TEMPERATURE DEPENDENT LUMINESCENCE OF $CaWO_4$ AND $CdWO_4$

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ABSTRACT

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The relative efficiencies and decay times of alpha particle induced scintillations of $CaWO_4$ and $CdWO_4$ were investigated as a function of temperature in the range 10°K to 375°K. Their behavior at intermediate and high temperatures is in agreement with that expected from the Mott-Seitz-Kröger configurational coordinate model. Values of E_Q, thermal quenching energy, of 0. 34 and 0. 31 ev were found for $CaWO_4$ and $CdWO_4$, respectively. As the temperature was decreased below 60°K, an increase in the decay times and a decrease in the relative efficiencies were found. This behavior can be explained qualitatively by assuming a trapping level.

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By

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I. INTRODUCTION

Both $CdWO_4$ and $CaWO_4$ crystals have been known to be good scintillators for some time.[1] Because of their high densities and high atomic numbers, the crystals have relatively high photo-efficiencies. However, they have the disadvantage of a long scintillation decay time which makes them poor for high counting rate experiments. It is only recently that their scintillation properties have been studied in some detail in connection with their use for certain specific investigations.[2,3] These investigations included a search for the natural alpha activities of tungsten in $CaWO_4$ and $CdWO_4$ and the relative energy response of $CaWO_4$ to various sources of excitation.

I have undertaken a study of the effect of temperature on the scintillation efficiencies and decay times of $CaWO_4$ and $CdWO_4$ crystals primarily to ascertain whether the scintillation response could be improved by operating in a particularly favorable temperature range. Kröger[4] has previously investigated the relative luminescent efficiencies of $CaWO_4$ and $CdWO_4$ as a function of temperature using excitation from ultraviolet light ($\lambda = 2537$ Å) in the temperature region from $80^\circ K$ to $480^\circ K$. In the experiment reported here alpha particles from Po^{210} were used as the source of excitation in the temperature region from $10^\circ K$ to $375^\circ K$. Measurements were also made over a limited temperature range using Cs^{137} gamma rays.

II. EXPERIMENTAL ARRANGEMENT

Various crystals of $CaWO_4$ and $CdWO_4$ with dimensions of about 10 mm x 5 mm x 3 mm were used. The crystals were polished such that one side was flat. This side was placed in direct contact with a light pipe. On the side opposite the flat side, a drop of $Po^{210}NO_3$ solution was placed and evaporated to dryness. A counting rate of roughly 6000 counts/minute was used with all crystals. The crystal and the remaining exposed end of the light pipe were covered with a thin layer of MgO, aluminum foil, and black electrical tape. Using this arrangement, little difficulty with light trapping is experienced.[5] A thermocouple and carbon resistance thermometer were mounted in contact with the aluminum foil. The light pipe and crystal were placed in the probe as indicated in Fig. 1.

The temperature of the crystal was measured with a constantan-copper thermocouple in the region from 30°K to 375°K. Below 30°K it was measured with an Allen-Bradley 56 ohm, 1/10 watt, carbon resistance thermometer.

The measurements were divided into five overlapping temperature regions, corresponding to the appropriate temperature baths. In order to obtain temperatures above those of the cooling baths a variable current was passed through a Manganin heating wire wrapped around the probe. The temperature was held to within a variation of 3°K during the 10-minute counting runs in the liquid helium region while for similar runs in the other temperature regions the deviations were less than 1°K. For each

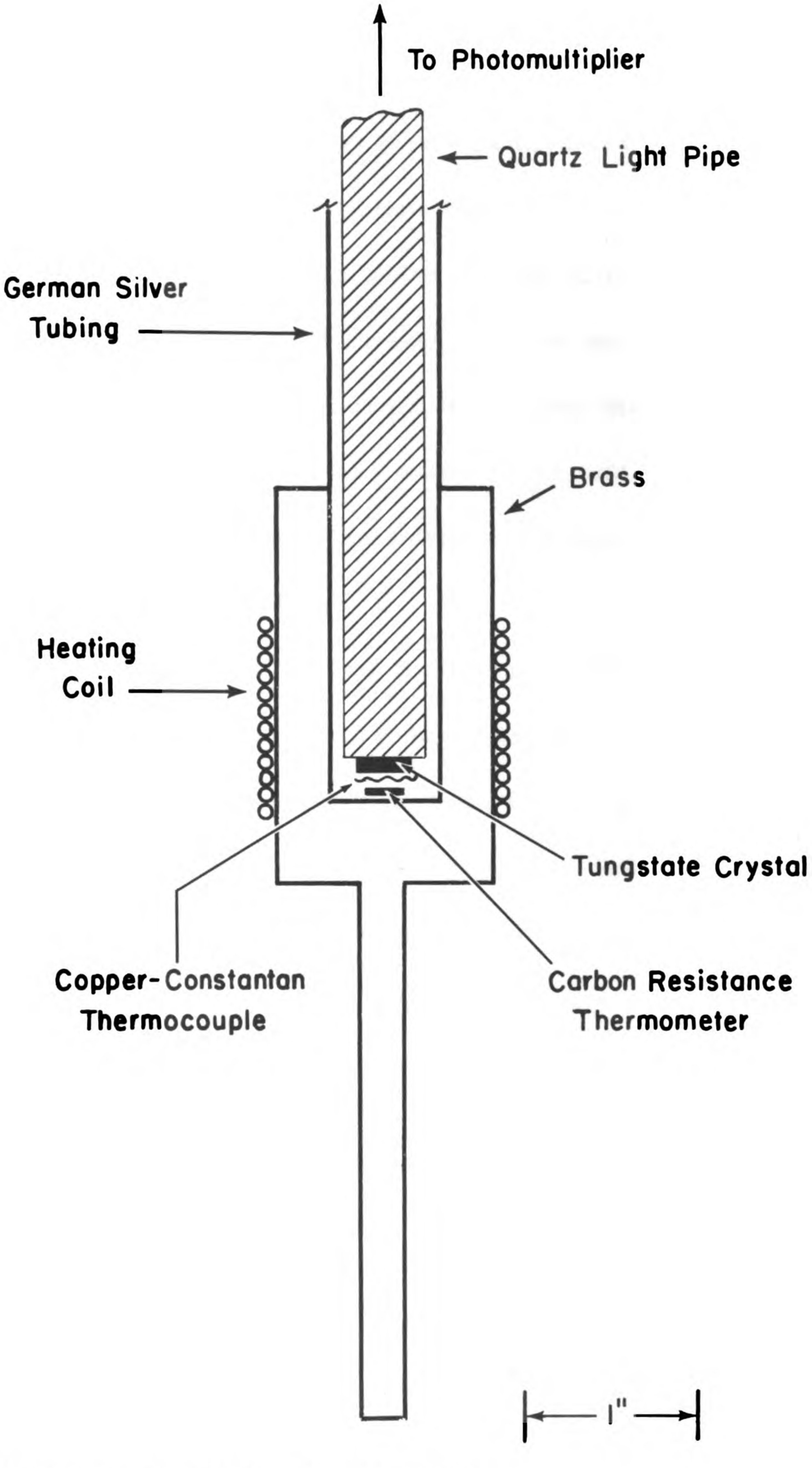

Figure 1. Cross sectional diagram of probe.

point 30 minutes were allowed for temperature equilibrium to be reached throughout the crystal before the data were taken.

To detect the scintillations the light pipe was mounted on RCA 6342 photomultiplier. The anode RC time constant was $\sim 10^{-3}$ sec, and the preamplifier consisted of a conventional White cathode follower. As long as the scintillation decay time is small compared to the anode time constant, the decay time can readily be determined from the rise time of the output pulse and the amplitude of the output pulse will be proportional to the scintillation efficiency.* The photomultiplier temperature was monitored and maintained constant to within 2^{o}C. For various runs light pipes of lucite or quartz were used. The failure to detect any differences in the relative scintillation efficiencies and decay times using the two different light pipes makes it reasonable to assume that any wavelength shifts in the detected luminescence radiation were relatively small. This conclusion is in accord with the results of Kröger[4] who found little change in the emission spectrum in going as low as 80^{o}K using ultraviolet excitation.

As a further precaution an RCA 6903 photomultiplier (quartz window) was also used for runs in the region of 10^{o}K to 90^{o}K. No noticeable change was observed in the scintillations.

A Tektronix 531 oscilloscope was used to observe the output of the preamplifier. The trace of the scope was photographed using exposure times sufficiently long to determine a reliable average of the amplitude and decay time. As a check on and to supplement these measurements a model A-61

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*Appendix I.

amplifier (modified for long rise time pulses) and a 256 channel pulse height analyzer were also used to determine the average pulse height at each temperature. The amplifier-analyzer response was measured using a variable rise time pulser and a correction factor depending on the rise time of the pulse was determined. This factor was used to correct the pulse height data. Measurements were made on the crystal at room temperature before and after each experimental run and were found to agree.

III. RESULTS AND THEIR INTERPRETATION

The analyzer data were compared with the photographic data and the results agreed to within 10% for the relative scintillation efficiencies. Figures 2 and 3 are the results obtained for $CaWO_4$ and $CdWO_4$ with the Po^{210} alphas. The efficiency data represent an average of the results as determined by the two methods. The reciprocals of decay time and relative efficiency are plotted against the reciprocal of the temperature to facilitate the comparison with theory. The efficiency at 273°K is arbitrarily chosen as 100%. The uncertainties in the relative efficiencies and decay times are estimated to be ± 10%.

Within the limits of the experimental accuracy, data obtained using Cs^{137} gamma rays as a source of excitation in a limited region above and below room temperature agree with the results using Po^{210} alphas in the same temperature range. These results are also in agreement with those of Gillette.[5] The absolute scintillation efficiency is greater for gamma ray excitation.[2, 3] Although artificial crystals of $CaWO_4$ were used in this work, previous experience has shown that one obtains similar scintillations using a natural $CaWO_4$ (scheelite) crystal at room temperature.

Relatively little theoretical work has been done on the problem of luminescence in pure (unactivated) crystals. The most recent work on temperature quenching dealing with crystals of the type used here appears to have been done by Kröger[4] and P. T. Botden.[6] The model advanced to explain their work on temperature quenching using ultraviolet excitation also is in agreement with the results reported here for $CaWO_4$ and $CdWO_4$

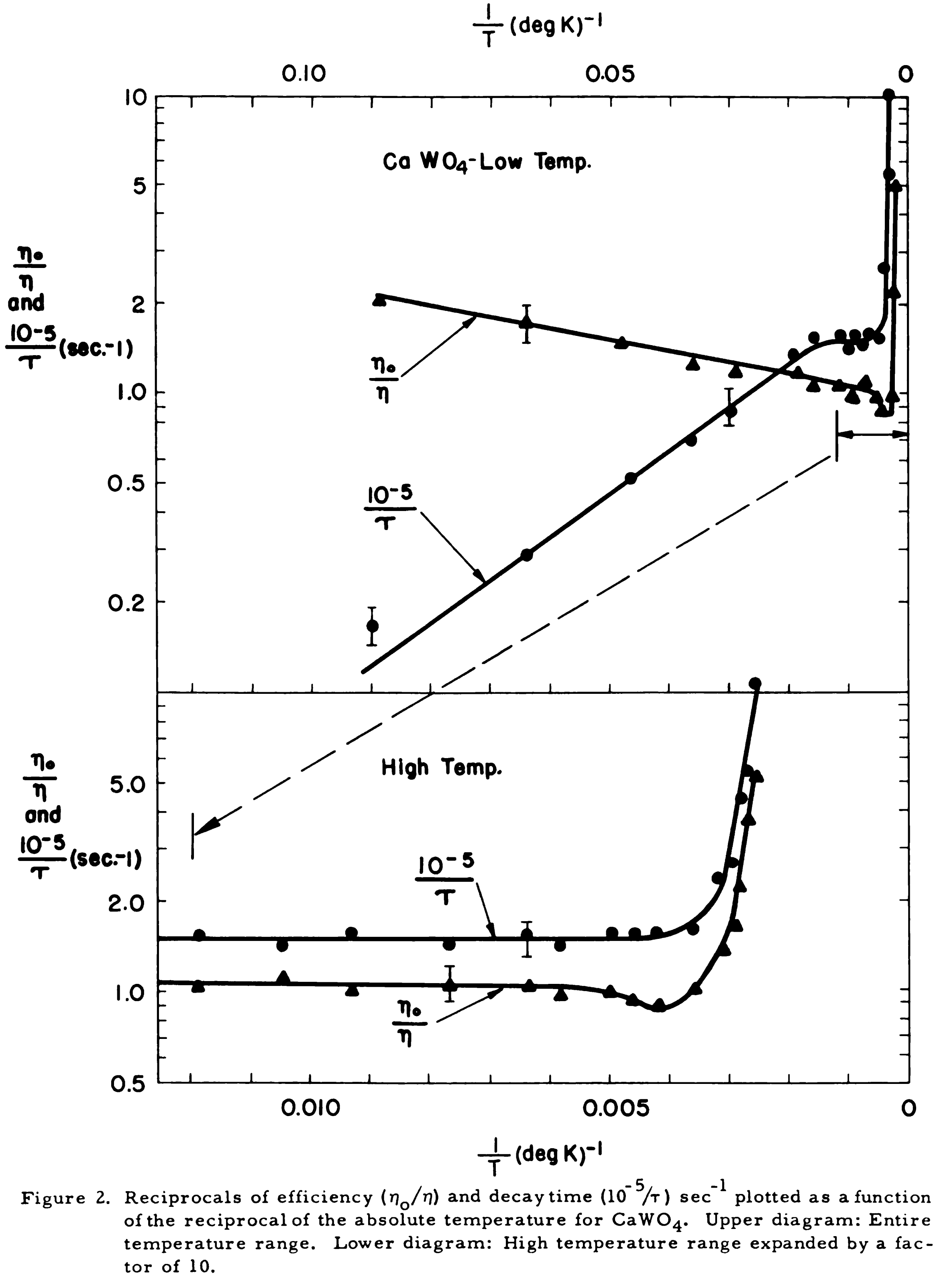

Figure 2. Reciprocals of efficiency (η_o/η) and decay time ($10^{-5}/\tau$) sec^{-1} plotted as a function of the reciprocal of the absolute temperature for CaWO$_4$. Upper diagram: Entire temperature range. Lower diagram: High temperature range expanded by a factor of 10.

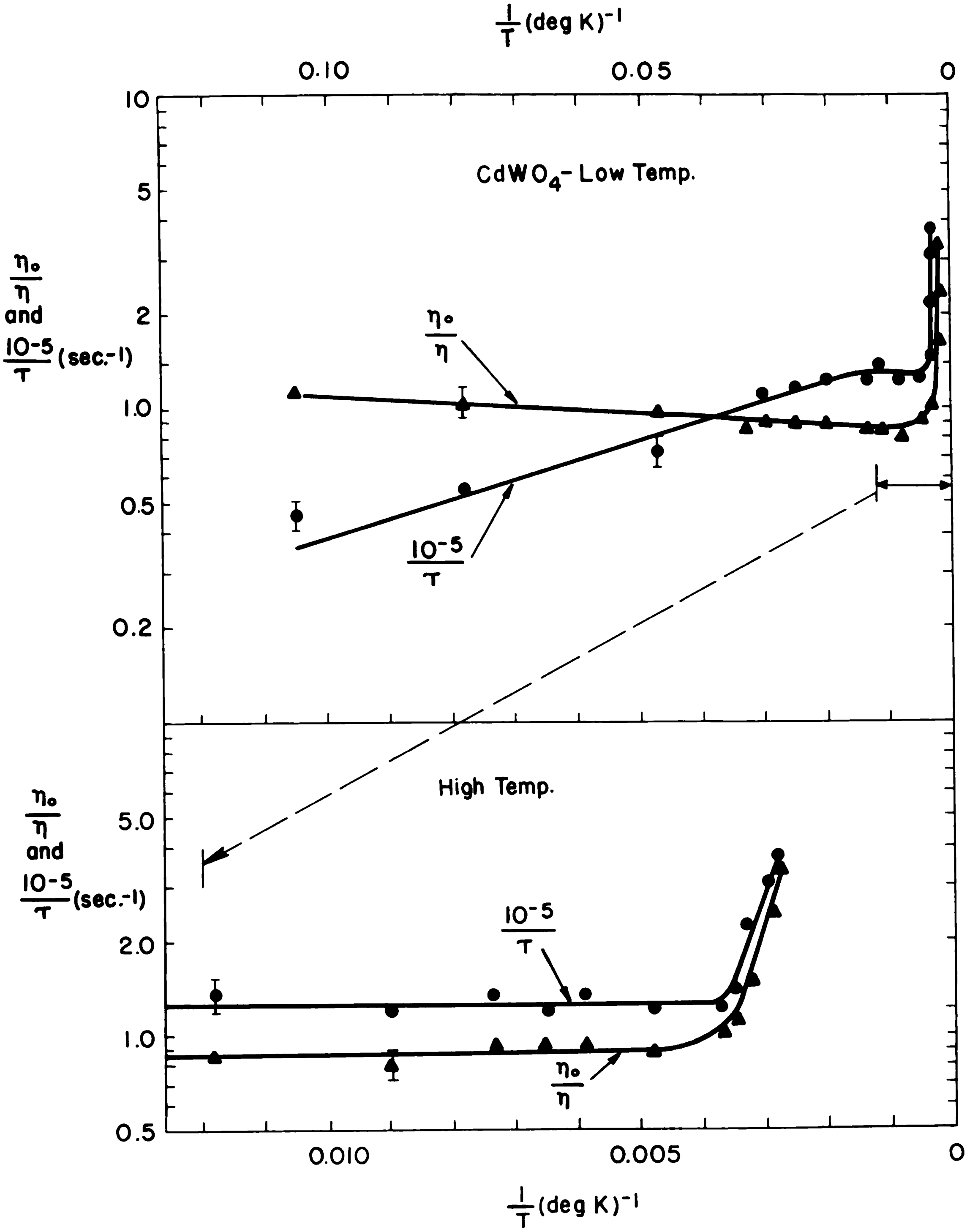

Figure 3. Reciprocals of efficiency (η_o/η) and decay time ($10^{-5}/\tau$) sec^{-1} plotted as a function of the reciprocal of the absolute temperature for CdWO$_4$. Upper diagram: Entire temperature range. Lower diagram: High temperature range expanded by a factor of 10.

in the temperature range above about 60°K. For this temperature region Kröger uses the picture of configuration coordinates as applied to luminescence by Seitz,[7] with the modification as proposed by Gurney and Mott.[8] Figure 4 is a configurational coordinate diagram showing the ground state and only one excited state of a luminescent center. The ordinate of the curves is the total energy of the system, including both ionic and electronic terms. The abscissa is a configuration coordinate which specifies the configuration of the ions around the center. The equilibrium position of the ground state in Figure 4 is at A. If the center is excited, it is raised to the excited state at B. A new equilibrium is obtained at C, with the energy difference between B and C given up as phonon emission. The center then decays from C to D by photon emission and again the energy difference between D and A is given up as phonon emission. The decay from C to D is assumed to be temperature independent. Gurney and Mott proposed that an alternate return to the ground state could occur by a non-radiative transition at E if the excited state at C is given sufficient thermal energy, E_Q. Thus, the photon is not emitted and thermal quenching results. This leads to the following equations[9] for the luminescence efficiency and decay time.*

$$\eta = [1 + S/P_L \exp(-E_Q/kT)]^{-1} \tag{1}$$

$$\frac{1}{\tau} - \frac{1}{\tau_L} = S \exp L - E_Q/kT) \tag{2}$$

where η is the efficiency for luminescence, S is a constant, P_L is the

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*Appendix II.

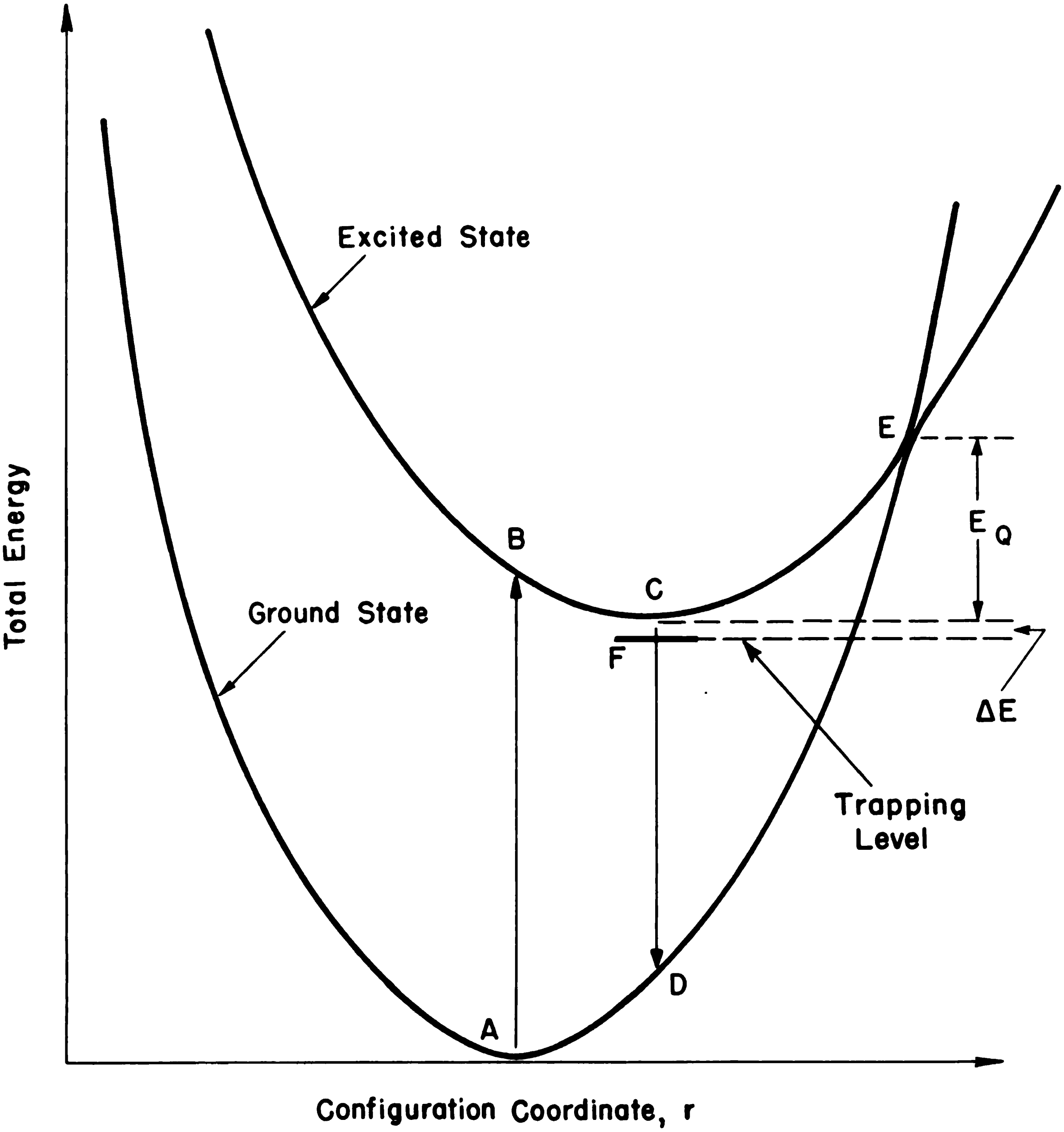

Figure 4. Configuration coordinate diagram.

probability of luminescence with no thermal quenching and equal to $1/\tau_L$, E_Q is the energy difference between states C and E of the excited state, and τ is the measured decay time. It is seen from the data presented in Table I that the value of E_Q determined from the decay time data and scintillation efficiency data agree very well. The value obtained for $E_Q = 0.34$ ev for $CaWO_4$ agrees with that obtained by Botden[6] using ultraviolet light ($\lambda = 2537$ Å) as the source of excitation. It is interesting to note that the E_Q values obtained for $CaWO_4$ and $CdWO_4$ are approximately equal. Table I contains also the values τ_L and S obtained for the two tungstate crystals.

The decay time of $CaWO_4$ at room temperature, $\tau = 5$ microseconds is found to agree with the value given by Dixon and Aitken.[3] The decay time of $CdWO_4$ at room temperature is 7.1 microseconds.

The model used here to picture the luminescence behavior above $\sim 60^\circ K$ does not describe the small dip noted in the luminescence curve for $CaWO_4$ at $\frac{1}{T} = 0.004\ (\mathrm{deg.\,K})^{-1}$. This dip does not have a corresponding variation in the decay time data and does not appear in the $CdWO_4$ data.

In the discussion above it is assumed that both the radiative transition probability and the proportion of the absorbed exciting radiation actually absorbed in fluorescent centers are constant and independent of temperature. According to this picture the luminescence decay times and efficiencies should remain constant below the temperature quenching region. This is in obvious disagreement with the experimental results. However, by a relatively simple modification one can obtain qualitative

TABLE I. Results obtained from the $CaWO_4$ and $CdWO_4$ scintillation efficiencies and decay times

	E_Q from		τ_L, sec	S, sec^{-1}
	Scintillation efficiency data, ev	Decay time data, ev		
$CaWO_4$	(0.34 ± 0.03)	(0.34 ± 0.03)	$(6.7 \pm 0.7) \times 10^{-6}$	$(1.6 \pm 0.8) \times 10^{10}$
$CdWO_4$	(0.30 ± 0.03)	(0.32 ± 0.03)	$(7.8 \pm 0.8) \times 10^{-6}$	$(0.8 \pm 0.8) \times 10^{10}$

agreement between the model and experiment for both the high and low temperature regions.

The proposed modification is as follows:

Assume there exists a metastable level F lying an energy ΔE below C and that this level is preferentially excited from B. See Figure 4. The center may be thermally excited to C from F with a probability proportional to $\exp(-\Delta E/kT)$, where it may decay from C to D by photon emission. Also the center may be de-excited from F to D by an unobserved transition whose rate may or may not be a function of temperature. It should also be assumed that the probability of the de-excitation by the unobserved transition is small compared to that of the thermal excitation to C at temperatures above 60°K. From this picture one would expect the decay time of the transition from C to D to increase and the scintillation efficiency to decrease (approximately as exponentials) as the temperature is decreased below $\Delta E/k$; this is the trend that is observed. If one assumes that the de-excitation of the trapping level by the nonradiative transition is independent of the temperature then one obtains relations for the luminescence efficiency and decay times that are somewhat similar to Eqs. (1) and (2). If one assumes that the state C is de-excited only by a luminescent transition in this temperature region, then the luminescence efficiency is given by the relation

$$\eta = [1 + P_T/S' \exp(\Delta E/kT)]^{-1} \tag{3}$$

where P_T is the probability per unit time for the excitation of the trapping level via the unobserved transition, and S' is a constant.

Since the decay leading to luminescence goes by a cascade of levels, the luminescence decay is not a simple exponential in time and hence the decay time data are not easily compared with the formulas. Applying equation (3) to the data, one obtains $\Delta E \approx .0023$ ev for $CaWO_4$ and $\Delta E \approx .0026$ ev for $CdWO_4$ with $P_T/S' \approx .010$ and .016 for the two crystals respectively.

Assuming the decay time from the trapping level is temperature independent, an order of magnitude for the decay time from the trapping level by the non-radiative transition can be estimated to be $\gtrsim 50$ microseconds.

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APPENDIX I

Time Constant and Decay Time Relations

Figure 5 is the schematic diagram of the preamplifier. Figure 6 is a simplified diagram of the photomultiplier anode circuit and block diagram of the electronics. Where R is the photomultiplier anode resistance to ground and C is the distributed capactiance to ground. If the scintillation decay is assumed to be exponential,

$$I(t) = A/\tau\, e^{-t/\tau} \qquad (4)$$

where I(t) is the current, A is a constant, τ is the decay time, and t is time. By simple circuit analysis,

$$I(t) = V/R + CdV/dt \qquad (5)$$

where V is the voltage across the anode resistance. Equating (4) and (5) and solving for V(t), using the initial condition that V(t) = 0 at t = 0, equation (6) is obtained.

$$V(t) = A/C \left(\frac{RC}{RC - \tau}\right)\left(e^{-t/RC} - e^{-t/\tau}\right) \qquad (6)$$

If the anode circuit is made to integrate, $RC >> \tau$, then

$$V(t) = A/C\,(1-e^{-t/\tau}) \qquad (7)$$

In the experiment, one measure V(t) C/A as a function of t and is thus able to obtain τ.

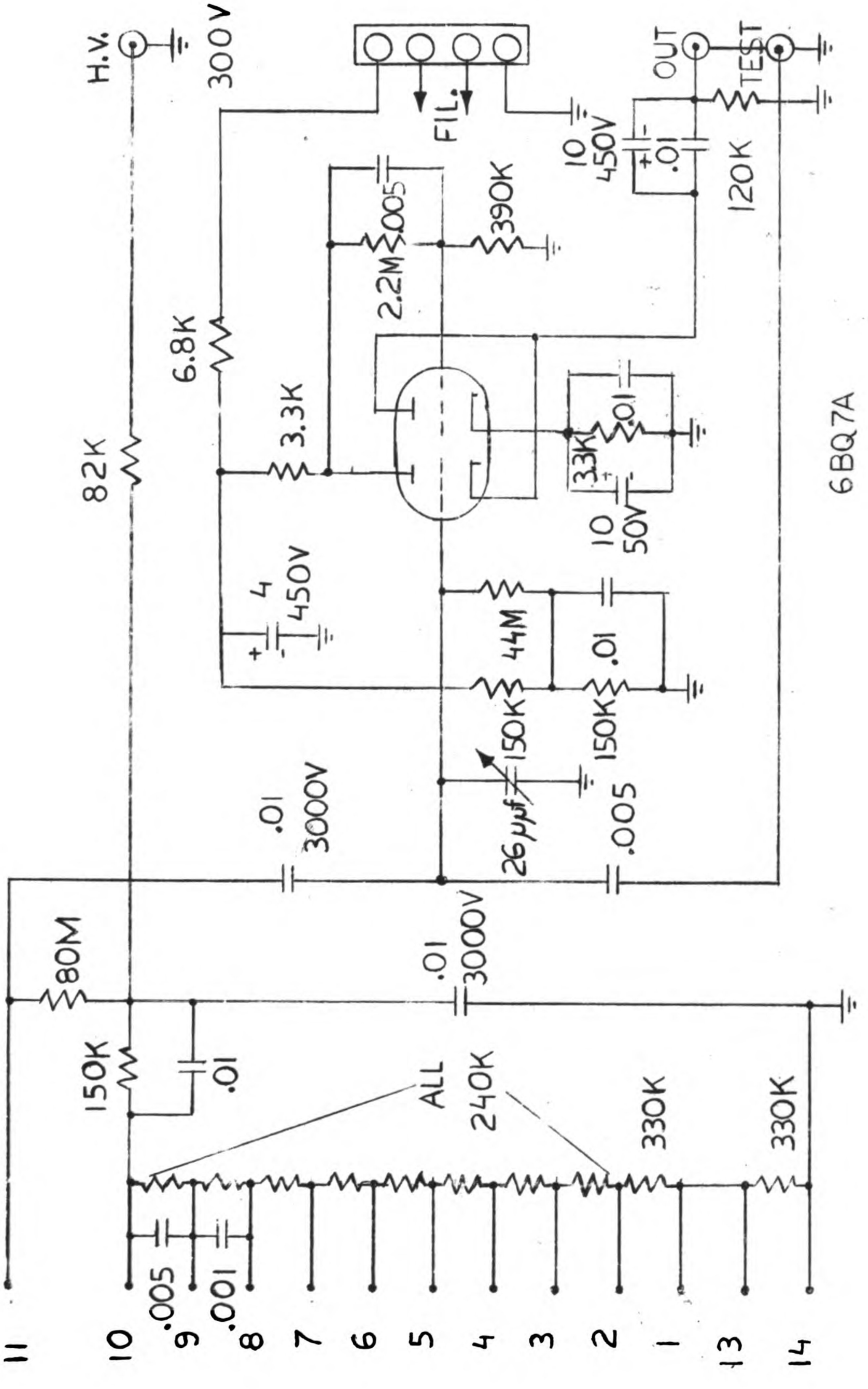

Figure 5. White cathode follower preamplifier circuit

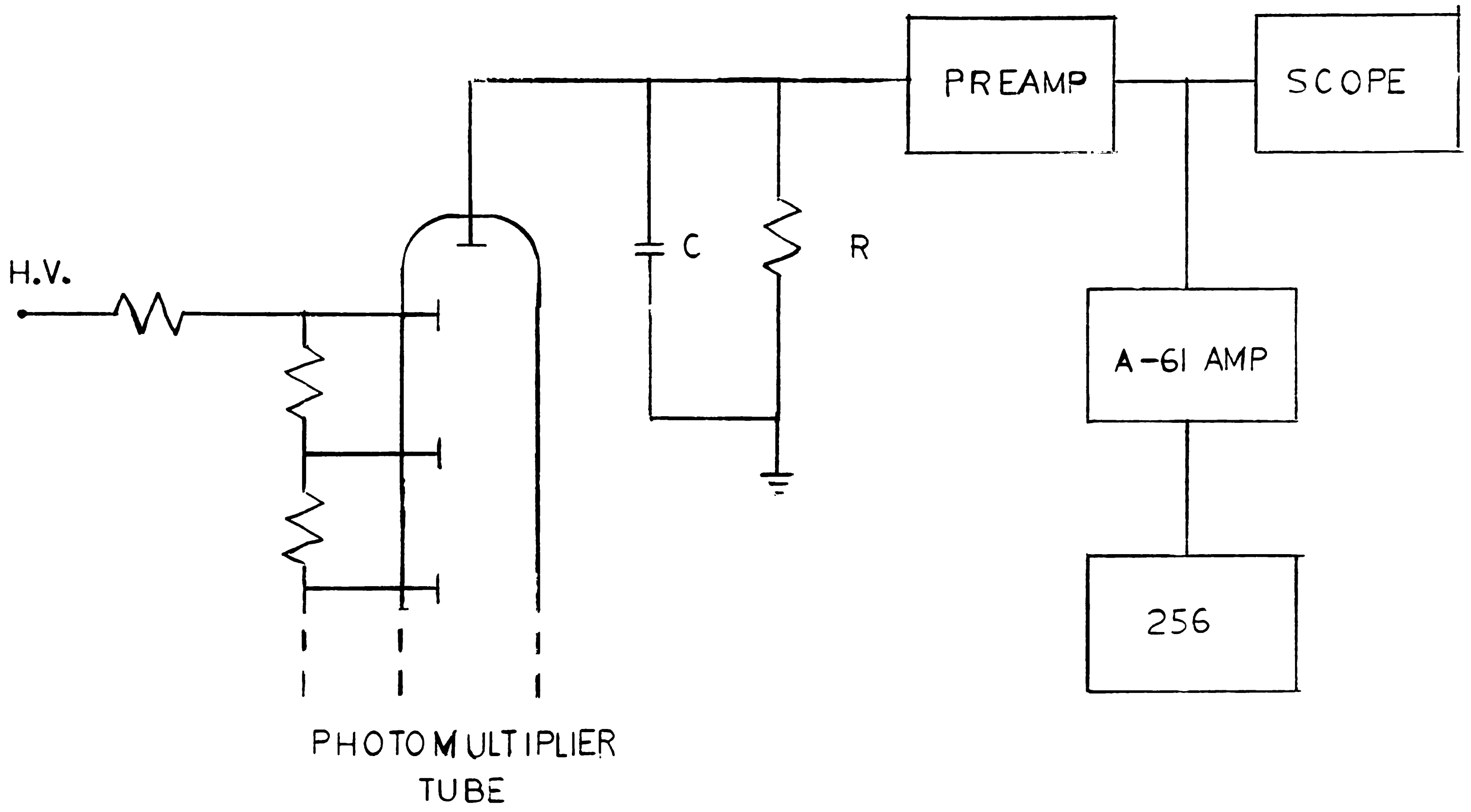

Figure 6. Simplified diagram of the photomultiplier anode circuit and block diagram of detection system. "Preamp." signifies White cathode follower preamplifier, "Scope" oscilloscope, "Amp." amplifier, "256" the 256-channel pulse height analyzer.

APPENDIX II

Efficiency and Decay Time Relation

The efficiency for luminescence η in the high temperature region is given by,

$$\eta = P_L/(P_L + P_Q) \tag{8}$$

where P_L is the probability per unit time of a luminescence transition and P_Q is the probability per unit time for thermal quenching. P_L and P_Q are two competing processes. P_L is assumed to be independent of the temperature and P_Q to be temperature dependent. Gurney and Mott proposed that P_Q could be represented by $S\exp(-E_Q/kT)$.[8] Substituting this into equation (8), the following results are obtained.

$$\eta = [1 + S/P_L \exp(-E_Q/kT)]^{-1} \tag{1}$$

The decay time τ is given by,

$$1/\tau = 1/\tau_L + 1/\tau_Q \tag{9}$$

where $\tau_L = 1/P_L$ is the decay time for luminescence independent of temperature and $\tau_Q = 1/P_Q$ is the decay time for temperature quenching. Using the assumption of Gurney and Mott, equation (2) is obtained.

$$(1/\tau - 1/\tau_L) = S \exp(-E_Q/kT) \tag{2}$$

In the experiment, τ_L is assumed to be the decay time in the temperature region 60°K to 250°K.