

# Transient measurements using thermographic phosphors

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Received 15 December 2005; accepted 20 March 2006

Available online 22 January 2007

## Abstract

The decay of thermographic phosphors has been used to measure temperature in a wide variety of applications. Because measurements of a single temperature are obtained from intensity decay in time, the use of phosphors is predicated on the fact that the temperature does not change during the decay. This may not be valid in some engineering applications. A new model for phosphor data reduction designed to recover transient effects is presented. A heated wire experiment is used to determine the efficacy of the approach. Results for a particular microsecond phosphor indicate that transients can be resolved, but not to a great deal of accuracy. Nevertheless, the steady model predicted temperatures that were 10 °C off compared to the transient model during high heating.

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*Keywords:* Thermographic phosphor; Transient temperature measurement

## 1. Introduction

Thermographic phosphors have proven to be useful and accurate for a variety of thermal measurement applications [1]. In fact, phosphor thermometry can often be used where traditional temperature measurement is difficult. For example, phosphors are particularly suitable for non-contact remote thermometry where thermophysical properties are not known [2,3]. Phosphors can be used for a wide range of temperatures and in harsh environments [4].

Phosphor decay time, emission frequency and line width, and intensity are all temperature dependent and can theoretically be used in thermometry, but phosphor decay is generally the most reliable way to measure temperature. The decay time of phosphors varies from nanoseconds to hours, so in general, a phosphor must be selected such that the decay time is much smaller than any transients in the system. Consequently, the temperature during the decay can be considered constant. This assumption is critical to the validity of existing data reduction models.

For extremely fast transients or situations where the transients are of primary interest, traditional phosphor models

do not hold. The present work describes a new model for phosphor data reduction when temperature transients exist during the decay and compares estimates from the new model to traditional steady techniques.

## 2. Theory

Steady-state temperatures can be extracted from phosphor intensity measurements by calculating the decay time of an excited phosphor that is allowed to relax. The decay time is usually found by fitting an exponential,

$$I(t) = I_o \exp\left(-\frac{t}{\tau}\right), \quad (1)$$

to measured intensity data. In the foregoing expression,  $I_o$  is the initial intensity (at  $t = 0$ ), and  $\tau$  is the decay time. This result is usually presented without derivation because of its simplicity and widespread acceptance of its validity. Even though a rigorous fit requires a non-linear method, quality estimates can be obtained by fitting a line to the logarithm of the data. The intercept represents the logarithm of the initial intensity, and the slope is  $1/\tau$ . This linearization fails when the measurement noise results in negative values of intensity. In this case, the logarithm can not be calculated and the points must be thrown away, resulting in a biased estimator. Therefore

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points at the end of the decay are sometimes ignored to reduce the bias. The errors associated with this procedure are usually small because the sensitivity of the measurement with respect to the parameter  $\tau$  are small near the end of the decay essentially because the measurement noise is comparable to or larger than the signal. Therefore, little additional information is provided at large times. Consequently, the approach has proved quite successful for steady-state measurements.

If we consider transient measurements where the temperature and, therefore, the decay change during the decay, then Eq. (1) is no longer applicable. In other words, there is no parameter in the physical model that can capture transients associated with the decay time. To reintroduce transient effects, we consider the governing equation for phosphor emission through recombination of excitation centers [4].

$$\tau(t) \frac{dI(t)}{dt} + I(t) = 0. \quad (2)$$

When  $\tau$  is assumed constant the solution is Eq. (1). A transient solution can be obtained if we assume a Taylor series expansion for  $\tau$  neglecting all non-linear terms ( $\tau(t) = \tau_o + \xi t$ ), such that  $\xi = d\tau/dt$  represents the transient contribution. The solution becomes

$$I(t) = I_o \left( \frac{\tau}{\tau + \xi t} \right)^{1/\xi}, \quad (3)$$

where  $I_o$  is the initial intensity as before. This is a more general solution to the phosphor decay and should collapse to the steady solution given by Eq. (1) in the limit of no transients ( $\xi \rightarrow 0$ ). If we use the Mercator series for the logarithm, then

$$\lim_{\xi \rightarrow 0} I_o \left( \frac{\tau}{\tau + \xi t} \right)^{1/\xi} = \lim_{\xi \rightarrow 0} I_o \left( 1 + \frac{\xi t}{\tau} \right)^{-1/\xi} \quad (4)$$

$$= \lim_{\xi \rightarrow 0} \exp \left\{ \ln I_o - \frac{1}{\xi} \ln \left( 1 + \frac{\xi t}{\tau} \right) \right\} \quad (5)$$

$$= \lim_{\xi \rightarrow 0} \exp \left\{ \ln I_o - \frac{1}{\xi} \left[ \frac{\xi t}{\tau} - \frac{1}{2} \left( \frac{\xi t}{\tau} \right)^2 + \frac{1}{3} \left( \frac{\xi t}{\tau} \right)^3 - \dots \right] \right\} \quad (6)$$

$$= \lim_{\xi \rightarrow 0} I_o \exp \left[ -\frac{t}{\tau} + \frac{\xi}{2} \frac{t^2}{\tau^2} - \frac{\xi^2}{3} \frac{t^3}{\tau^3} + \dots \right] \quad (7)$$

$$= I_o \exp \left( -\frac{t}{\tau} \right). \quad (8)$$

Despite this equivalence for constant  $\tau$  (i.e.  $\xi = 0$ ), computation of Eq. (3) may be difficult for small  $\xi$  because of the numerical infinities.

An alternative approach considers the transition rate  $W$  instead of the decay time.

$$\frac{dI(t)}{dt} + W(t)I(t) = 0, \quad (9)$$

where  $W = 1/\tau$  for steady conditions. If we assume a Taylor series expansion of the transition rate ignoring all non-linear

terms ( $W = \nu + \zeta t$ ), the solution becomes

$$I(t) = I_o \exp \left[ -t \left( \nu + \frac{\zeta}{2} t \right) \right]. \quad (10)$$

Here,  $\nu \approx 1/\tau$  is interpreted as the decay rate instead of the decay time, and  $\zeta = d\nu/dt$  represents the transient component.

This formulation is more amenable to computations because the steady result (Eq. (1)) is recovered for  $\zeta = 0$  and  $\nu = 1/\tau$ . Furthermore, we can linearize the fit by taking the logarithm of the data as we did for the steady case. As before, the errors are presumably negligible because the noise overwhelms the signal for large times and no additional information is available.

In some instances it may be important to relate the change in decay rate  $\xi$  to the parameters in Eq. (10) [5]. If we write the transition rate  $W$  in terms of the decay time

$$\nu + \zeta t = \frac{1}{\tau_o + \xi t}, \quad (11)$$

and assume that  $\nu = 1/\tau_o$  for  $t = 0$ , then the change in decay time becomes

$$\xi = -\frac{\zeta}{\nu} \frac{1}{\nu + \zeta t}. \quad (12)$$

If  $\zeta = 0$ , then  $\xi = 0$ , meaning that the decay does not contain any transients. We also note that  $\xi = -\zeta/\nu^2$  for  $t = 0$ , which provides a way to convert the parameters from Eq. (10) to the parameters from Eq. (1). The change in decay time  $\xi$  can be useful for predicting heating rates [5].

Characteristics of the model can help us understand the ability of the model to extract transient effects. Fig. 1 shows the normalized intensity

$$I^*(t) = \frac{I(t)}{I_o} = \exp(-t^* - D^* t^{*2}) \quad (13)$$

given for different amounts of transient effects denoted by the dimensionless group  $D^* = \zeta/2\nu^2$ . When  $D = 0$  the steady case is recovered. The normalized time  $t^* = t\nu$  can be interpreted as the number of decay times. The interesting feature of this model is the fact that positive and negative values of  $D^*$  do not produce equivalent deviations from the linear case. Depending on whether the phosphor experiences heating or cooling, the parameter  $\zeta$  could be positive or negative. However, we are limited on the negative side to small deviations, because large deviations result in physically unrealistic decay curves. For strongly negative  $D^*$ , the emission actually increases. Although there may be some physical basis for this behavior (thermoluminescence), the governing physics is slightly different than what is presented here. Therefore, we will assume that the changes in the decay rate are modest (i.e. small  $\zeta$ ) and disregard the extreme cases. As demonstrated later, the magnitude of  $D^*$  considered in the present case is much less than unity, so we do not expect to enter into any physically unrealistic regimes.

Additional insight can be gleaned from the sensitivity coefficients, which are obtained by differentiating the model

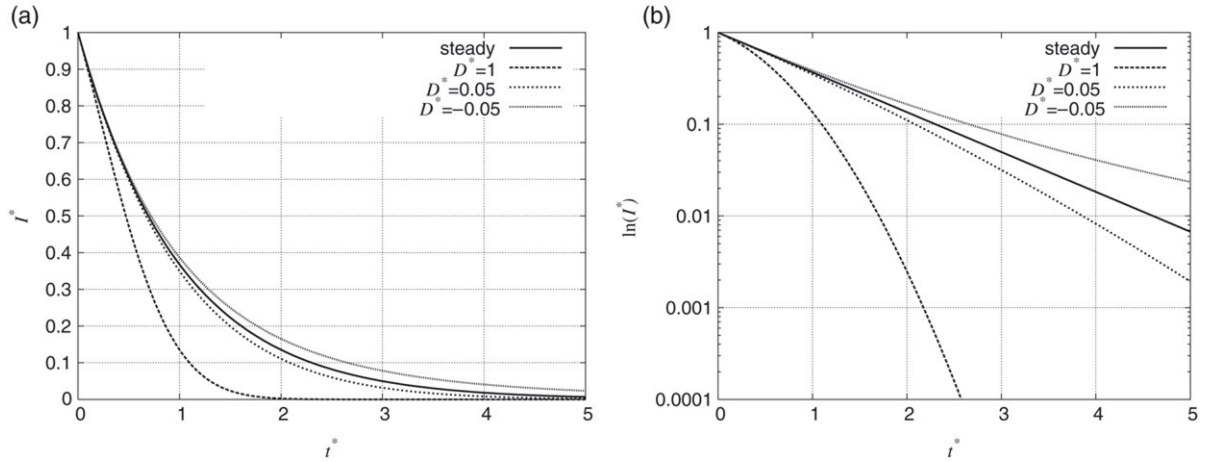


Fig. 1. Normalized intensity as a function of number of time constants for various values of the non-dimensional group  $D^* = \zeta/2\nu^2$ . Both plots are of the same data; (a) shows the intensity, and (b) shows the log of the intensity. Note that the steady case is a line on the log plot.

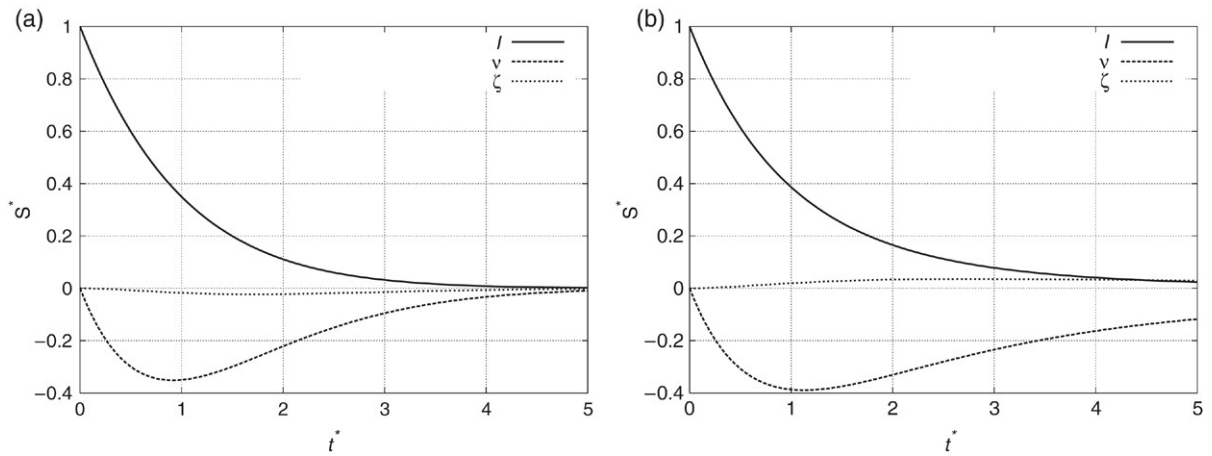


Fig. 2. Normalized sensitivity coefficients for (a)  $D = 0.05$  and (b)  $D = -0.05$ .

with respect to the parameters, given as

$$S_I = \exp \left[ -t \left( \nu + \frac{\zeta}{2} t \right) \right], \quad (14)$$

$$S_\nu = -I_o t \exp \left[ -t \left( \nu + \frac{\zeta}{2} t \right) \right], \quad (15)$$

$$S_\zeta = -\frac{I_o}{2} t^2 \exp \left[ -t \left( \nu + \frac{\zeta}{2} t \right) \right]. \quad (16)$$

We immediately notice that none of these values are linearly dependent, which means that we should be able to estimate all three parameters simultaneously. The normalized sensitivities are plotted in Fig. 2. Again it is clear from the figures that the parameters are not linearly dependent. However, the sensitivity coefficient for  $\zeta$  is considerably smaller than that of the other parameters, which means that the confidence interval on the estimate will be large. Yet, the sensitivities are non-linear in the parameters, so different heating scenarios will result in different levels of sensitivity. For example, a value of  $D^* = 0.1$  (more heating) results in sensitivities of similar magnitude; a value of

$D^* = 0$  (no heating) results in a zero sensitivity. For positive  $D^*$  (heating), the sensitivities all approach zero for large  $t^*$  suggesting that the data for  $t^* > 3$  will not improve the estimate of any of the parameters significantly. We also notice that at least two time constants worth of data are required to reduce the uncertainty in the estimate of the  $\zeta$  parameter. For negative  $D^*$  (cooling), we notice that the greatest sensitivity in the  $\zeta$  parameter is for later times. However, we know that at later times, the noise is much greater than the signal. Therefore, we expect a large uncertainty in the estimates of negative  $\zeta$ .

### 3. Experiments and data

To evaluate the ability of a transient model to recover transient features, test data were developed to mimic actual test conditions. The experimental setup consists of a 36 gauge NiCr wire treated with  $Mg_4FGeO_4:Mn$  phosphor whose calibration curve is shown in Fig. 3. Both decay time and decay rate are shown, but the calibration data were developed using decay time  $\tau$  in Eq. (1). We showed that for the steady state, the decay rate is simply the inverse of decay time  $\nu = 1/\tau$ . The

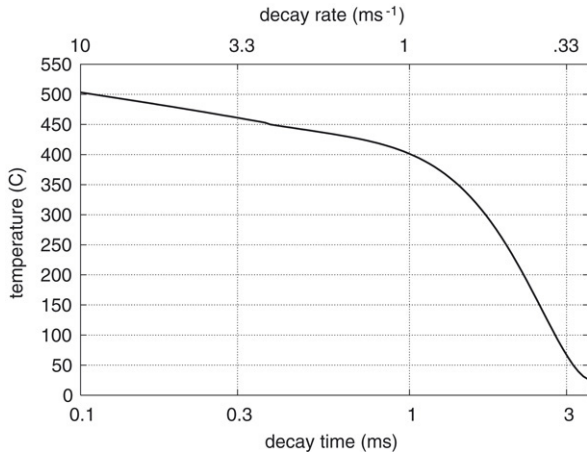


Fig. 3. Calibration curve for  $\text{Mg}_4\text{FGeO}_4:\text{Mn}$  phosphor in terms of decay time. The unit  $\text{ms}^{-1}$  is equivalent to kHz, but kHz is not used because the process is not cyclical.

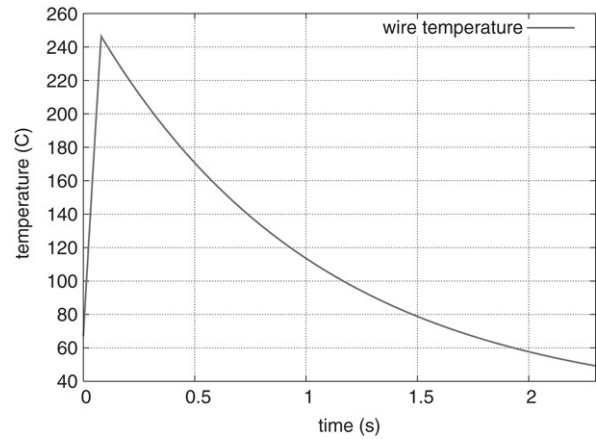


Fig. 5. Wire temperature as predicted from a lumped model knowing the generation rate.

Power is applied to the wire for a short time (80 ms) and then turned off allowing the wire to cool for a total cycle time of 2.3 s. This cyclic heating is accomplished by the *pulsed current generator* in Fig. 4. The *delay generator* provides a trigger to fire the laser at a fixed time relative to the heating pulse. Therefore, each phosphor measurement occurs at the same time during the heating pulse where the temperature and rate of temperature rise are the same. Therefore, multiple measurements can be averaged to reduce noise in the data.

#### 4. Results

The time of the laser pulse is adjusted to collect phosphor data at various times during the pulse. Based on the power input to the wire, we can approximate the expected temperature history of the wire during the heating/cooling cycle from a lumped model as

$$\frac{T(t) - T_\infty - GR}{T_i - T_\infty - GR} = \exp\left(-\frac{t}{RC}\right), \quad (17)$$

where  $G$  is the generation rate,  $R$  is the convective resistance,  $T_i$  and  $T_\infty$  are the initial and ambient temperatures, respectively, and  $C$  is the thermal capacitance of the NiCr wire. Note that this formulation can also be used during cooling where  $G = 0$  and  $T_i$  is equal to the peak temperature after heating. Although we do not know  $R$  and  $C$ , we can estimate the product  $RC$  by setting the final temperature of the cooling phase to the initial temperature of the heating phase. This assumption is valid for a steady periodic system. Now we have two equations (one for heating and one for cooling) and two unknowns ( $R$  and  $RC$ ) as long as we make some reasonable assumptions about the ambient and initial temperatures. The generation rate  $G$  is measured. From this crude model, which is shown in Fig. 5, the expected temperature rise can be estimated. During heating, the total temperature rise is  $\sim 180^\circ\text{C}$  over 80 ms heating time. Therefore an average heating rate is  $\Delta T/\delta t = 2250 \text{ K s}^{-1}$ . At the temperatures of interest, we see that the decay time is of the order of 2.5 ms from Fig. 3.

Therefore, we might expect the temperature to rise by  $\sim 18^\circ\text{C}$  over three decay times, which is the portion of the

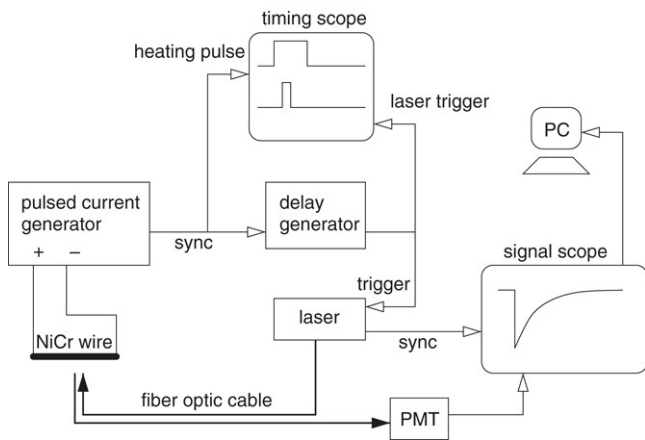


Fig. 4. Experimental setup used to measure temperature of a heated wire.

phosphor was applied to the NiCr wire by dipping the wire in an alcohol/phosphor slurry. The coating dried in a few minutes at room temperature.

The phosphor was excited with a nitrogen laser, which provides an instantaneous excitation compared to the decay. Data were collected with a photomultiplier tube (PMT) for a short period of time before the laser pulse to determine the measurement offset usually found in detection equipment. PMTs are light detectors that are useful in low intensity applications such as fluorescence spectroscopy. Due to high internal gain, PMTs are very sensitive detectors. This also means that the signal often contains a good bit of noise. The setup is shown in Fig. 4. Emission data with a peak emission intensity of  $-0.8 \text{ V}$  were collected for a total shot time of 0.01 s, which resulted in 3–4 decay times (depending on temperature).

When steady-state data are collected, multiple measurements can be made and averaged to reduce the experimental noise. For transient measurements, we only get a single shot. However, we have devised a steady-periodic heating scheme that allows us to average measurements as long as the measurements are taken at the same time during the heating cycle.

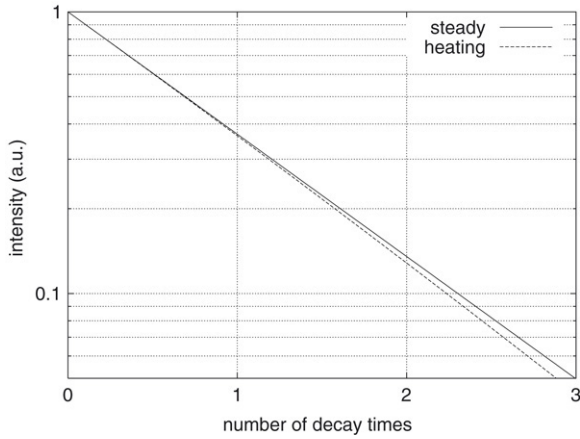


Fig. 6. Expected decay curves for the steady model with  $\tau = 0.0025$  and the transient model with  $\xi = 0.013$ .

Table 1  
Heating parameters for a single decay measurement

$t_i = 0$ s	$t_f = 0.0075$ s	Rate
$\tau_i = 0.0025$ s	$\tau_f = 0.0024$ s	$\xi = -0.13$
$T_i = 146.98$ °C	$T_f = 165.73$ °C	$2500$ K s <sup>-1</sup>
$\nu_i = 400$ s <sup>-1</sup>	$\nu_f = 416.67$ s <sup>-1</sup>	$\zeta = 2222$ s <sup>-2</sup>

The initial and final times refer to the beginning of a phosphor decay measurement and three decay times later. The rate is computed as  $A_f - A_i / \Delta t$ , where  $A$  is the variable of interest.

decay where reasonable data can be collected. Consequently, the steady-state decay time will change from 0.0025 s to  $\sim 0.0024$  s or nearly 4%. While this change may seem modest, we can compare the emission of a phosphor governed by Eq. (3), where  $\xi \approx \Delta\tau / \Delta t = -0.0001$  s/0.0075 s =  $-0.013$  to the steady solution for  $\tau = 0.0025$ . Fig. 6 shows the steady model (Eq. (1)) along with the transient model (Eq. (3)) on a log plot. The steady case is linear on a log plot, but the heating case is not. If we assume that the non-linear (heating) response is the measurement and try to predict temperature using the steady model by fitting a line to the curved response, we underestimate the temperature by  $\sim 10$  °C, which would place the estimate at the average of the initial temperature and the temperature at three decay times.

Measurement noise will further increase confidence intervals on the parameter estimates. To evaluate this effect, we generate artificial data with normally distributed random noise. Table 1 shows the parameters that govern the temperature change for a single decay during the heating. The values are representative of the heating seen in Fig. 5 of the lumped model. The amount of noise added is characterized by the standard deviation of the normally distributed random noise.

The sum of squares of the residual,

$$\chi^2 = \frac{\sum_{i=1}^N [I_i - I(t_i)]^2}{N - p}, \quad (18)$$

where  $N$  is the number of data points and  $p$  is the number of estimated parameters, gives an idea of the error associated

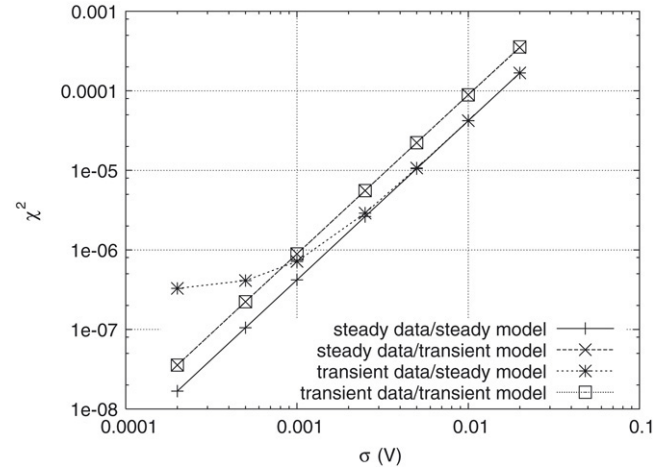


Fig. 7. RMS of the residual ( $\chi^2$ ) as a function of measurement noise.

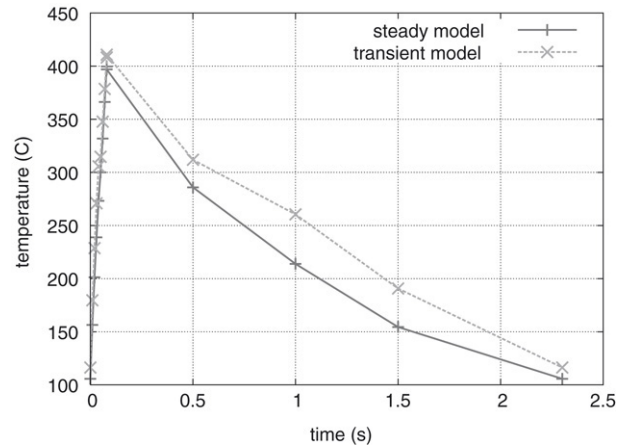


Fig. 8. Temperature estimates of the heated wire from phosphor decay measurements using both a steady model and a transient model.

with the fit. Fig. 7 shows the error in the fit as a function of the added noise. If the model matches the data, then the error should be a linear function of the noise. In this case, the steady model does not match well with the transient data as expected, but only for small noise levels. If the noise level is large, then these errors overwhelm the errors associated with the model not fitting the data well. Also we notice that the transient error is larger than the steady error. This is expected because of the increased number of degrees of freedom in the transient model and does not indicate a “worse” fit compared to the steady model.

Fig. 8 shows the temperature of the heated NiCr wire as estimated from phosphor measurements using both the steady model and the transient model.

We concede that the transient model will have more uncertainty in the estimates, for the simple fact that the number of degrees of freedom is larger due to the additional parameter being estimated compared to the steady model. Therefore, the estimates may contain more variability. Nevertheless, the trend is undeniable. The transient estimate is indeed everywhere greater than estimates from the steady model.

## 5. Conclusions

Thermographic phosphors have been used to measure steady temperatures in the past, but transient measurements, where the temperature changes significantly during the decay of the phosphor, have not been addressed. A new model for capturing transient temperatures with thermographic phosphor measurements was presented. The sensitivity of the additional free parameter required to describe the transient effect is small for small values of the non-dimensional group  $D^* = \zeta/2v^2 < 0.05$ . Nevertheless, estimates indicate that the transient model can predict the temperature at the beginning of the phosphor decay more accurately than the steady model. We also found that measurement noise greater than 1% of the maximum signal mitigates the effectiveness of the transient model over the steady model. This threshold is also a function of  $D^*$  and could improve with larger  $D^*$ . Therefore, additional tests need to be designed using different phosphors and different heating rates to explore larger values of the dimensionless group  $D^*$ .

## Acknowledgment

This work was supported in part through a summer faculty fellowship from the Heating, Cooling and Power Group in the Engineering Science and Technology Division at Oak Ridge National Lab.

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