

X-RAY-INDUCED LUMINESCENCE FROM HYDROXYL-DOPED SILICA FIBERS -- D. W. Cooke, E. H. Farnum, F. W. Clinard, Jr., B. L. Bennett (Los Alamos National Laboratory) and A. M. Portis (UC-Berkeley)

## OBJECTIVES

The objectives of this work are to 1) measure the luminescence emitted from low- (~ 1 ppm) and high- (~ 600 - 800 ppm) OH-doped silica fibers subjected to continuous x irradiation as a function of temperature and time, 2) analyze the emission in terms of Gaussian lineshapes, 3) compare the time and temperature dependence of each peak, and 4) utilize the results to gain a better understanding of the origin of the radiation-induced luminescence. Our goal is to understand the x-ray-induced luminescence in pristine silica fibers so that we may proceed to an investigation of luminescence in neutron-irradiated fibers.

## SUMMARY

Fiber optics is expected to play a very important role in ITER diagnostics. Minutes of the 2nd Meeting of the ITER Physics Expert Group on Diagnostics outlined several plasma parameters that must be measured to ensure machine protection and plasma control. Many of these parameters (total radiated power, plasma line-averaged density, plasma rotation, impurity species monitor, etc.) are expected to require optical techniques for assessment. And regardless of the specific tool applied, it is evident that fiber optics form the basis for many of the diagnostic measurements. It is envisioned that fibers, in some cases, may be very close to the plasma with limited possibility for neutron and gamma shielding. Therefore it is imperative to fully understand the behavior of candidate fibers under extreme conditions, viz., exposure to mixed radiation fields at elevated temperatures.

The present consensus is that silica fibers comprised of low-OH silica cores and F-doped cladding are the best candidates for use in optical diagnostic systems in a high-fluence radiation environment. There are, however, two main concerns regarding their use: 1) radiation-induced attenuation, and 2) radiation-induced visible luminescence. Both properties affect the transmission and subsequent evaluation of diagnostic signals and, consequently, must be either sufficiently ameliorated or properly characterized to be useful. Accordingly, we have examined the visible luminescence of silica fibers subjected to continuous x irradiation as a function of temperature and time. Two types of fibers were investigated: 1) low OH fiber (containing ~ 1 ppm OH, as stated by the manufacturer, and labeled anhydroguide), and 2) high OH fiber (containing ~ 600 - 800 ppm OH, as stated by the manufacturer, and labeled superguide). These fibers were obtained from Fiberguide Industries, Inc., and were used in the as-received state [1].

In the temperature interval 7 - 300 K, anhydroguide exhibits two well-defined luminescence peaks at about 520 and 670 nm with the exact position being dependent upon temperature. Superguide is characterized by one broad peak near 590 nm with evidence of a second very weak peak near 620 nm. Generally we find that luminescence peak intensities decay with increasing temperature, the exception being the 670-nm peak of anhydroguide. The time dependence of each luminescence peak was measured at various fixed temperatures, and was found to exhibit exponential-type decay. Rate equations were written to explain the time dependent intensities in terms of exciton and luminescence center creation and annihilation.

Although we do not yet have an electronic model to adequately describe the observations, the results clearly show that x-ray-induced luminescence from low-OH silica fibers is very weak at room temperature. This observation has been made only for fibers subjected to ionizing radiation (in the absence of neutron-induced knock ons), but it suggests that recent observations of intense visible emission from neutron-irradiated fibers may be attributable to Cherenkov radiation, which at elevated temperatures (~ 250°C, for

example) is expected to be much more intense than luminescence. This implies that present concern over neutron-induced luminescence in silica fibers may be less important than Cherenkov radiation.

## PROGRESS AND STATUS

### Introduction

The anticipated use of fiber optics for ITER diagnostics requires an assessment of their optical characteristics during and after exposure at various temperatures to mixed neutron and  $\gamma$  radiation fields. Recent observations of intense visible emission emanating from silica fibers during neutron exposure have raised questions about the origin of this light and its possible interference with diagnostic signals. To gain a better understanding of the nature of this emission and its impact on transmission of diagnostic signals, we have embarked upon a systematic investigation of radiation-induced luminescence in silica fibers.

### Experimental Procedure

Silica fibers containing <1 ppm of OH (hereafter referred to as fiber "A") and ~ 600 - 800 ppm OH (hereafter referred to as fiber "S") were obtained from Fiberguide Industries, Inc. [1] and tested in the as-received condition. They each consisted of a pure fused-silica core with fluorine-doped (~ 4 mole %) cladding and either nylon (fiber A) or aluminum (fiber S) jackets. Core/cladding/jacket diameters were 200/220/280  $\mu\text{m}$ . Luminescence measurements were done by placing the fibers on an aluminum sample block in a continuous-flow cryostat, evacuating the chamber, exposing them to continuous x irradiation (25 keV effective energy; ~ 13 Gy/s exposure rate) as a function of either temperature (~ 7 - 300 K) or time, and collecting the emission with a CCD-based optical multichannel analyzer. In some cases the emission was directed to a cooled photomultiplier tube for detection. In this latter arrangement we collected total light emitted by the fiber without regard for wavelength information. Typically, data were taken in the interval 300 - 800 nm, corrected for the non-linear response of the spectrophotometer, plotted in energy units and fitted with Gaussian lineshapes.

### Results

#### Anhydroguide

Figure 1 shows the x-ray-induced luminescence from fiber A taken at 7.3 K. The spectra consist of two well-defined Gaussian bands (dashed lines) centered at 521 and 671 nm (these maxima shift to lower wavelength by about 20 nm as temperature increases to 150 K). The fitted composite of the two bands is shown by the thin solid line where intensities are plotted as optical multichannel analyzer (OMA) counts. Temperature dependences of the peak intensities are shown in Fig. 2. Although we have not yet attempted to write rate equations describing the *temperature* dependence of luminescence peaks in silica fibers, we did find that a simple exponential adequately described the 521-nm peak decay. The 671-nm peak exhibits an initial increase with increasing temperature followed by a decrease. No attempt was made to fit the latter peak intensity to a functional form. Data of Fig. 2 were taken from the fitted Gaussian curves and the statistical errors are smaller than the plot symbols. The total time required to obtain a full spectrum at each temperature was 15 seconds (total OMA integration time), which is also the x-ray exposure time. That is, the specimens were exposed to x radiation only during the 15-second measurement interval. Data in Fig's. 1 and 2 were taken by cooling the sample to 7.3 K and recording spectra during warming. Hysteresis of the data were examined by also observing spectra upon cooling; only minimal effects were found. The dependence of the peak intensities was investigated by maintaining the sample temperature at 7.3 K and observing the change in intensity as the sample was subjected to continuous x-ray exposure. Results of this experiment are shown in Fig. 3.

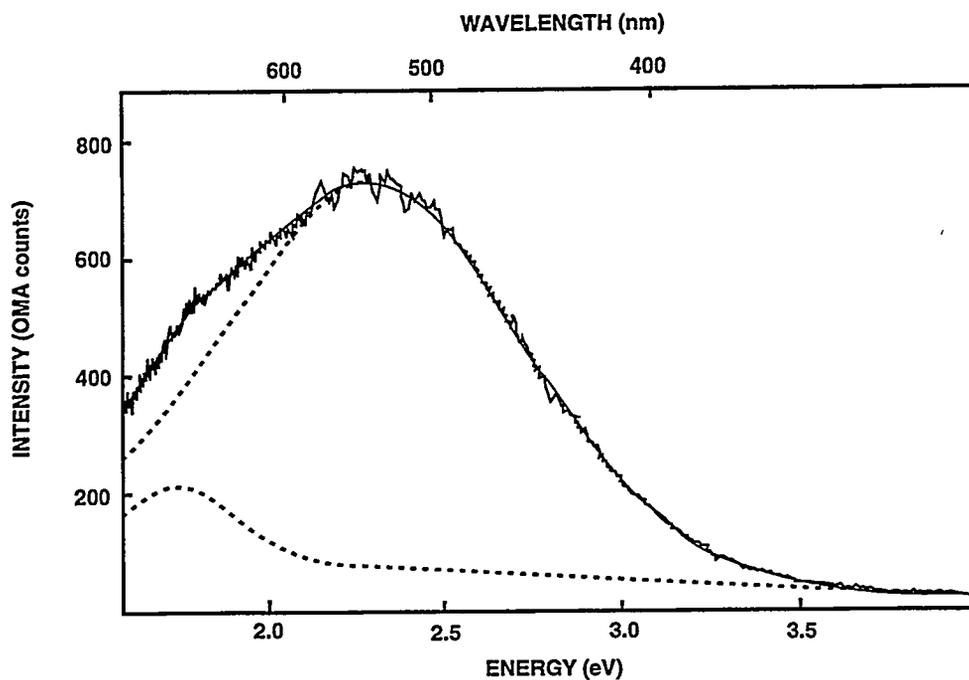


Fig. 1. X-ray-induced luminescence from silica fiber A taken at 7.3 K. Dashed lines are the deconvoluted Gaussian peaks (521 and 671 nm) and the solid line is the composite fit.

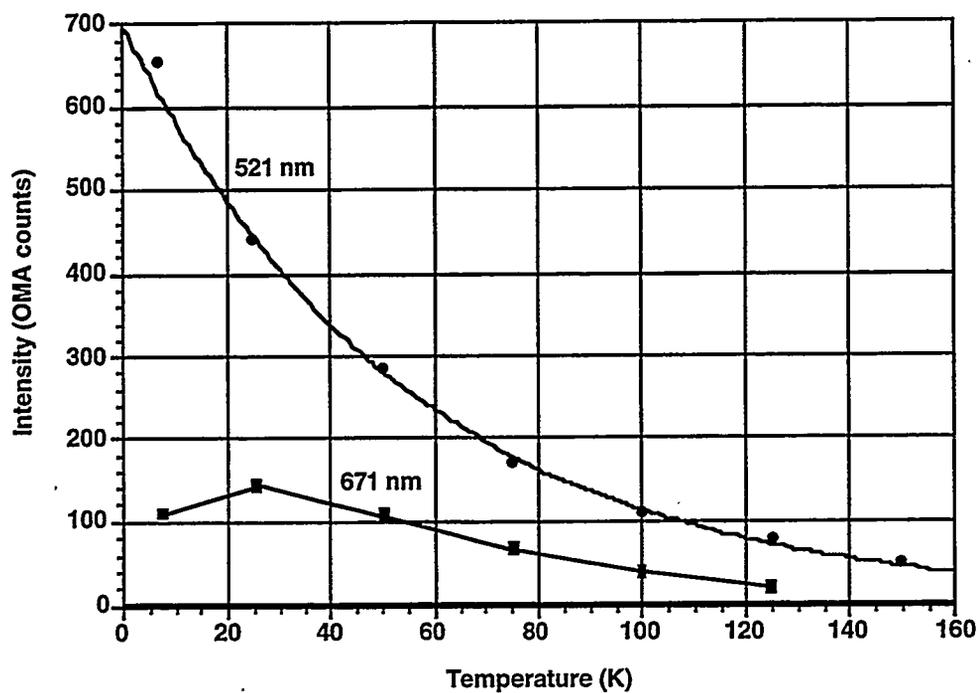


Fig. 2. Temperature dependence of luminescence peaks in silica fiber A. Solid line of upper curve is an exponential fit whereas the lower solid line is only a guide to the eye.

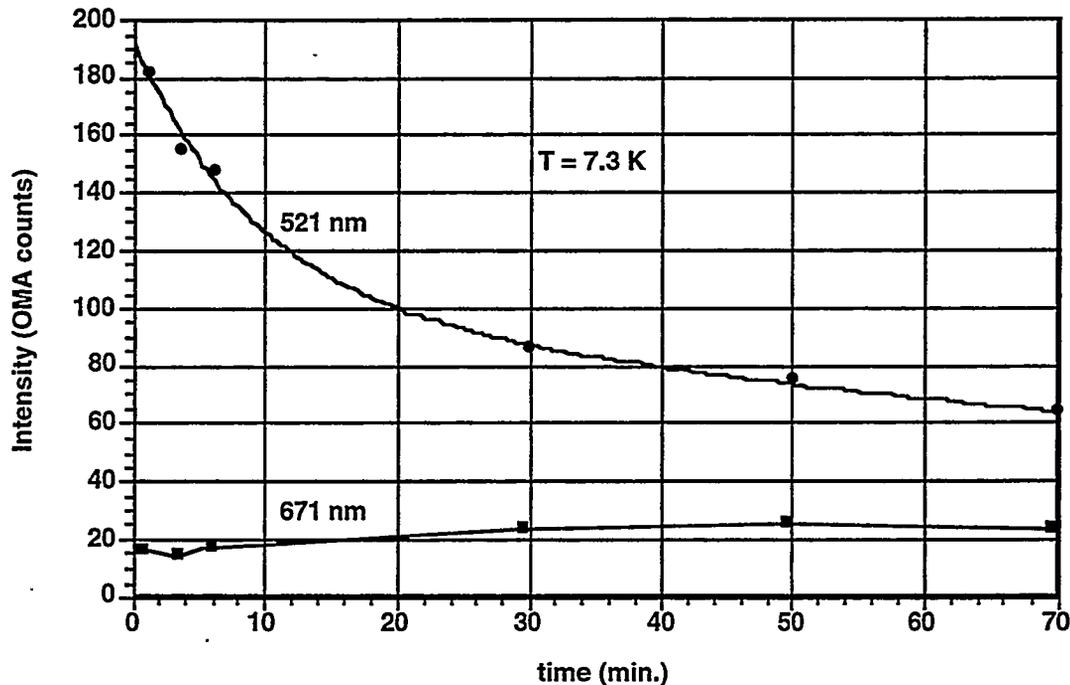


Fig. 3. Time dependence of luminescence peaks in silica fiber A. Solid line of upper curve is a fit to Eq. (7) of text and the lower curve is a guide to the eye.

### Superguide

X-ray-induced luminescence from fiber *S* taken at  $T=8$  K is shown in Fig. 4. The spectrum was taken under similar conditions as those previously described for fiber A. Unlike fiber A, however, the spectrum does not exhibit two well-defined peaks. Instead there exists one main peak with maximum at 596 nm and a hint of a second very weak peak near 660 nm. This latter peak was sufficiently weak at all temperatures that we did not attempt to separately fit it with an individual Gaussian lineshape. A reasonably good fit to all of the spectra for fiber *S* was obtained by invoking a single Gaussian lineshape, which is shown as the thin solid line of Fig. 4.

Temperature dependence of the luminescence intensity for fiber *S* is shown in Fig. 5. It is clear that a simple exponential (shown as the solid curve) cannot properly describe the relaxation. We postpone efforts to model the temperature dependence of the luminescence intensity at the present time and focus only on the time dependent data shown in Fig's. 3 and 6. Subsequent work will address the temperature dependence of the luminescence.

To gain an understanding of the time dependence of the x-ray-induced luminescence of pristine silica, we plotted the total light output as a function of irradiation time at a *fixed* temperature. For this particular experiment we directed the luminescence onto a cooled photomultiplier tube (PMT) and plotted intensity vs. time in seconds. Notice that the ordinate is measured in units of PMT current instead of OMA counts as in Fig. 3. Surprisingly, we found that in the interval  $8 \leq T \leq 60$  K, the overall luminescence intensity decays with a rate constant that is *independent* of temperature (the model will be described in the discussion section). For  $T \geq 80$  K the rate constant changes such that for  $T \geq 125$  K there is no measurable decay in the intensity as a function of time.

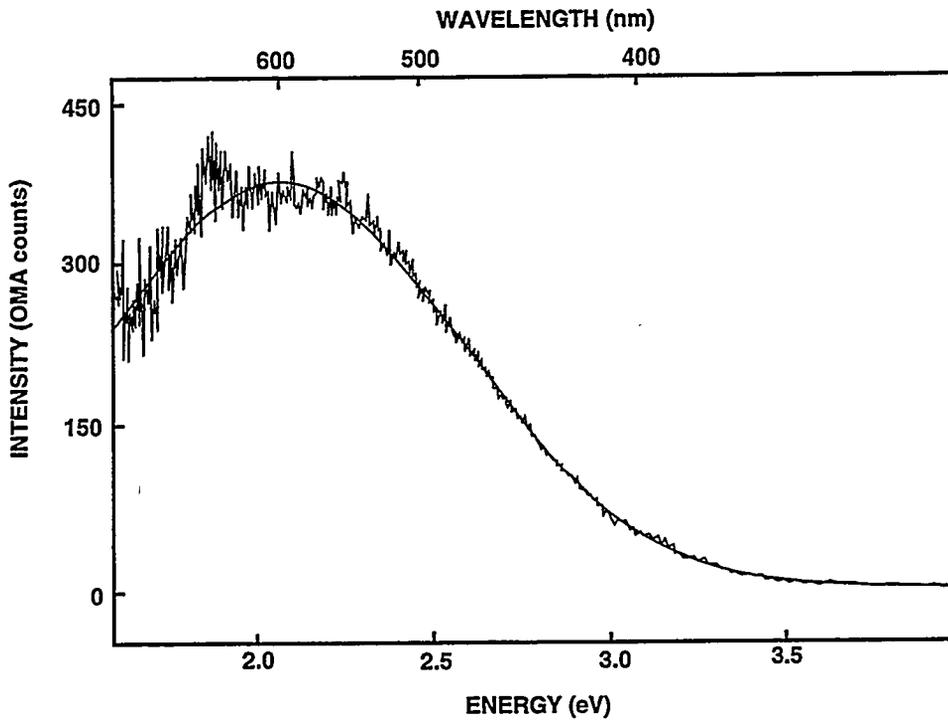


Fig. 4. X-ray-induced luminescence from fiber *S* taken at  $T = 8$  K. The solid line is a Gaussian fit to the data.

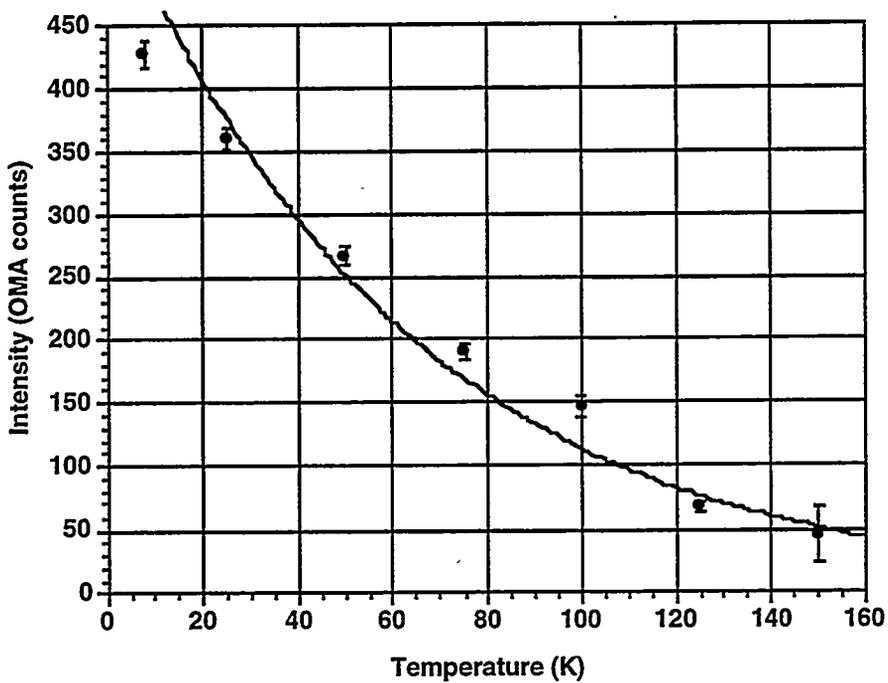


Fig. 5. Temperature dependence of luminescence from fiber *S*. The solid line is a simple exponential similar to the one shown in Fig. 2 and is included only for comparative purposes.

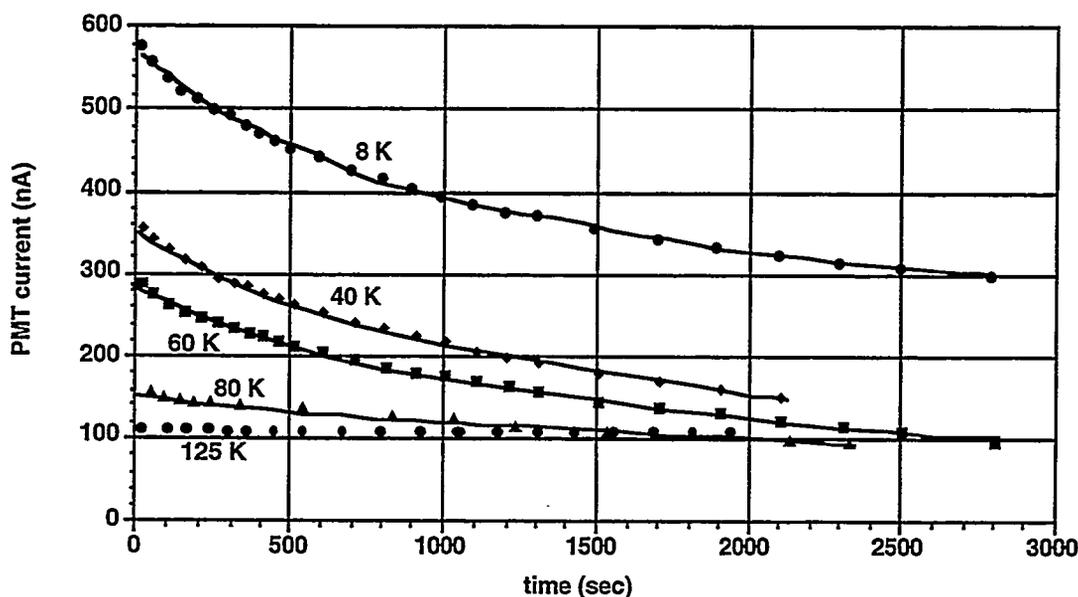


Fig. 6. Time dependence of the x-ray-induced luminescence intensity of fiber *S* taken at several fixed temperatures. The solid lines are fits to Eq. (7) of text.

### Discussion

We now develop rate equations to describe the *time* dependence of the luminescence intensity at fixed temperatures in silica fibers. In subsequent work we will address the temperature dependence. Primarily we are presently attempting to model the behavior exhibited in Fig's 3 and 6.

We assume that x radiation produces energetic electrons, which produce both lattice defects and excitons. Radiation-produced excitons are either self-trapped, likely decaying nonradiatively, or are trapped at a defect with the possibility of radiative recombination. Self-trapping is certainly expected to involve phonons and thus should be temperature dependent; increasing the temperature should increase the probability of their decay. For the present work, however, we concentrate on the time dependence.

Under x-ray excitation the rate of increase in exciton concentration  $n$  is described by the equation:

$$\frac{dn}{dt} = \alpha - \beta n - \sum_i D_i n N_i \quad (1)$$

The parameter  $\alpha = AI$ , with  $I$  the intensity of the x-ray radiation, gives the exciton production rate and  $\beta = BI + C$  gives the decay rate. The parameter  $D_i$  gives the capture rate (velocity times cross-section) by  $N_i$  recombination centers.

Now we allow for the possibility that recombination centers may be created under irradiation. These centers may be destroyed either by the action of the radiation or through thermal processes. Some of the generation of these centers will be first-order, increasing at a rate proportional to  $I$  and some second-order, increasing at a rate proportional to  $n^2$ . We simplify the discussion by *assuming* that the generation is first-order and thus proportional to  $I$ :

$$\frac{dN_i}{dt} = \alpha_i - \beta_i(N_i - N_i^0) \quad (2)$$

Here  $\alpha_i = A_i I$  is the rate of generation of recombination centers and  $\beta_i = B_i I + C_i$  is the decay rate, where  $B_i I$  represents power-induced decay and  $C_i$  represents thermal decay.  $N_i^0$  is a fixed concentration of recombination centers. At constant radiation intensity the concentration of recombination centers increases as:

$$N_i = N_i^0 + (\alpha_i / \beta_i)(1 - e^{-\beta_i t}) \quad (3)$$

We further assume that the exciton relaxation rate  $\beta + \sum_i D_i N_i$  is much greater than the relaxation rates  $\beta_i$  of the recombination centers. This assumption allows us to take for the instantaneous exciton concentration the steady state value corresponding to the current concentrations of the recombination centers:

$$n = \frac{AI}{BI + C + \sum_i D_i N_i} \quad (4)$$

where the  $N_i$  are given by Eq. (3).

Much of the exciton recombination is nonradiative while some recombination may be radiative and identified as luminescence. We separate the recombination rate into two terms:

$$D_i = D_i^n + D_i^r \quad (5)$$

where  $D_i^n$  is the nonradiative fraction and  $D_i^r$  is the radiative fraction. The luminescence intensity of the  $j$ 'th center is from Eqs. (1), (4) and (5):

$$L_j = D_j^r n N_j = \frac{D_j^r N_j}{BI + C + \sum_i D_i N_i} AI \quad (6)$$

The decrease in  $L_j$  with increasing *temperature* is a consequence of the increase in  $C$  and possibly the  $D_i$  with temperature. The decrease in  $L_j$  with *time* is a consequence of the increase in the  $N_i$  with time. Where a particular  $L_j$  is found to increase with time, this increase may be a consequence of a growth in the corresponding  $N_j$  with time.

Substituting Eq. (3) into Eq. (6) gives for the decay in the luminescence of the  $j$ 'th center:

$$L_j = D_j^r n N_j = \frac{D_j^r \left[ N_j^0 + (\alpha_j / \beta_j)(1 - e^{-\beta_j t}) \right]}{BI + C + \sum_i D_i \left[ N_i^0 + (\alpha_i / \beta_i)(1 - e^{-\beta_i t}) \right]} AI \quad (7)$$

The asymptotic value of  $L_j$  from Eq. (7) is:

$$L_j = D_j^r n N_j = \frac{D_j^r (N_j^0 + \alpha_j / \beta_j)}{BI + C + \sum_i D_i (N_i^0 + \alpha_i / \beta_i)} AI \quad (8)$$

As the temperature is increased, the asymptotic value can be expected to decrease as a result of an increase in  $C$  but may be compensated somewhat by increases in the  $\beta_j$  in the denominator. At sufficiently high power, the luminescence is expected to saturate at the value:

$$L_j = D_j^r n N_{rj} \approx D_j^r \left( N_j^0 + \frac{A_j}{B_j} \right) \frac{A}{B} \quad (9)$$

The model calculations were compared to experimental results by fitting the data of Fig's 3 and 6 (under simplifying assumptions) to Eq. (7). Excellent fits were obtained as shown by the solid lines in Fig's 3 and 6, thereby supporting our conclusion that the decrease in luminescence intensity is attributable to an increase in recombination center concentration. Moreover, it was found that the recombination center rate constants for data taken at 8, 40 and 60 K were essentially equivalent;  $\langle \beta_i \rangle = 4.94 \times 10^{-4} \text{ s}^{-1}$ .

Therefore the rate of increase in recombination center concentration is independent of temperature in this interval. The value of the rate constant changes for  $T \geq 80 \text{ K}$  and we speculate that this thermal dependence is likely due to increased mobility of an as yet unknown species, possibly H or O. Identification of these defects must await our planned optical absorption and electron spin resonance studies. However, it is well established that non-bridging oxygen hole,  $E'$ , and peroxy radical centers are the main defects induced in silica by x radiation, and the conversion of  $E'$  centers to peroxy radicals is controlled by the diffusion of molecular oxygen [2]. Radiolytically-produced atomic hydrogen is also known to exist below about 130 K in OH-containing silica and may play a role in the luminescence process [2]. Further work is required to identify the luminescence centers and their interconversions.

Our current results clearly demonstrate that x-ray-induced luminescence in pristine silica fibers of both low and high OH content decays with temperature and time, and is very weak at room temperature. Similar studies are now underway to examine the behavior of neutron-irradiated fibers. It is important to establish the role and relative intensities of radiation-induced luminescence and Cherenkov emission in fibers subjected to neutron exposure. If the Cherenkov emission dominates at temperatures of interest in ITER applications as suggested by other data [3], attention should be focused on ways to mitigate this problem rather than luminescence. Of course there still remains the problem of radiation-induced absorption in silica, which is certainly due to the production and/or interconversion of defects. The usefulness of silica fibers for ITER diagnostics may depend upon how well we understand the production, destruction and interconversion of these defects. Because precursors are believed to play a role in radiation hardening of silica [4] and because interconversion of defects depends upon radiation dose, temperature and time [5], it is necessary to study both pristine and neutron-irradiated silica at low temperatures where initial defects still exist. As our present data demonstrate, below about 80 K there is a temperature independent rate of decay of luminescence intensity that we speculate to be associated with the mobility of either H or O. Our aim is to understand the defects, model the kinetics, and predict ways to ameliorate the luminescence (and absorption) in silica fibers.

## FUTURE PLANS

We are presently investigating luminescence of silica fibers which have been irradiated to high neutron fluences ( $10^{23} \text{ n-m}^2$ ) at the Los Alamos Spallation Radiation Effects Facility. Luminescence data similar to that reported in the present work will be taken on these specimens and compared to the pristine fibers. Optical absorption measurements on both sets of fibers will be conducted to ascertain expected correlations between absorption and luminescence centers. These data should aid identification of the radiation-induced defects.

## REFERENCES

- [1] Fiberguide Industries, Inc., 1 Bay Street, Stirling, NJ 07980.
- [2] D. L. Griscom, *J. Ceram. Soc. Jpn.* **99**, 923 (1991).
- [3] S. F. Paul, J. L. Goldstein, R. D. Durst and J. R. Fonck, *Rev. Sci. Instrum.* **66**, 1252 (1995).
- [4] D. L. Griscom, *J. Appl. Phys.* To be published.
- [5] L. Zhang, V. A. Mashkov and R. G. Leisure, *Phys. Rev. Lett.* **74**, 1605 (1995).