

Observation of a Simple Lithium-Associated Electron Trap in Crystalline SiO₂

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A defect consisting of an extra electron trapped at a four-coordinated silicon atom and stabilized by an adjacent interstitial lithium ion has been observed in quartz. It is formed by a double irradiation, first between 150 and 300 K to release the lithium ion from its associated Al³⁺ and then at 77 K to trap an electron at the free lithium ion. The *c*-axis ESR spectrum shows a splitting of 0.9 G from a ⁷Li and 404.7 G from a ²⁹Si (thus, the defect does not resemble a lithium atom). Pairs of these defects may be responsible for the lack of electronic paramagnetism in quartz after room-temperature irradiation.

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The determination of the identities of electron trapping centers in the various forms of SiO₂ has been a long-standing problem.¹⁻³ Electron-spin-resonance (ESR) experiments reveal large concentrations of holelike centers in both silica and single-crystal quartz after room-temperature irradiation; however, there are no corresponding ESR spectra representing equivalent concentrations of trapped electrons. It is possible that paramagnetic electron centers are present but are difficult to observe because of either extremely long or short spin-lattice-relaxation times. It is equally possible that the electrons are trapped in pairs, thus forming diamagnetic electron centers. Alkali ions are often suspected of being a key participant in these unseen electron centers in SiO₂, primarily because they have a positive charge and they are nearly always present, either as network modifiers in silica or simply as interstitials in quartz.

The lack of paramagnetism in amorphous chalcogenide semiconductors⁴ has led to the concept of negative-*U* centers⁵ and, thus far, the silicon vacancy in crystalline silicon is the best known example of such a defect.^{6,7} Extending this concept of a negative-*U* defect to quartz provides a plausible explanation for the apparent lack of paramagnetic electron traps after room-temperature irradiation. In the present Letter, we suggest that the newly observed defect described herein could combine in pairs during room-temperature irradiation and then decay at higher temperatures by releasing not one but two electrons.

In this Letter, we describe the observation of a simple lithium-associated $S = \frac{1}{2}$ electron trap in quartz. This defect is thermally stable below 180 K and is formed by radiation whenever isolated interstitial lithium ions drift along the open channels characteristic of the quartz structure. The *c*-axis ESR spectrum ($g_c = 1.9995$) shows a small hyperfine splitting (0.9 G) due to one ⁷Li nucleus and a large hyperfine splitting (404.7 G) due to one ²⁹Si nucleus. Based on these observations, we suggest that the defect consists of an extra electron stabilized by an interstitial lithium ion in the otherwise perfect lattice. The most important and

surprising feature of this defect is the localization of the unpaired spin density on one of the adjacent four-coordinated silicon ions instead of on the lithium itself. Thus, contrary to our naive expectation, trapping of an electron by a lithium ion during irradiation at 77 K does not result in a lithium atom analogous to the hydrogen atom⁸ found in SiO₂. Instead, our model is similar to the lithium-compensated germanium centers⁹⁻¹¹ and the silver-atom center¹² previously observed in quartz. Following the notation scheme proposed by Weil,² we label our new defect the [SiO₄/Li]⁰ center.

Our data were obtained from an unswept bar of synthetic quartz provided by Thermo-Dynamics, Inc. of Shawnee Mission, Kansas. Samples with dimensions of 7×3×2 mm³ in the *X*, *Y*, and *Z* directions, respectively, were cut from the +*X* growth region. Defects were produced with x rays from a Machlett OEG-60 tube (50 KV, 30 mA) positioned 5 cm from the sample. Each irradiation lasted 5 min, during which time the sample was either placed in a stream of nitrogen gas precooled to the desired temperature or immersed in a styrofoam container of liquid nitrogen or ice water. The ESR spectrometer was an IBM Instruments (Bruker) Model ER200D operating at 9.283 GHz with 100-kHz field modulation. All ESR spectra were taken with the sample at 77 K by using a finger Dewar extending into an IBM 4102ST rectangular cavity.

The ESR spectrum shown in Fig. 1 was taken with the magnetic field parallel to the *c* axis. It consists of a central four-line spectrum, with splittings of 0.9 G, surrounded by a pair of similar, but less intense, four-line spectra located 188.6 G above and 216.1 G below the central set. The four lines within each set are due to a single ⁷Li nucleus (93% abundant, $I = \frac{3}{2}$) while the widely split weaker lines are due to a single ²⁹Si nucleus (4.7% abundant, $I = \frac{1}{2}$). These two widely split sets of lines are approximately 40 times smaller than the center set, which is in agreement with the natural abundance of ²⁹Si. Because of an extremely long spin-lattice-relaxation time, all ESR data from the [SiO₄/Li]⁰ center were taken with the spectrometer's

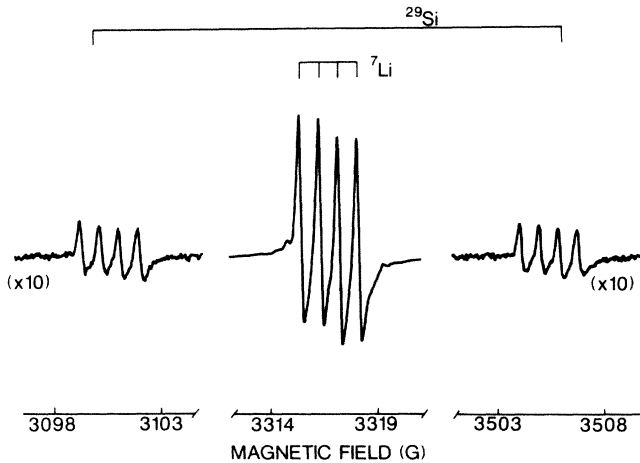


FIG. 1. ESR spectrum of the $[\text{SiO}_4/\text{Li}]^0$ center. These data were taken at 77 K with the magnetic field parallel to the crystal's c axis. The gain was increased by a factor of ten when recording the two outer sets of four lines.

lock-in amplifier set "out of phase." Similar relaxation behavior has been reported for E' and E'' centers in quartz.^{13,14}

Our assignment of the four-line ESR spectra in Fig. 1 to a lithium nucleus instead of sodium, was initially based on the relative distribution of alkali ions normally found in synthetic quartz. Martin¹⁵ has shown that this distribution predominantly favors Li^+ in commercially grown quartz even though the mineralizer is mostly Na_2CO_3 with only a small amount of Li_2CO_3 added. To provide more convincing proof for the nuclear identity, an electron-nuclear double-resonance (ENDOR) experiment was performed.¹⁶ With the static magnetic field parallel to the c axis, a pair of ENDOR lines were observed at 4.271 and 6.700 MHz when sitting on the next-to-lowest line in the central ESR spectrum (i.e., at 3320.4 G and 9.2890 GHz). The average of 5.486 MHz for these two ENDOR lines leaves no doubt that the nucleus is lithium. A second pair of ENDOR lines, thus far unidentified, were at 5.478 and 6.786 MHz.

An angular-dependence study of the primary set of ESR lines arising from defects with no ^{29}Si nucleus was made in the plane perpendicular to the crystal's X axis (i.e., about a twofold symmetry axis). These results are shown in Fig. 2. For most paramagnetic defects in quartz, rotation of the magnetic field away from the c axis in the X plane causes each of the ESR lines to split into three components; however, in the case of the $[\text{SiO}_4/\text{Li}]^0$ center, this rotation splits the lines into only two components (the solid curve being doubly degenerate in Fig. 2). This degeneracy requires that the $[\text{SiO}_4/\text{Li}]^0$ center be symmetrical about a twofold axis of the crystal (i.e., the lithium interstitial ion lies on the twofold axis passing through the adjacent

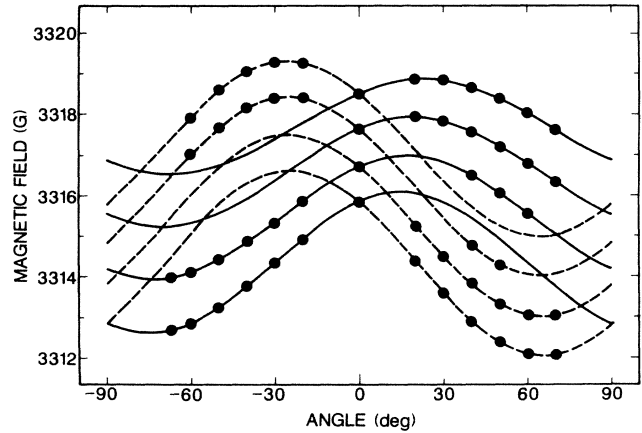


FIG. 2. Angular dependence of the central ESR spectrum for rotation of the magnetic field in the X plane. The points are experimental data, while the dashed and solid (doubly degenerate) curves were computer generated from the parameters given in Table I.

silicon ion having the large spin density). The ESR data, represented by the points in Fig. 2, were taken at thirteen angles ranging from -67° to $+70^\circ$ and were fitted with the following spin Hamiltonian:

$$H = \mu_B \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} - g_N \mu_N \mathbf{N} \cdot \mathbf{I}.$$

Final values for the g and A matrices, obtained from diagonalizing the 8×8 Hamiltonian matrix, are listed in Table I along with parameters from analogous germanium-associated centers in quartz. The root-mean-square deviation between the computer-generated and the measured line positions for the 86 lines used in our fitting was 0.068 MHz, which compares favorably with the 1.0-MHz experimental linewidths.

Figure 3 shows the results of a pulse-anneal experiment to determine the thermal stability of the $[\text{SiO}_4/\text{Li}]^0$ centers. Each data point was taken at 77 K and represents the amount of ESR signal remaining after the sample was held at the indicated anneal temperature for 5 min. The defect has two decay steps, one near 109 K and the other near 187 K. We suggest that the lower-temperature step occurs when holes are released from other traps in the crystal and migrate to the $[\text{SiO}_4/\text{Li}]^0$ centers. Because none survive the 187-K step, we suggest that it corresponds to the intrinsic decay of the $[\text{SiO}_4/\text{Li}]^0$ centers. In a separate investigation, we have observed an intense thermoluminescence peak in the 180–190 K region which correlates with the ESR spectrum of the $[\text{SiO}_4/\text{Li}]^0$ center.¹⁷

Our identification of the $[\text{SiO}_4/\text{Li}]^0$ center as an extra electron trapped by an interstitial lithium ion in the otherwise perfect lattice is strongly supported by the unique nature of its formation conditions. We have found that these centers are formed by a two-step irra-

TABLE I. Spin-Hamiltonian parameters for the $[\text{SiO}_4/\text{Li}]^0$ center and related defects in quartz. The principal directions are θ , the polar angle (relative to $+Z$), and ϕ , the azimuthal angle (relative to $+X$ with positive rotation being from $+X$ to $+Y$). Estimates of errors in the present work are $\Delta g = \pm 0.00003$, $\Delta A = \pm 0.05$ MHz, and $\Delta\theta$ and $\Delta\phi = \pm 1^\circ$.

Center	Matrix	Principal values	Principal directions		Refs.
			θ	ϕ	
$[\text{SiO}_4/\text{Li}]^0$	g	1.998 99	25°	270°	a
		2.000 74	90°	0°	
		2.001 66	65°	90°	
	A (^7Li) (MHz)	2.49	1°	270°	a
		2.75	89°	90°	
4.11		90°	0°		
Ge(II)	g	1.9929	159°	90°	b
		2.0001	90°	0°	
		2.0007	69°	90°	
$[\text{GeO}_4(A)/\text{Li}^+]^0$	g	1.9907	25°	90°	c
		2.0003	90°	0°	
		2.0019	65°	270°	

^aPresent work.

^bJ. Isoya, J. A. Weil, and R. F. C. Claridge, *J. Chem. Phys.* **69**, 4876 (1978).

^cReference 10.

diation process, first at an intermediate temperature (between 150 and 300 K) and then at 77 K. This double irradiation is needed because of the conflicting requirements imposed by (1) the minimum temperature at which radiation can form "free" lithium ions in quartz and (2) the maximum temperature at which the $[\text{SiO}_4/\text{Li}]^0$ centers remain stable. Past work has shown that interstitial lithium ions are located adjacent to

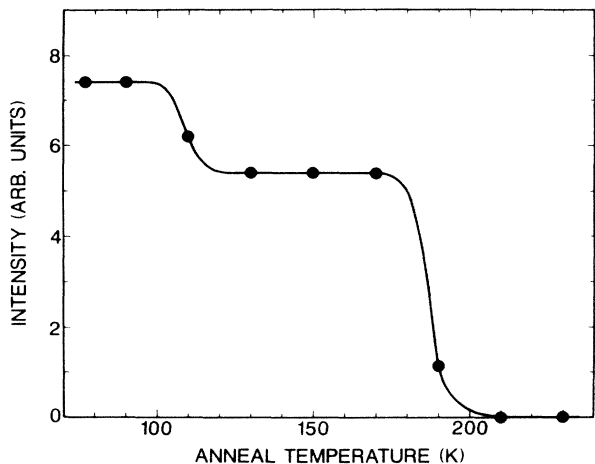


FIG. 3. Thermal-anneal behavior of the $[\text{SiO}_4/\text{Li}]^0$ center. Each data point was taken at 77 K after holding the sample at the indicated anneal temperature for 5 min.

substitutional aluminum ions in as-grown quartz,¹⁵ and also that the lithium ions can be moved away from these trapping sites by ionizing radiation whenever the sample temperature is near or above 200 K.¹⁸ Thus, the $[\text{SiO}_4/\text{Li}]^0$ centers, which are only stable below 180 K, cannot be efficiently formed by the same irradiation that moves lithium ions away from the aluminum sites. In practice, an as-grown sample must be irradiated at the intermediate temperature to release the lithium ions from their aluminum traps, then immediately cooled to 77 K before the lithium ion can diffuse to another impurity or defect site, and finally irradiated at 77 K to form the $[\text{SiO}_4/\text{Li}]^0$ center.

The solid curve in Fig. 4 shows how the production of $[\text{SiO}_4/\text{Li}]^0$ centers depends on the temperature of the intermediate irradiation. Each data point represents the concentration of these centers after a double irradiation, first at the indicated intermediate temperature and then at 77 K. Following each double-irradiation step, the sample was heated to 300 K before continuing to the next intermediate temperature. For comparison, the dashed curve in Fig. 4 illustrates the temperature dependence of $[\text{AlO}_4]^0$ center formation in quartz, which, as shown in Ref. 18, is directly related to the radiation-induced dissociation of the lithium-aluminum pair. It is clear from Fig. 4 that the phenomena represented by the two curves are related. For example, the formation of $[\text{SiO}_4/\text{Li}]^0$ centers reaches a maximum at the maximum slope of the dissociation curve. At temperatures above 250 K, the lithium ions have sufficient thermal energy to diffuse

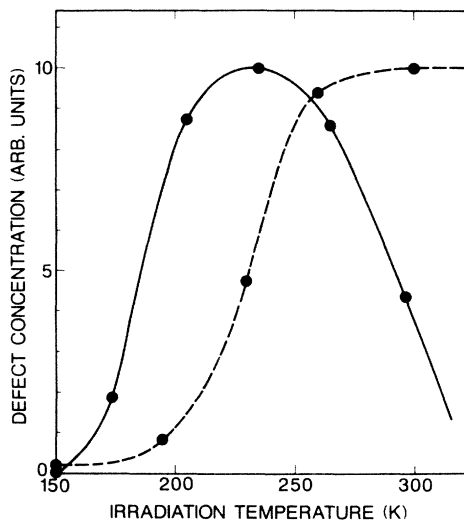


FIG. 4. The formation curve (solid line) for the $[\text{SiO}_4/\text{Li}]^0$ center illustrates the dependence on the temperature of the intermediate irradiation. The dashed curve, consisting of normalized data taken from Fig. 9 in Ref. 18, shows the temperature dependence of the radiation-induced dissociation of alkali ions from aluminum.

to more stable trapping sites and the production of $[\text{SiO}_4/\text{Li}]^0$ centers decreases.

In summary, we have observed a new defect in quartz wherein an extra electron is trapped by an alkali ion. From the production criteria and hyperfine splittings, we show that the extra electron is trapped primarily at a four-coordinated silicon ion with the adjacent interstitial lithium ion providing stability. Furthermore, we suggest that defects of this same type should be formed in silica and in the oxide-interface regions of silicon devices, although their stability is not expected to extend to room temperature. Most importantly, the simplicity of this new center in quartz should provide the insight necessary to develop models of the more complex alkali-electron traps present at room temperature in all forms of SiO_2 . In this latter regard, if two $[\text{SiO}_4/\text{Li}]^0$ centers were to be formed simultaneously about a common silicon ion during room-temperature irradiation, then a diamagnetic center would result and its thermal stability might be significantly greater than one $[\text{SiO}_4/\text{Li}]^0$ center alone. This would represent an effective negative- U behavior. Then, when the diamagnetic center thermally decays by releasing an electron, the remaining center would immediately become unstable and release the second electron.

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