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Correlated ESR and thermoluminescence study of the $[SiO_4/Li]^0$ center in quartz

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The thermally stimulated luminescence (TSL) peak in quartz near 190 K, which appears only after undergoing double-irradiation, has been studied in parallel with an electron-spin-resonance (ESR) spectrum appearing under the same double-irradiation procedure. This study revealed a full correlation between the 190-K peak and the new four-line ESR spectrum due to the defect we have labeled the $[SiO_4/Li]^0$ center. Both were formed under exactly the same conditions, both were absent after subjecting the quartz crystal to heavy doses of radiation near room temperature, and both were eliminated by hydrogen sweeping (i.e., electrodiffusion) of the crystal. In addition to the correlation, specific characteristics of the 190-K TSL peak are described. These include an effect in which radiation caused the kinetics of the 190-K peak to change from first to nearly second order. At the same time the peak temperature dropped by about 6 K. The explanation of these results is shown to follow from the kinetic theory of TSL.

I. INTRODUCTION

Point defects play an important role in many of the optical and precision frequency control applications of quartz crystals. This is best illustrated in the case of quartz oscillators where the quality of resonators is known to depend directly on impurity content.[1] Thus, the identification and characterization of point defects in quartz provides insight to basic physical mechanisms and also leads to improved device performance. Thermoluminescence, or thermally stimulated luminescence (TSL), is one of the more sensitive techniques available for the investigation of defects in insulator materials. This has resulted in a large number of TSL studies of defects in quartz, many of which are summarized in the review article by Arnold[2] and, more recently, the monograph by McKeever.[3] Another sensitive technique used in the investigation of point defects is electron spin resonance (ESR), and Weil[4] has provided a comprehensive review of the present state of knowledge of paramagnetic defects in crystalline quartz. In the present paper, we combine these two techniques (TSL and ESR) in a study of the $[SiO_4/Li]^0$ center in quartz.

In a recent investigation of the TSL of quartz at low temperatures, Malik *et al.*[5] observed a very intense emission in the 180—210-K region. Their effect was unusual because the peak did not appear if the as-received sample was simply irradiated at or near 77 K and then warmed at a constant rate. Instead, a double irradiation procedure was required wherein the first irradiation was carried out at some intermediate temperature between 145 and 300 K and the second one near 77 K. Subsequent warming after this double irradiation resulted in the intense TSL peak. Halperin and Katz[6] independently observed the same phenomenon under somewhat different conditions. In their case, it was also found that a double irradiation was necessary, but that both irradiations could be at the same low temperature (actually any temperature below 160 K) if the sample was simply heated to an intermediate temperature in the range 160—350 K after the first but before the second irradiation. Warming at a constant rate after the second irradiation produced the intense TSL peak with a maximum near 190 K. Henceforth, we will refer to this emission as the "190-K" peak. The kinetics of this TSL peak was close to first order, its thermal activation energy was 0.60 eV, and its spectral dependence peaked at 390 nm.[7]

Both Malik *et al.*[5] and Halperin and Katz[6,7] realized that the 190-K peak was probably connected with the movement of the interstitial alkali-metal impurities along the *c*-axis channels in the quartz lattice. However, they were unable to determine the nature of the specific defects involved. ESR is known to provide detailed information, primarily via hyperfine interactions, about the chemical structure of point defects. We, therefore, undertook an investigation of the 190-K peak in quartz using both TSL and ESR. Samples for the two techniques were taken from the same bars of quartz and the irradiating and heating procedures were kept as similar as possible. Because of this careful coordination during the application of the two techniques, our study proved productive and an ESR spectrum related to the 190-K TSL was observed.

This $S=\frac{1}{2}$ ESR spectrum consists of four equally spaced lines arising from a weak hyperfine interaction with a nearly 100% abundant $I=\frac{3}{2}$ nucleus. Its *c*-axis g value is 1.9995 and the corresponding hyperfine splitting is 0.9 G. Because of an extremely long spin-lattice relaxation time, the spectrum is much more intense when viewed with the spectrometer's phase detector set "out of phase." A more detailed description of the newly observed ESR spectrum has been published elsewhere.[8] It is shown there that the four-line spectrum arises from a defect in which an extra electron is trapped at a four-coordinated silicon and stabilized by an adjacent interstitial lithium ion in the *c*-axis channel. Adhering to the notation scheme of Weil,[4] this defect was labeled the $[SiO_4/Li]^0$ center.

In the present work, we concentrate mainly on the correlation between the 190-K TSL peak and the $[SiO_4/Li]^0$ center as monitored via its ESR spectrum.

II. EXPERIMENTAL PROCEDURE

The crystals of cultured quartz used in the present work were obtained from two sources. Samples referred to as TDQ had dimensions of $10\times10\times1.5$ mm^3 in the X, Y, and Z directions, respectively, and were cut from the $+x$-growth region of a bar supplied by Thermo Dynamics, Shawnee Mission, KS. These TDQ samples were unswept. Other samples referred to as PQ-I were cut from a bar of z-growth material provided by Sawyer Research Products, Eastlake, OH. Initially, three blocks approximately 1 cm in each dimension were cut from the PQ-I bar, and then hydrogen and lithium were separately swept (i.e., electrodiffused) into two of the blocks. Lithium sweeping was carried out at 485 °C in an electric field of 14 V/cm for a period of 5.5 h. Prior to the sweeping, a LiCl salt was deposited on the crystal face at the negative electrode. Hydrogen sweeping was done in a hydrogen atmosphere at 485 °C for a total of 117 h with an electric field of 640 V/cm. Plates between 2 and 2.5 mm thick in the Z direction were then cut from each of the three PQ-I blocks for use in the TSL measurements.

The TSL data were obtained from samples mounted on the cold finger of an Air Products Displex closed-cycle refrigerator. The refrigerator shroud contained a fused silica exit window for the emitted light and a thin aluminum entrance window (0.1-mm thick) for the excitation radiation. A Machlett OEG-60 x-ray tube operating at 55 kVP and 18 mA was used for all excitations of the TSL. The tungsten target of the tube was 5 to 6 cm from the quartz sample. Several samples were electron irradiated at room temperature with a Van de Graaff accelerator (1.7 MeV and 0.5 μA/cm^2 incident on the sample).

Light emitted from the samples was condensed by lenses and focused on the entrance slit of a Spex Minimate grating monochromator which in the present work was set on zero wavelength to transmit white light. An RCA C31034 photomultiplier followed by a Keithley 600 B electrometer and a recorder were used to acquire the glow curves. The rate of heating in the TSL measurements was approximately 10°/min. A constant rate of heating over the range of 15 to 305 K was accomplished by adding a manually controlled variable resistor to the heater circuit. ESR data were obtained from an IBM Instruments (Bruker) ER200D spectrometer operating at 9.283 GHz with a 100-kHz modulation frequency. Sample size was $2\times3\times7$ mm^3. All ESR measurements were made at 77 K using a finger Dewar of our own construction.

Two distinct methods were used to produce the 190-K glow peak and its analogous effect in ESR. These were (1) the "intermediate-warming" method and (2) the "two-temperature irradiation" method. In the first method,[6] the sample was x-ray irradiated at a low temperature (15 K for TSL and 77 K for ESR), then warmed and kept for 5 min at an intermediate temperature, and finally cooled and x-ray irradiated again at the same low temperature after which the TSL or ESR data were taken. In the second method,[5] the sample was x-ray irradiated at the intermediate temperature, then cooled and x-ray irradiated again at a low temperature (15 K for TSL or 77 K for ESR) after which the TSL or ESR data were taken. In both methods, the intermediate temperature was in the range 160—300 K.

III. RESULTS

A. General TSL features

Figure 1(a) shows the glow curve of an unswept Sawyer crystal (PQ-I) obtained after 5 min of x-ray irradiation at 15 K. It contains a variety of glow peaks, all of which have been reported before except the one at 72 K. The 190-K peak does not appear in Fig. 1(a). The glow curve for the Li-swept PQ-I sample (not shown) was almost the same as that of the unswept sample, with only minor differences occurring in the relative intensities of some of the peaks. This is in agreement with the observation of Martin[9] that the interstitial alkali ions in as-grown commercial quartz are nearly all lithium. The glow curve for the H_2-swept PQ-I crystal, shown in Fig. 1(b), differed from the unswept and Li-swept samples. The hydrogen sweeping eliminated all the TSL peaks above 110 K as well as the 72 K peak. The other peaks (at approximately 37, 78, 85, 93, and 109 K) were unchanged. Results similar to those of the hydrogen-swept sample were obtained from unswept samples if they were first subjected to a 10-Mrad electron irradiation (1.7 MeV) at room temperature.

Unswept and Li-swept samples were subjected to a complex series of treatments to determine the production conditions for the 190-K glow peak. "Formation" curves obtained through repeated application of the intermediate-warming method (described in Sec. II) are shown in Fig. 2. Each data point in this figure represents

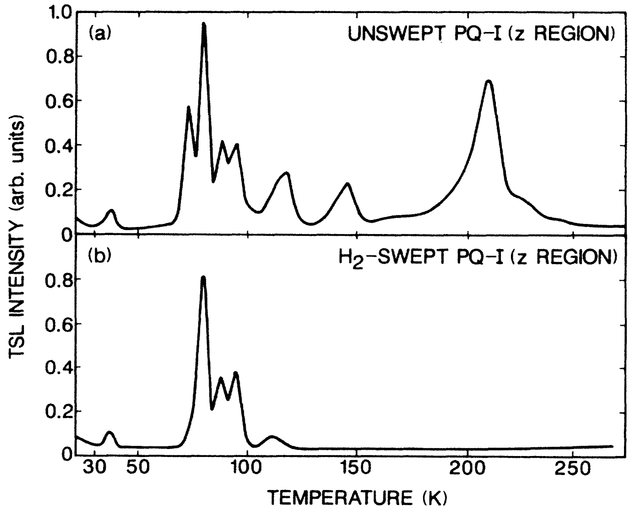

FIG. 1. Thermally stimulated luminescence from synthetic quartz following an irradiation at 15 K. Trace (a) was taken from an unswept (i.e., as-grown) sample and trace (b) was taken from a hydrogen-swept sample.

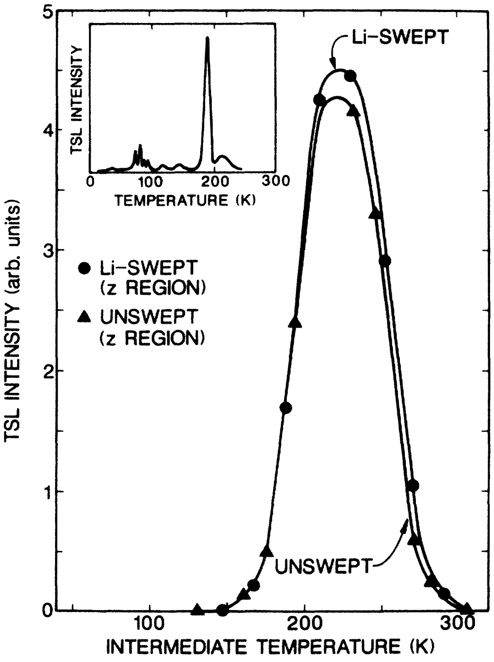

FIG. 2. Formation curves for the 190-K TSL peak. The intermediate-warming production method was used, and each data point represents the intensity of the 190-K peak for the indicated intermediate temperature. The inset shows the glow curve corresponding to an intermediate temperature of 210 K.

the intensity of the 190-K peak as determined from a glow curve taken with the corresponding intermediate temperature. Thus, these formation curves illustrate how the intensity of the 190-K peak rises and then falls as the intermediate temperature used in the production scheme is systematically increased. As an example, the glow curve obtained with an intermediate temperature of 210 K is reproduced in the insert. The 190-K peak is seen to dominate this particular glow curve.

The formation curves shown in Fig. 2 are almost identical for the unswept and Li-swept crystals. Even the maximum intensities of the 190-K peaks differ by only a few percent. The high-temperature side of the formation curve for the Li-swept sample seems slightly shifted to higher temperatures compared to that of the unswept sample. This, however, is within the limits of accuracy for our measurements. The peak temperatures of the TSL (at a heating rate of 10°/min) were near 188 K for both the unswept and Li-swept samples. The thermal activation energies obtained from initial-rise curves[10] were also found to be the same, 0.60 eV, for both crystals. The shape of the 190-K peak suggests[11] that the kinetics of the transitions involved in the 190-K peak is close to first order ($\mu_g = 0.42$, see Ref. 11). This, again, was found to be the same for both crystals.

B. Correlation of the 190-K peak with an ESR spectrum

Thermo Dynamics quartz (TDQ) was used in this portion of our investigation. Y-plate samples for TSL were cut from the $+x$-growth region of the bar, and samples for ESR were taken from adjacent positions. When searching for an ESR spectrum related to the 190-K TSL peak, the procedure was kept as similar as possible to that already known to produce the 190-K peak. The different experimental techniques involved in TSL and ESR, of course, prevented exact duplication of the procedures. Our approach proved successful and a four-line ESR spectrum, previously assigned to the $[SiO_4/Li]^0$ center,[8] was found. The connection between the newly observed ESR spectrum and the 190-K glow peak will be shown in the following paragraphs. It should be noted that the TDQ samples were unswept, and that the interstitial alkali ion is thought to be primarily lithium.[9]

The data in Fig. 3 suggest that the $[SiO_4/Li]^0$ center is the trapping level from which electrons are released during production of the 190-K peak. This figure shows the annealing behavior of the $[SiO_4/Li]^0$ ESR spectrum after its formation by 15 min of x-ray irradiation at 273 K followed by 10 min of x-ray irradiation at 77 K. In this pulse anneal experiment, the crystal was held for 5 min at an elevated temperature and then returned to 77 K where the intensity of the ESR spectrum was monitored. Repeating this procedure at sequentially higher temperatures gave the set of plotted points. The $[SiO_4/Li]^0$ center has two decay steps, one near 109 K and the other near 187 K. In our earlier paper,[8] we suggested that the lower-temperature step occurs when holes are released from other traps in the crystal and migrate to the $[SiO_4/Li]^0$ centers. Because none of the $[SiO_4/Li]^0$ centers survive the 187-K step, we suggested that it corresponds to the release of an electron from the $[SiO_4/Li]^0$ center. Also included in Fig. 3 is a glow curve taken after similar initial irradiations. It contains a very small peak at 109 K and a much larger peak near 187 K. Comparing the relative intensities of these two TSL peaks with the corresponding drops in intensity of the ESR spectrum, we conclude that the 190-K TSL peak is produced when elec-

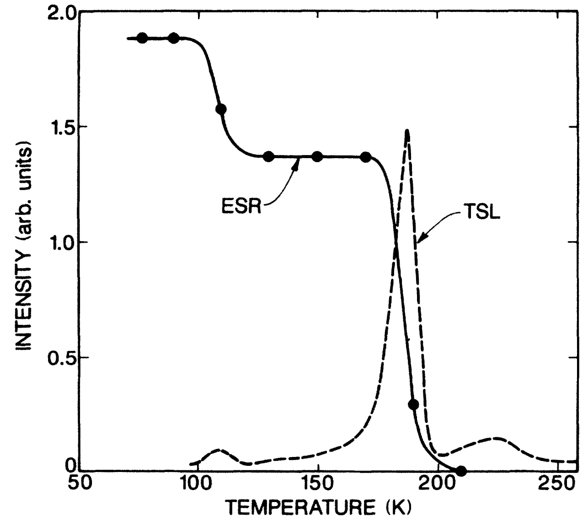

FIG. 3. Thermal anneal behavior of the $[SiO_4/Li]^0$ ESR spectrum. A glow curve containing the 190-K peak is plotted on the same temperature scale for comparison.

trons released from the $[SiO_4/Li]^0$ centers recombine with holes at unidentified defects. If the 190-K peak were due to electron-hole recombination at the $[SiO_4/Li]^0$ center, then we would expect the intensities of the 109 and 187 K TSL peaks to have approximately the same ratio as the observed drops in the ESR spectrum. It is obvious that these ratios are not the same.

Additional evidence of a correlation between the $[SiO_4/Li]^0$ ESR spectrum and the 190-K TSL peak is obtained from production studies. Figure 4 illustrates the formation curve resulting from the intermediate warming method (see Sec. II). At each intermediate temperature, the ESR data point was obtained by monitoring the ESR spectrum after the final low-temperature irradiation but before applying the temperature ramp for the glow curve. The ESR results described by the circles and by the diamonds in this figure were obtained from two independent sets of measurements, and, in each case, the ordinates were normalized to fit near the maximum of the curve. The agreement between the 190-K TSL intensity and the $[SiO_4/Li]^0$ ESR intensity is remarkable. This is even more striking when one considers the unavoidable differences in the TSL and ESR procedures.

Figure 5 shows the formation curve for a TDQ sample using the two-temperature irradiation method (see Sec. II). The abscissa in this case is the temperature of the initial irradiation at the higher temperature preceding the second irradiation (at 15 K for TSL or 77 K for ESR). Both the TSL and ESR intensities in this case were higher by about a factor of 3 compared to those obtained by the intermediate-warming method and shown in Fig. 4. Again, the agreement between the two spectra is very good.

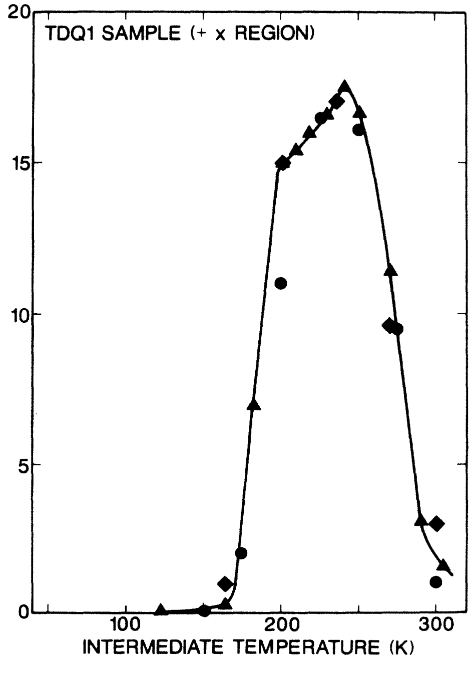

FIG. 4. Formation curves for the $[SiO_4/Li]^0$ ESR spectrum (circles and diamonds) and the 190-K TSL peak (triangles) obtained by the intermediate-warming method.

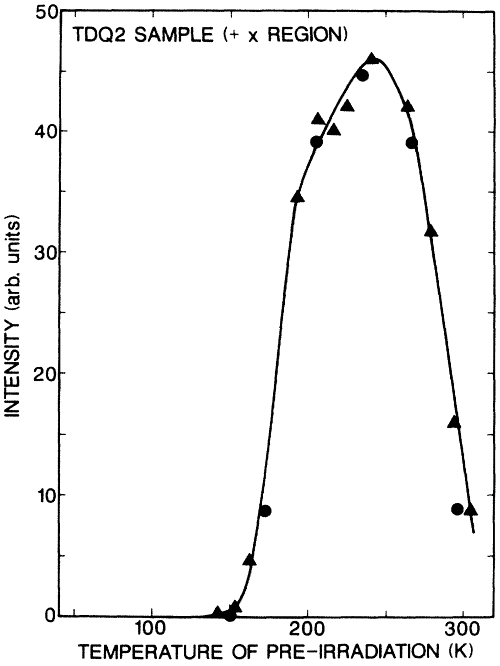

FIG. 5. Formation curves for the $[SiO_4/Li]^0$ ESR spectrum (circles) and the 190-K TSL peak (triangles) obtained by the two-temperature irradiation method.

C. Additional irradiation effects

Two effects observed in the formation curves obtained by the two-temperature irradiation method, and shown in Fig. 5, warrant a short description. First, the accumulated x-ray dose at the higher temperatures (above about 180 K) caused the 190-K TSL peak to decrease in intensity. Thus, for example, returning to the 240-K value of the intermediate temperature after finishing the entire set of formation points presented in Fig. 5 gave an intensity only about 60% of the original value given at 240 K in the figure. Furthermore, after a TDQ sample was subjected to a 10-Mrad electron irradiation (1.7 MeV) at room temperature, the 190-K peak could not be induced and the glow curve looked very much like that obtained from the H_2-swept crystal [see Fig. 1(b)].

Another interesting effect was the change in the kinetics that occurred during production of the 190-K peak by the two-temperature irradiation method. The transition from first to second order, when the intermediate temperature approached 180 K, is demonstrated in Fig. 6. Curve 1 gives the 190-K peak (on an increased ordinate scale—$\times 10$) as formed by a 5-min x-ray irradiation at 163 K followed by a second irradiation at 15 K. The shape of the curve ($\mu_g = 0.41$) indicates[11] first-order kinetics. Curve 2 was obtained with the first irradiation at 240 K. Its symmetry ($\mu_g = 0.48$) indicates a kinetics closer to second order, which means[11] that retrapping is now considerably higher than with the irradiation at only 163 K. Note also the shift of the peak to lower temperatures. The thermal activation energies were found to be equal (0.60 eV) in both the first- and second-order kinetics peaks.

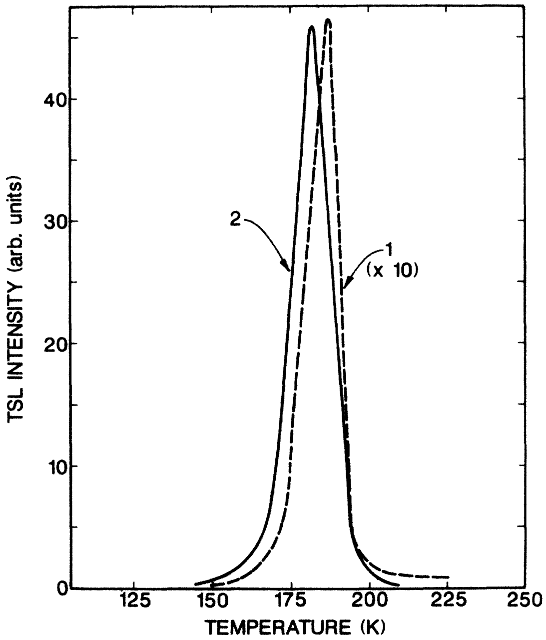

FIG. 6. Illustration of the change in kinetics when using the two-temperature irradiation method to produce the 190-K TSL peak. The intermediate temperature for curve 1 was 163 K and for curve 2 was 240 K. These gave first- and second-order kinetics, respectively. Also, note that curve 2 is a factor of 10 larger than curve 1.

IV. DISCUSSION

We have shown in the present work that the 190-K TSL peak in alpha quartz is directly associated with the $[SiO_4/Li]^0$ center. The ESR spectrum from this defect was identified during the initial stages of our study, then correlations of the TSL and ESR responses were obtained for a variety of production conditions. During the course of the investigation, two major questions arose. First, why is such a complex experimental procedure required to produce the 190-K TSL peak (and corresponding ESR spectrum), and second, why is there a change in the kinetics of the TSL peak for different production conditions? These will now be further considered.

A TSL peak is usually produced by irradiating at a fixed temperature and then warming the sample at a constant rate while monitoring the emission. However, production of the 190-K peak in quartz was not this simple because the sample had to be subjected to a "preconditioning" treatment prior to the final irradiation and warming step. In either the intermediate-warming or the two-temperature irradiation method, subjecting the sample to an intermediate temperature between 160 and 300 K was a crucial step in forming the $[SiO_4/Li]^0$ center and the subsequent 190-K TSL.

To explain how these methods lead to the production of the 190-K peak, attention must be focused on the known behavior of interstitial lithium ions in quartz. These ions serve as charge compensators for the ever-present substitutional aluminum impurities; furthermore, in as-grown crystals, the aluminum and lithium impurities are associated with each other in the form of neutral $[AlO_4/Li^+]^0$ centers. The interstitial lithium ion must be moved away from the aluminum and into the perfect lattice before the 190-K TSL peak can be produced. Once in the perfect lattice, the lithium ion can then trap an extra electron during a subsequent irradiation and form a $[SiO_4/Li]^0$ center.

In the case of the intermediate warming method, the initial low-temperature x-ray irradiation causes radiation-induced holes to become trapped at $[AlO_4/Li^+]^0$ centers, thus forming lithium-perturbed aluminum-hole defects known as the $[AlO_4/Li^+]^+$ centers.[12] These latter defects have an interstitial lithium ion on one side of the substitutional aluminum and a hole trapped at an oxygen ion on the other side of the aluminum. The concentration of the $[AlO_4/Li^+]^+$ centers is limited by the comparatively low concentration of electron traps in the crystal. Then, during the intermediate-warming step that follows the first irradiation, the Li^+ ion which is only loosely bound in the $[AlO_4/Li^+]^+$ center can migrate away from the aluminum along the *c*-axis channel, thus leaving behind an $[AlO_4]^0$ center.[13] The Li^+ ion will not diffuse far from its original position near the aluminum provided the temperature does not exceed 300 K. The second low-temperature x-ray irradiation allows "free" electrons to be trapped at these Li^+ ions, which are located in the otherwise perfect lattice, and this completes the formation of the $[SiO_4/Li]^0$ center. Then, subsequent warming of the crystal releases an electron from this center at 190 K which, in turn, leads to a TSL peak when this electron recombines with a hole at another site in the lattice.

The two-temperature irradiation method involves the same thermally activated mechanism for removal of the lithium ion from the aluminum. Irradiating the quartz at temperatures near or above 200 K produces $[AlO_4/Li^+]^+$ centers, but they are thermally unstable at these higher temperatures and immediately decay by releasing a Li^+ ion which then slowly diffuses along the *c*-axis channel.[14] Thus, the two steps in the intermediate warming method (initially irradiating at a low temperature followed by warming to an intermediate temperature) are replaced by a single step in the two-temperature irradiation method (irradiating at the intermediate temperature).

As further support for the role played by lithium, we found we could not produce the 190-K peak in samples that had been H_2 swept or that had been heavily irradiated at room temperature (i.e., to doses greater than 10 Mrad at rates approaching 2 Mrad/min). In the former case, there were no lithium ions remaining in the crystal and thus no $[SiO_4/Li]^0$ centers could be created. In the latter case, the interstitial lithium ions rapidly migrated to unidentified "deep" traps after their radiation-induced release from aluminum sites. Once captured at these deep traps, the lithium ions are unable to participate in the subsequent formation of $[SiO_4/Li]^0$ centers. The elevated temperature [i.e., room temperature (RT)] and the intense radiation field combine to enhance the mobility of lithium ions and prevent us from stabilizing them in the unperturbed lattice.

The change in kinetics of the 190-K TSL peak, from first order to nearly second order, provides evidence for the retrapping of electrons. This effect, illustrated in Fig.

6, occurs as the intermediate irradiation temperature approaches 180 K. Presumably, a greater variety of electron traps are produced at the higher intermediate irradiation temperatures. When these additional electron traps remain unpopulated after the final low-temperature irradiation in the TSL procedure, there will be an increase in the probability for retrapping of released electrons and this should shift the kinetics toward second order.[11] To our knowledge, such a radiation-induced shift in the kinetics of a TSL peak has not been previously reported, nor has the accompanying shift towards lower temperature of the maximum of the peak.

This somewhat unexpected temperature shift can be shown to follow directly from the expressions for the thermal activation energies of first- and second-order TSL peaks.[10] The expression for first-order kinetics is

$$E_1=(1.72/\tau_1)kT_{m1}^2(1-2.58\Delta)$$

and that for second order is

$$E_2=(2/\tau_2)kT_{m2}^2(1-3\Delta) ,$$

where E_1 and E_2 are the thermal activation energies, τ_1 and τ_2 are the temperature differences between the peak temperature and the half-intensity temperature on the low-temperature side of the glow peak, k is Boltzmann's constant, and T_{m1} and T_{m2} are the peak temperatures. The correction factor Δ is equal to $2kT_m/E$. Our results give equal thermal activation energies ($E_1=E_2=0.60\pm0.02$ eV) and equal τ values ($\tau_1=\tau_2=7.5$ K). The value of Δ is 0.053 assuming an average T_m of 185 K. Inserting these values in the equations for E_1 and E_2, then dividing the two expressions and taking the square root gives $T_{m2}/T_{m1}=0.94$. This translates into an expected shift of 17 K for the peak position as it changes from first to second order. In our present case, the change is not from pure first order to pure second order and thus the observed shifts of 6 to 7 K seems reasonable.

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