups in this cluster are situated on either side of the c-axis channel in the quartz lattice with the lithium nucleus situated on the twofold-crystal-symmetry x axis connecting the two silicon atoms. These SiO_4 groups were initially fixed at the positions they would occupy in the α-quartz lattice. Initially, the $Si—O_{1,2}$ and $Si'—O_{1,2}'$ bonds are short bonds, and $Si—O_{3,4}$ and $Si'—O_{3,4}'$ are long bonds (respectively, 1.6101 and 1.6145 Å at 94 K[12]). The hydrogen atoms, acting as bond terminators, initially lie along the appropriate oxygen-silicon directions with the O—H bond distance set at 0.96 Å. All the atoms, with the exception of the hydrogen atoms, were allowed to move during the subsequent geometry optimizations. Fixing the positions of the hydrogen atoms simu-

TABLE I. Net atomic spin densities ρ_A, net spin densities at the atomic nuclei $\rho(\mathbf{R}_A)$, and net ionic charges q_A (in units of $|e|$) as calculated for the cluster shown in Fig. 1 using an STO-6G basis.

Atom (A)	ρ_A	$\rho(\mathbf{R}_A)$	q_A
Si	0.001	0.013	1.45
O_1 ($=O_2$)	0.001	0.002	−0.52
O^3 ($=O_4$)	0.001	0.026	−0.47
Si′	0.285	2.627	1.07
O_1' ($=O_2'$)	0.112	0.883	−0.41
O_3'($=O_4'$)	0.114	0.113	−0.50
Li	0.142	0.040	−0.11
Total H	0.113	0.066	1.38

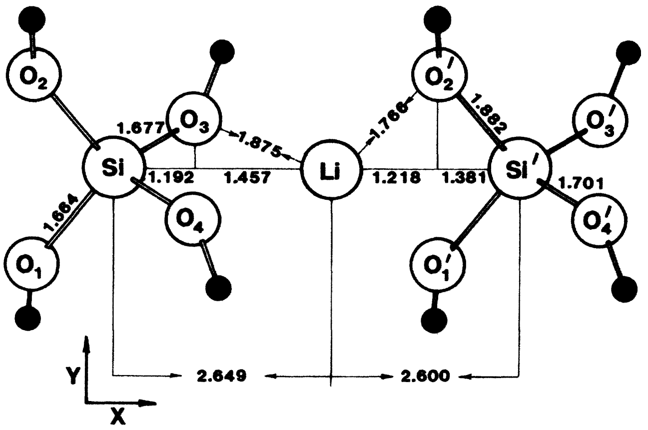

FIG. 1. 19-atom cluster used in the self-consistent field calculations to model the interstitial lithium defect in crystalline SiO_2. The distances cited (in Å) are for the final optimized (STO-3G) cluster.

lates the constraining effect of the rest of the quartz lattice. No conditions forcing twofold symmetry were imposed. The equilibrium positions obtained from this procedure show the lithium and two silicon atoms to lie within 0.001 Å of the x axis, with the lithium atom positioned slightly closer to Si' than to Si (by 0.05 Å). A plot of the total energy of the cluster versus distance of the lithium atom from Si is shown in Fig. 2 for the ground state of the defect. Here, the silicon and oxygen atoms were fixed at their optimized equilibrium positions. The ground state shows a minimum potential energy for the lithium atom at a position 2.649 Å from Si and 2.600 Å from Si'.

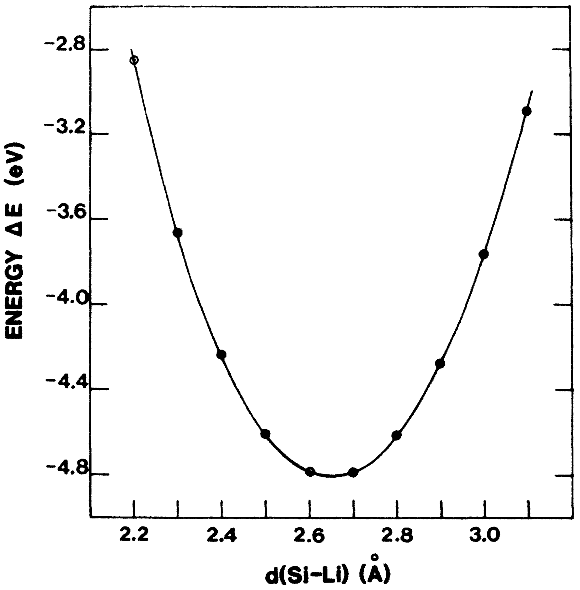

FIG. 2. Potential-energy curve for the ground ^2A state of the $[SiO_4/Li]^0$ center corresponding to the motion of the lithium atom between Si and Si' along the x axis. Here the silicon and oxygen atoms are fixed at their optimized equilibrium positions in the cluster. ΔE gives the energy of the cluster $[Si(OH)_4/Li/Si(OH)_4]^0$ relative to that of the separated lithium atom and $[Si(OH)_4/Si(OH)_4]^0$ cluster.

The net atomic spin densities ρ_A, net spin densities $\rho(\mathbf{R}_A)$ at the nuclei,[13] and net ionic charges $q_A|e|$, where A denotes the silicon, lithium, oxygen, and hydrogen atoms in the cluster, corresponding to the geometry-optimized ground-state energy minimum, are summarized in Table I. $\mathbf{R}_A$ is a vector from the origin to the atomic nucleus A in the geometry-optimized cluster. We observe that the ratio of the calculated spin densities at the nuclei give $\rho(\mathbf{R}_{\mathrm{Si}})/\rho(\mathbf{R}_{\mathrm{Li}})\cong 0.3$ and $\rho(\mathbf{R}_{\mathrm{Si'}})/\rho(\mathbf{R}_{\mathrm{Li}})\cong 65$. The ratio of the experimental silicon and lithium hyperfine constants suggests a value of the order of 10^2 for the dominant silicon ion with the spin density on any other silicon ion negligibly small. The calculated atomic spin densities, which give the fraction of the unpaired electron spin on each atom in the cluster, show that 85% of the unpaired spin is localized on the $Si'(O'H)_4$ group of atoms with the remainder localized on the lithium. A similar asymmetry in the two silicon spin densities has been observed for the interstitial silver atom, which also lies in the c-axis channel on the twofold axis connecting the two silicon ions.[14]

Our calculations for the $[SiO_4/Li]^0$ center predict a slightly negative net ionic charge for the lithium ion. Initially, we suspected that this negative net charge might be an artifact due to the use of minimal STO-NG basis sets in these calculations. However, calculations made using a STO-3G basis for a ten-atom cluster $[Si(OH)_4/Li]^0$, with the lithium situated along the x axis, respectively, on the long-bond and the short-bond side of the cluster (yielding energy minima for $d = 2.66$ and 2.60 Å), both gave a value for q_{Li} of -0.4. When the calculations were repeated using a split-valence 3-21G basis,[15] the value for q_{Li} came down only slightly, to -0.3, whereas the effective charges on the oxygen and the silicon atoms changed significantly from -0.6 and $+1.5$ to -1.0 and $+2.2$, respectively. It is worth noting that for this smaller cluster both calculations predict a much larger spin density for the lithium than for the silicon ion, just the opposite of that observed and that predicted by the 19-atom cluster calculation. No such major difference is found when calculations with the ten-atom cluster $[Al(OH)_4/Li]^+$ (8) are compared to those for the double cluster $[Al(OH)_4/Li/Si(OH)_4]^+$. The 3-21G results for the ten-atom cluster suggest that the net ionic charge of the interstitial lithium ion would turn out to be very nearly zero were the calculations to be performed for the 19-atom cluster using a 3-21G basis.

Naively, one might expect that the interstitial lithium ion could trap an electron to form a lithium atom, analogous to the hydrogen atom found in quartz.[16,17] Clearly the observed defect does not resemble a lithium atom in so far as spin density is concerned. Pleasingly our calculations give a net ionic charge of approximately zero for the lithium "atom," and at the same time predict spin densities at the ^{7}Li and ^{29}Si nuclei that agree quite well with the measured values. Analysis of the α- and β-spin molecular orbitals shows that the lithium "atom" forms sp^3-like hybrid orbitals and participates strongly in the formation of covalent bonds with the four oxygen ions that point in toward the c-axis channel and also tends to form sp_x bonds with the two silicon ions. This results in the spin density due to the trapped, unpaired electron being shared by the lithium "atom" and the SiO_4 group centered on Si′. It is worthwhile pointing out that lithium ions in oxides and hydroxides occur in tetrahedral sites.

A thermally stimulated luminescence (TSL) peak has been observed in quartz at 190 K following the same double-irradiation procedure used to form the $[SiO_4/Li]^0$ center.[18,19] Furthermore, a parallel study by Halperin and Katz[20] has revealed a full correlation between the 190-K TSL peak and the four-line EPR spectrum for this defect. From their analysis of the kinetics of the TSL peak, an activation energy of 0.6 eV was obtained for the release of the trapped electron. This energy indicates the position of the unpaired electron's energy level to be below the bottom of the conduction band (gap ~8.9 eV). Our calculations show this level to lie 8.1 eV above the highest-energy, valence-band, oxygen nonbonding level or ~0.8 eV below the bottom of the conduction band.

The relative stabilities of the $[SiO_4/Li]^0$ and the $[AlO_4/Li]^0$ centers can be estimated through the calculation of the energy required for the reaction:

$$[Al(OH)_4/Li/Si(OH)_4]^0 + [Si(OH)_4/Si(OH)_4]^0 \rightarrow [Si(OH)_4/Li/Si(OH)_4]^0 + [Al(OH)_4/Si(OH)_4]^0 ,$$

which gives $\Delta E = 5.7$ eV. All the clusters used to make these calculations are based on the one shown in Fig. 1, and represent, respectively, the $[AlO_4/Li]^0$ center, a (double) α-quartz unit, the $[SiO_4/Li]^0$ center, and the aluminum-hole center $[AlO_4]^0$. The calculation predicts the $[AlO_4/Li]^0$ center to be considerably more stable than the interstitial lithium center, as is experimentally known to be the case.

Thus far, we have been concerned with the neutral version of the interstitial lithium center. Of equal interest is the positively charged form of the defect. The results of our calculations for the ionized $[SiO_4/Li]^+$ defect strongly suggest that the conventional picture of a Li^+ ion being trapped at such a site through a combination of ionic attraction and lattice distortion is incorrect. In fact, the net ionic charge of the lithium ion in the ionized $[SiO_4/Li]^+$ defect is calculated to be +0.1, and the lithium ion is bound to the two SiO_4 groups on either side of the c-axis channel through the formation of strong covalent bonds with the four oxygen ions that point into the channel and with the two silicon ions. The implication is that alkali-metal diffusion in crystalline quartz should not be considered in terms merely of +1 ions moving through oxygen-line channels. Our calculations with hydrogen within SiO_4 clusters, to be reported, do not yield spin-density shifts away from the atom, in concert with its relatively higher $2p$ state. Similar differences between hydrogen and lithium have been found with silicon.[21]

In summary, a collaborative experimental[4] and theoretical research effort has resulted in the observation and identification of a new lithium-associated defect in quartz, which has been designated the $[SiO_4/Li]^0$ center. This center is possibly a precursor to the diamagnetic center in α-quartz responsible for the trapping of the lithium ions following room-temperature irradiation. The $[SiO_4/Li]^0$ center consists of a lithium "atom" trapped at an interstitial site in the c-axis channel at a twofold-symmetry axis in the lattice. The lithium "atom" is bonded (unequally) to the two SiO_4 groups on either side of the channel along the twofold axis, with the unpaired-electron spin density concentrated on the silicon ion nearest the lithium "atom."

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