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LASER-INDUCED FLUORESCENCE OF PHOSPHORS FOR REMOTE CRYOGENIC THERMOMETRY

D. L. Beshears
G. J. Capps
M. R. Cates
C. M. Simmons

Applied Technology Division

S. W. Schwenterly

Fusion Energy Division

Oak Ridge National Laboratory
Oak Ridge, Tennessee

Laser-induced fluorescence of phosphors for remote cryogenic thermometry

D. L. Beshears
G. J. Capps
M. R. Cates
C. M. Simmons
S. W. Schwenterly

Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37831-7280

ABSTRACT

Remote cryogenic temperature measurements can be made by inducing fluorescence in phosphors with temperature-dependent emissions and measuring the emission lifetimes. The thermographic phosphor technique can be used for making precision, non-contact, cryogenic temperature measurements in electrically hostile environments, such as high DC electric or magnetic fields. NASA is interested in utilizing these thermographic phosphors for mapping hot spots on cryogenic tank walls. Europium-doped lanthanum oxysulfide (La_2O_2S:Eu) and magnesium fluorogermanate doped with manganese ($Mg_4(F)GeO_6$:Mn) are suitable for low-temperature surface thermometry. Several emission lines, excited by a 337 nm UV laser, provide fluorescence lifetimes having logarithmic dependence with temperatures from 4 to 125 Kelvin. A calibration curve for both La_2O_2S:Eu and $Mg_4(F)GeO_6$:Mn are presented as well as emission spectra taken at room temperature and 7 Kelvin.

2. INTRODUCTION

Surface temperatures of moving objects, objects restricted from direct contact with a thermal probe, or large areas were temperature surveys are needed can be very difficult to measure with conventional techniques. One method of accomplishing these measurements is to coat the surface area of interest with a temperature dependent phosphor and induce fluorescence by excitation with ultraviolet radiation. The emission lifetime and intensity at certain wavelengths are directly dependent on temperature. Studies with various doped phosphors at high temperatures have been effected with great success and have added a new dimension to thermometry. A need for this remote thermal ability at cryogenic temperatures exists in areas such as space vehicles and exploratory machinery. This paper will investigate the use of lanthanum oxysulfide doped with europium (La_2O_2S:Eu) and magnesium fluorogermanate doped with manganese ($Mg_4(F)GeO_6$:Mn) for temperature measurements over the range of 4 to 80 K. Temperature calibration curves for La_2O_2S:Eu and $Mg_4(F)GeO_6$:Mn at cryogenic temperatures will be presented.

3. THERMOGRAPHY PHOSPHORS CHOSEN FOR CRYOGENIC MEASUREMENTS

Strong temperature dependence exist in the lanthanum oxysulfide phosphor because of the competition between nonradiative-lattice de-excitation processes and photon-emitting de-excitation within the europium electronic levels. The trivalent europium ion has several metastable states from which fluorescent emission occurs. Details of this interaction are described by Fonger and Struck.[1]

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From the studies by Fonger and Struck, as well as earlier Oak Ridge studies[1-4] of La_2O_2S:Eu, its temperature dependency from approximately 80 to above 500 K is well documented. The room temperature emission and excitation spectra for La_2O_2S:Eu are shown in Fig. 1.

The second phosphor chosen for our evaluation was $Mg_4(F)GeO_6$:Mn. The emission lifetime or fluorescent decay time exhibits a reproducible variation over a range of temperature between -180°C and +450°C.[5] We will explore the region between absolute zero and -180°C. Figure 2 shows the room temperature emission and excitation spectra for $Mg_4(F)GeO_6$:Mn.

Figures 3 and 4 show emission spectra for each of the phosphors for a given cryogenic temperature. In our initial screening process we found that both the La2O_2S:Eu and $Mg_4(F)GeO_6$:Mn showed excellent potential in the temperature range of interest. With the La_2O_2S:Eu the fluorescence lines of interest for the cryogenic temperatures were 418 and 446 nm, although we also monitored the 514-, 538-, and 624-nm lines. When looking at the $Mg_4(F)GeO_6$:Mn, the 657-nm lines showed cryogenic temperature dependence. We also monitored the 623- and 638-nm lines.

Measurements with La_2O_2S:Eu near room temperature have exhibited temperature dependency as to allow determinations with <0.5°C uncertainty.[4] In these initial feasibility studies, accuracy was not the issue but rather determining if phosphor thermography could be used to measure cryogenic temperatures in the region of 4 to 80 K. Thus, the main objective of this report is to present data which have been collected on La_2O_2S:Eu and $Mg_4(F)GeO_6$:Mn at temperatures ranging from 4 to 80 K.

4. DESCRIPTION OF THE THERMOGRAPHIC CRYOSTAT

The design objective was to provide a variable-temperature cryostat that could be used to investigate various phosphors' responses to cryogenic temperatures from liquid nitrogen (LN) down to liquid helium (LHe) temperatures. Such an apparatus was designed and fabricated and will be described in the following paragraphs.

The cryostat shown in Figs. 5 and 6 was designed to fit an existing research Dewar. Figure 7 gives a detailed cross-sectional view of the thermographic phosphor sample holder. The phosphor was placed in a 0.64-cm diam cup in the end of a copper spindle. A heater was wrapped around the spindle just below the phosphor cup. A thermocouple (Au-0.07%Fe vs chromel) junction was mounted just below the cup to provide for temperature measurements. The reference junction for this thermocouple was immersed in the LHe bath at 4.16 K. Thus, the temperature differentials relative to the LHe bath temperature could be measured. Using standard thermocouple tables, an accuracy of >1 K could be obtained. A vishay cryogenic linear temperature sensor (CLTS) was also mounted on the copper spindle to allow additional absolute temperature measurements with a precision of ~2 K.

The copper spindle was sealed into a 0.64-cm Swagelok fitting that was welded into a long, 1.91-cm-diam, stainless-steel tube. Thus, the measurements could be carried out with either vacuum or helium vapor around the phosphor. Two optical fibers were mounted in the tube to bring in the 337-nm ultraviolet (UV) light from a nitrogen laser and transmit the emitted light back out to the monochrometer. The Swagelok fitting could be unscrewed to allow a new phosphor to be evaluated. A piece of 1.27-cm-diam thin-wall stainless-steel tubing extended from the spindle down into the LHe bath. A 25-turn-length of 0.1-cm-diam copper wire was wrapped around this tube to provide a heat leak from the bath to the spindle. The thermocouple, CLTS, and heater leads come through this tube and exited into the bath. The leads were hermetically sealed into the end of the copper spindle with Stycast 2850FT epoxy.

In operation, the phosphor tube and Dewar were evacuated and purged with helium gas. The Dewar was then filled with LHe to the desired level. If the temperature desired was at or near LHe temperature, the level was raised until the copper spindle was immersed. The temperature of the phosphor could be increased by elevating the spindle with respect to the LHe level or energizing the heater to provide fine temperature control. The temperature could be controlled within 0.1 K during a measurement sequence on the phosphor.

5. SETUP FOR CRYOGENIC TEMPERATURE MEASUREMENTS

A schematic of the screening and calibration setup is shown in Fig. 8. A pulsed- nitrogen laser (337-nm wavelength) was used to produce the excitation signal. The signal was carried from the laser via an optical fiber (600-μm-diam, plastic-coated silica) to the sample that consisted of a thin packed film of the phosphor of interest. The phosphor was housed in the copper spindle cup described under in the previous section where the technique for controlling the temperature is also described. The cooling liquid was supplied by a 1000-L LHe storage Dewar to the cryogenic research Dewar.

The fluorescent emission signal was picked up by the same type of optical fiber mentioned previously and carried into a monochrometer where the wavelength was selected. The signal then entered the photomultiplier tube from which the amplified signal was displayed on a Tektronics 7854 waveform-analyzing oscilloscope. The fluorescent signals were then permanently stored on a computer via a GPIB interface. Fluorescent-emission spectral information was also obtained at different temperature levels by automatically varying the emission wavelength on the monochrometer and recording the output of the photomultiplier on a strip-chart recorder.

6. COLLECTING AND ANALYZING THE TEMPERATURE DATA

Several runs were made in each temperature range for the La_2O_2S:Eu, and each temperature datum was the average of four individual readings. This calibration study concentrated on a temperature range between 4 and 80 K, and several higher-temperature points were taken to verify concurrence with previously obtained data. The 446-nm-emission line representing the $^5D_3$ transition was examined, and a plot of the results of this investigation, as well as our earlier investigation, are shown in Fig. 9. The temperature, in Kelvin, is plotted against the log of the emission lifetime in microseconds.

Program limitations did not allow a thorough investigation of the $Mg_4(F)GeO_6$:Mn phosphor. A cursory at the $Mg_4(F)GeO_6$:Mn indicated that it could be use as a cryogenic thermometer. The 657-nm emission line was examined over the range of 13 to 145 K. The data are plotted in Fig. 12 as the temperature in Kelvin vs the log of the emission lifetime in milliseconds. In the future, we hope to be able to perform a more extensive and detailed calibration study of the $Mg_4(F)GeO_6$:Mn.

7. CONCLUSION

Both the europium-doped lanthanum oxysulfide, and manganese doped magnesium fluorogermanate phosphors can be used for remote cryogenic temperature sensing. Moving, inaccessible, or hazardous cold environments can be thermally investigated using these phosphor techniques. Additional research is needed to fully exploit the potential in this area. Different phosphors and rare earths should be investigated.

8. ACKNOWLEDGEMENTS

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9. REFERENCES

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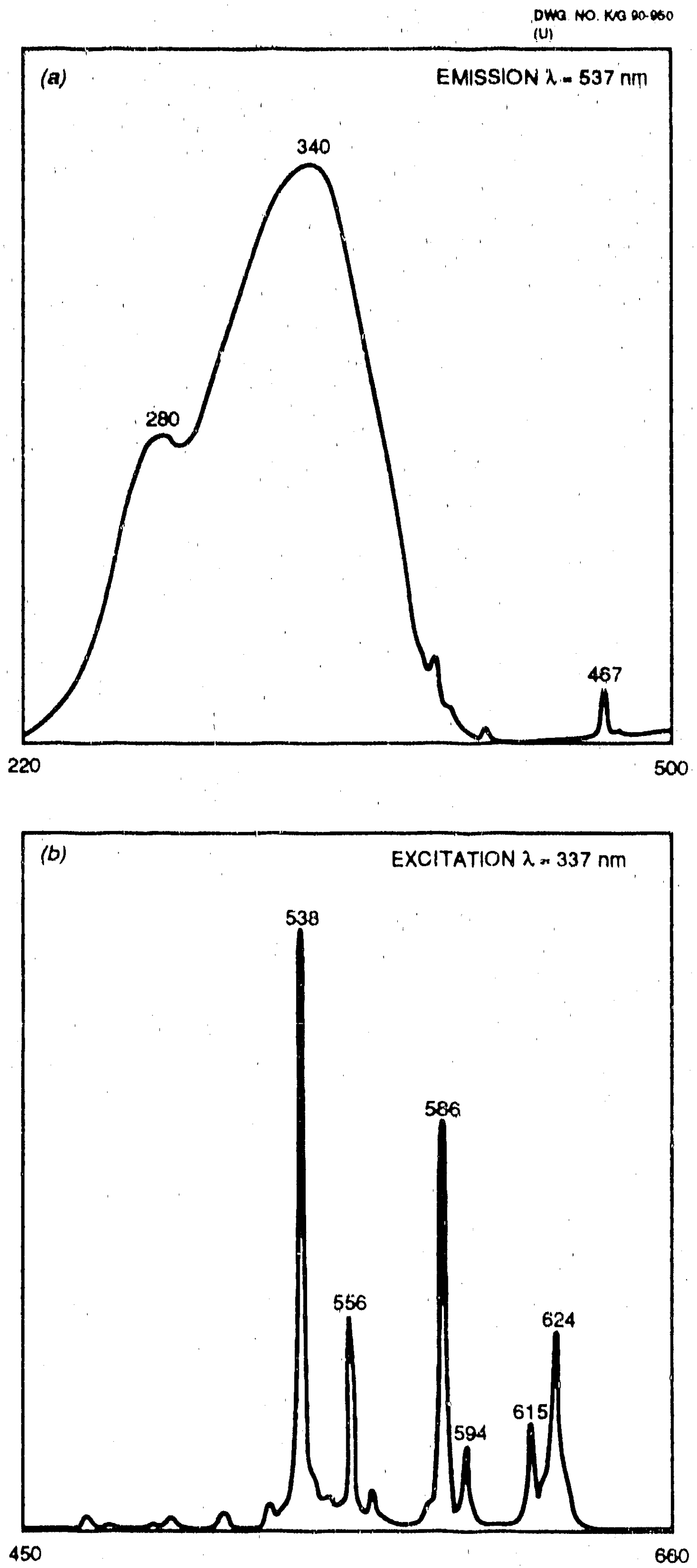

Fig. 1. Fluorescent excitation and emission spectra for La_2O_2S:Eu at room temperature. *(a)* excitation spectra, *(b)* emission spectra.

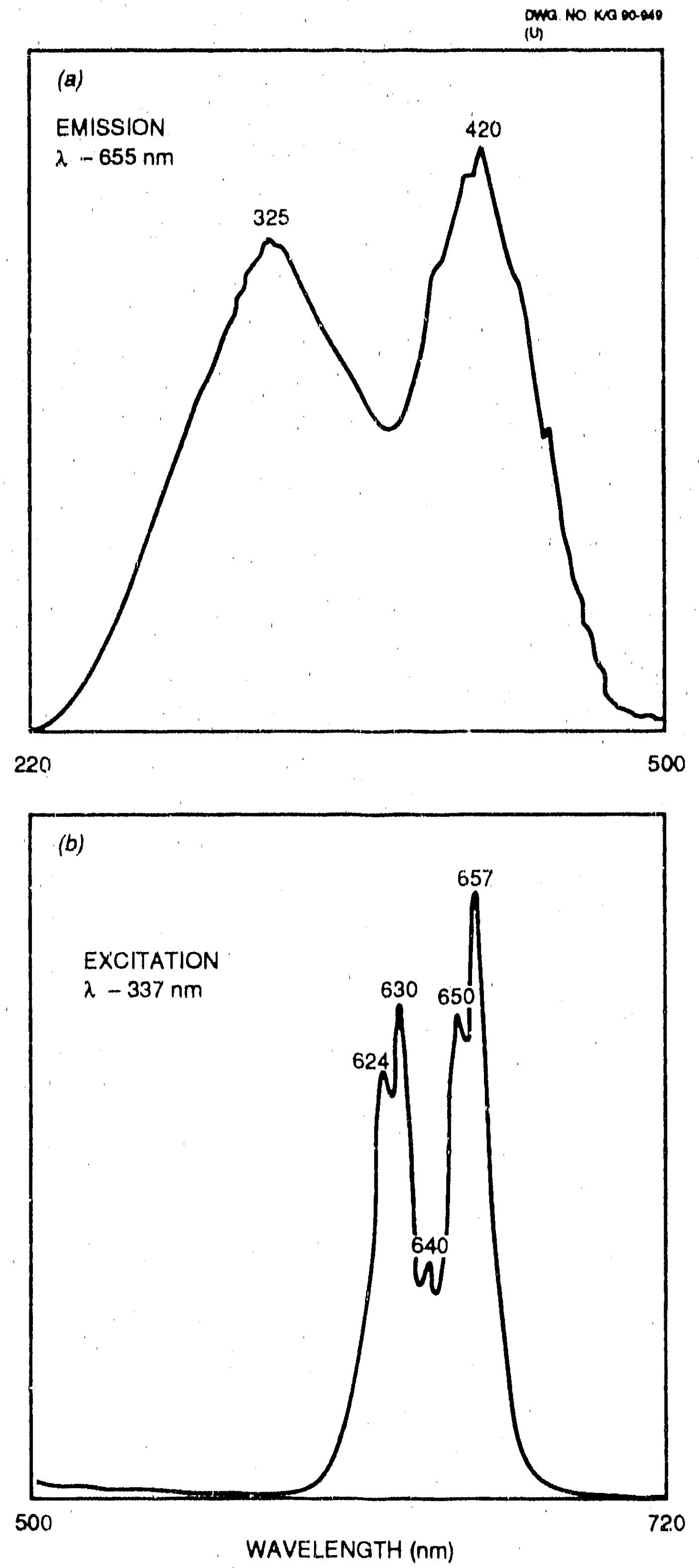

Fig. 2. Fluorescent excitation and emission spectra for $Mg_4(F)GmO_6$:Mn at room temperature. *(a)* excitation spectra, *(b)* emission spectra.

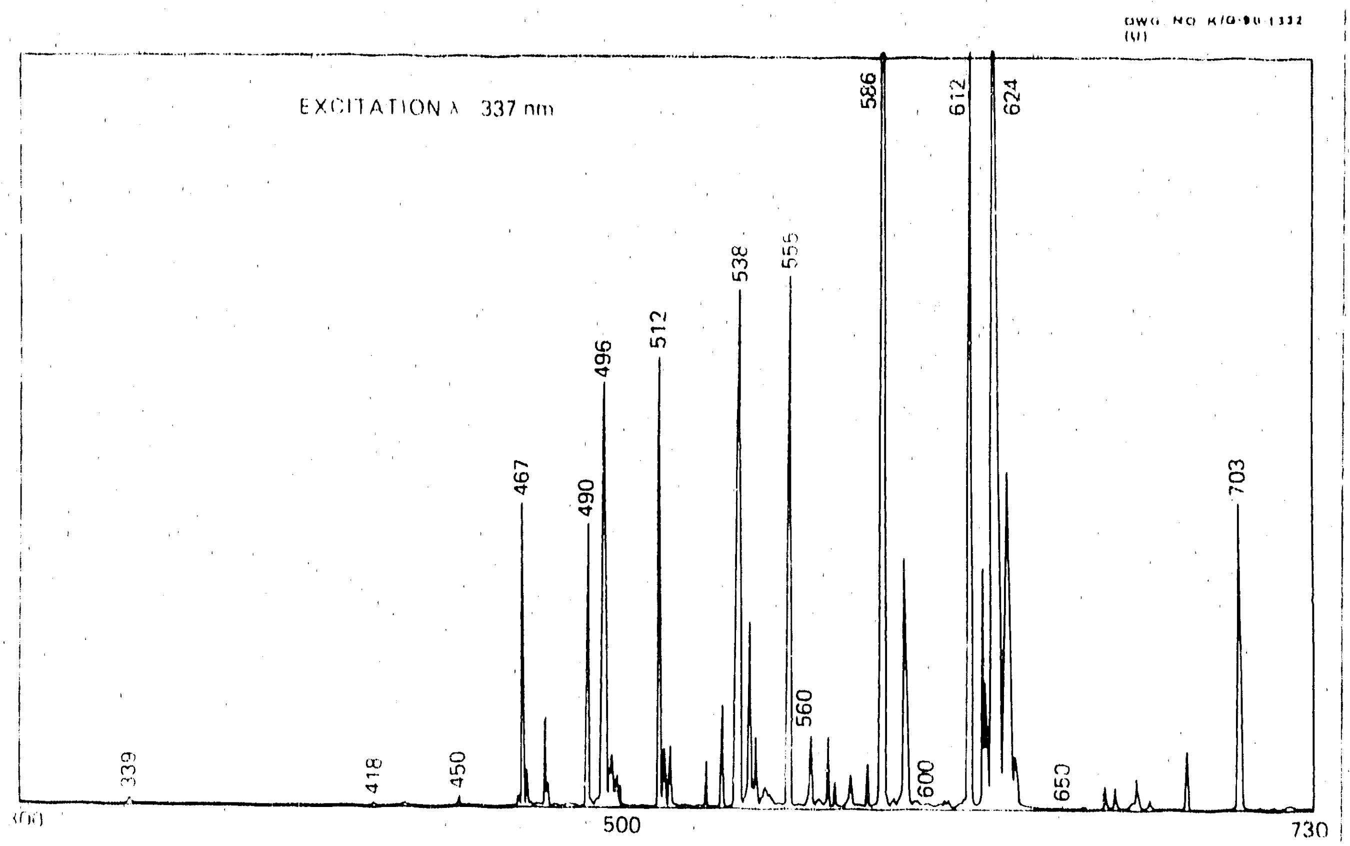

Fig. 3. Fluorescent emission spectra for La_2O_2S:Eu at 11K.

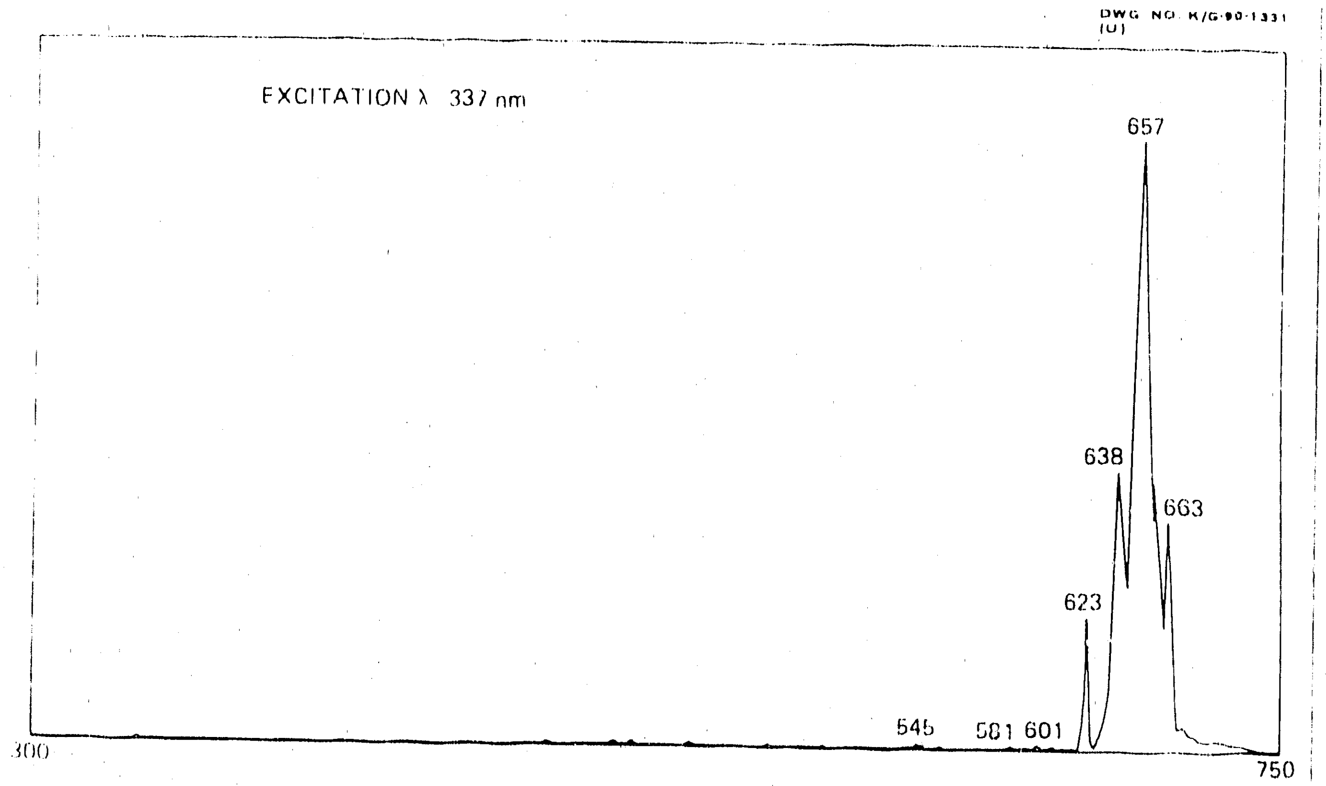

Fig. 4. Fluorescent emission spectra for Mg_4(F)GmO_6:Mn at 12K.

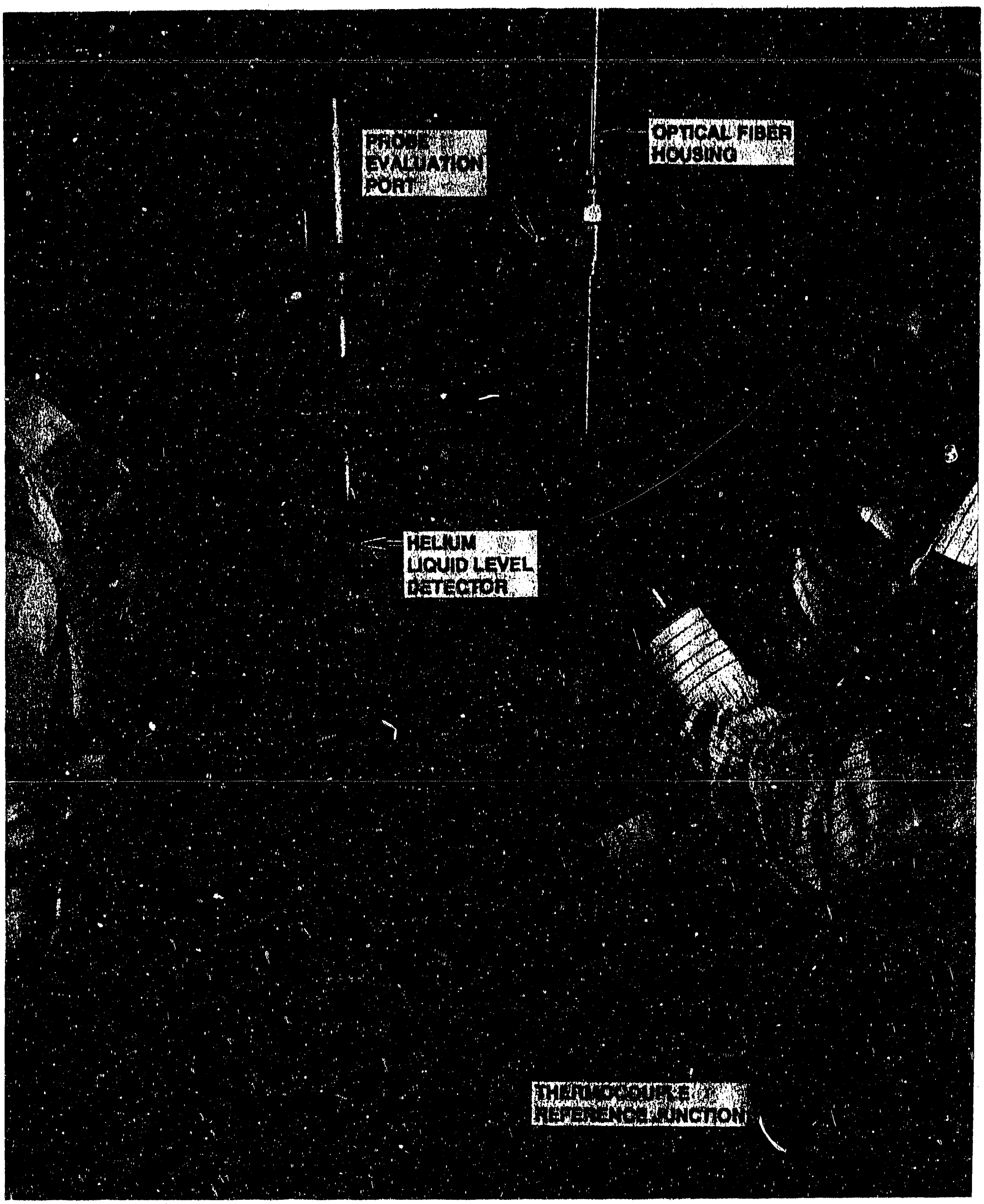

Fig. 5. Cryostat for thermographic phosphor experiments.

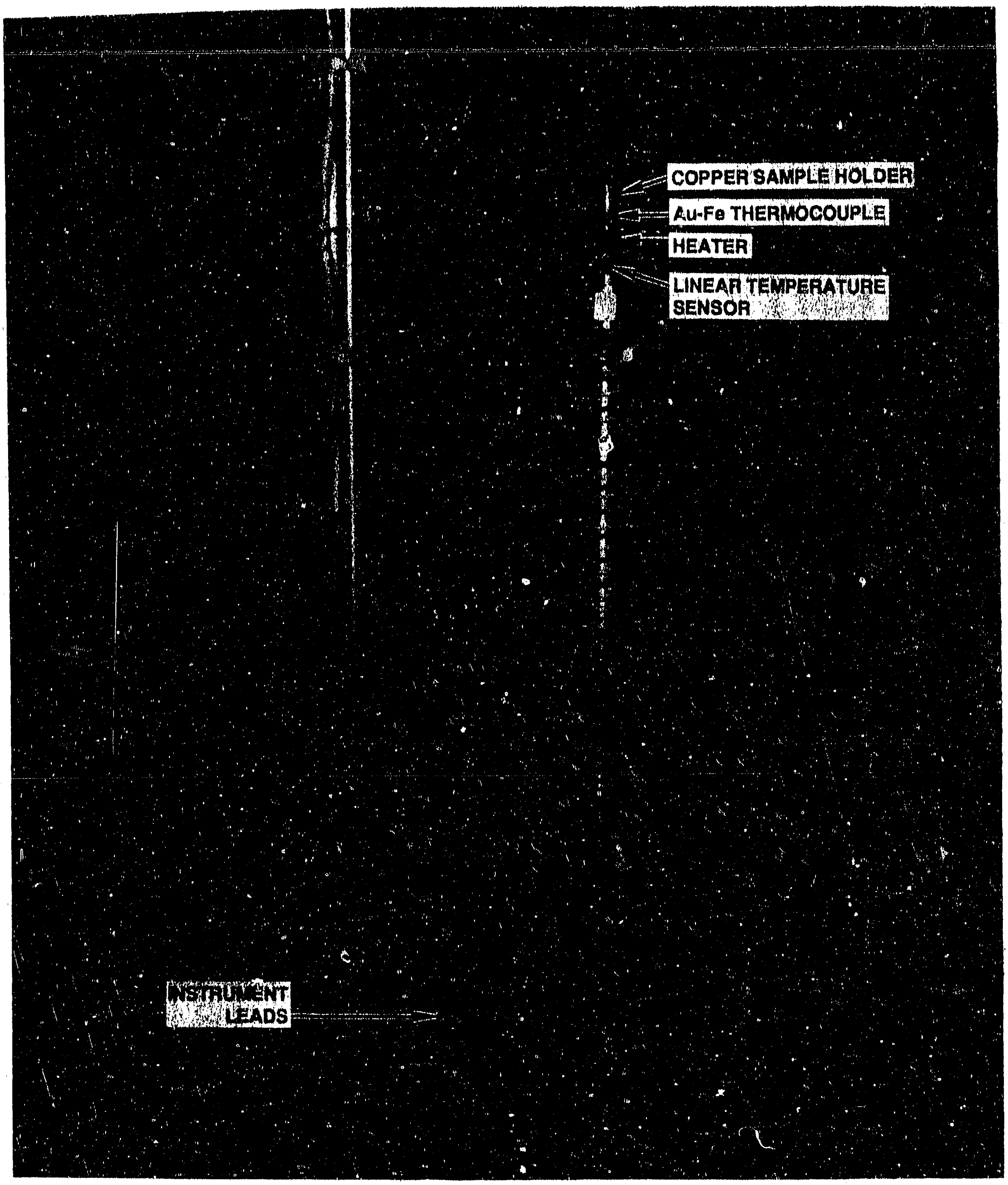

Fig. 6. Photograph of the cryostat sample holder.

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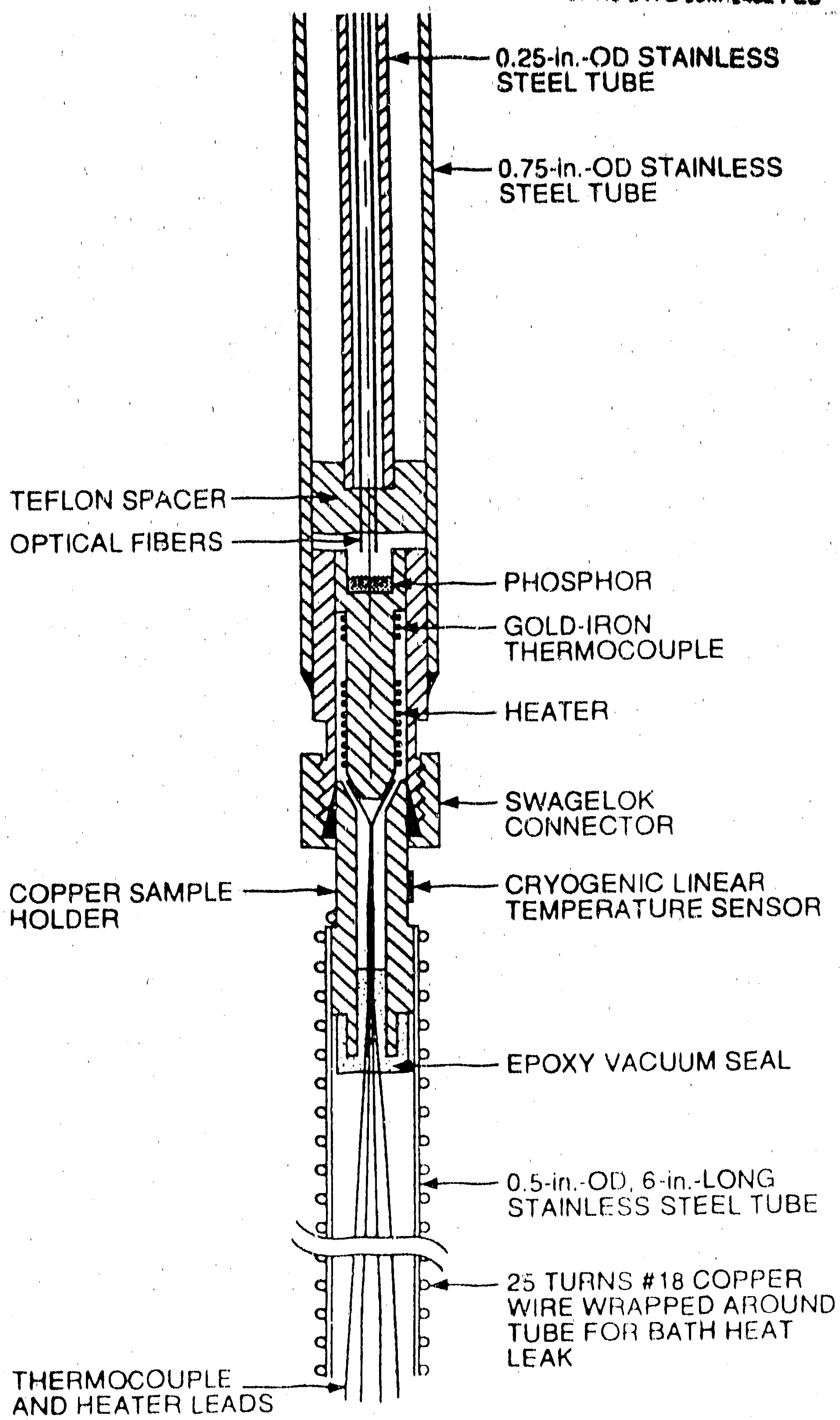

Fig. 7. Thermography sample holder.

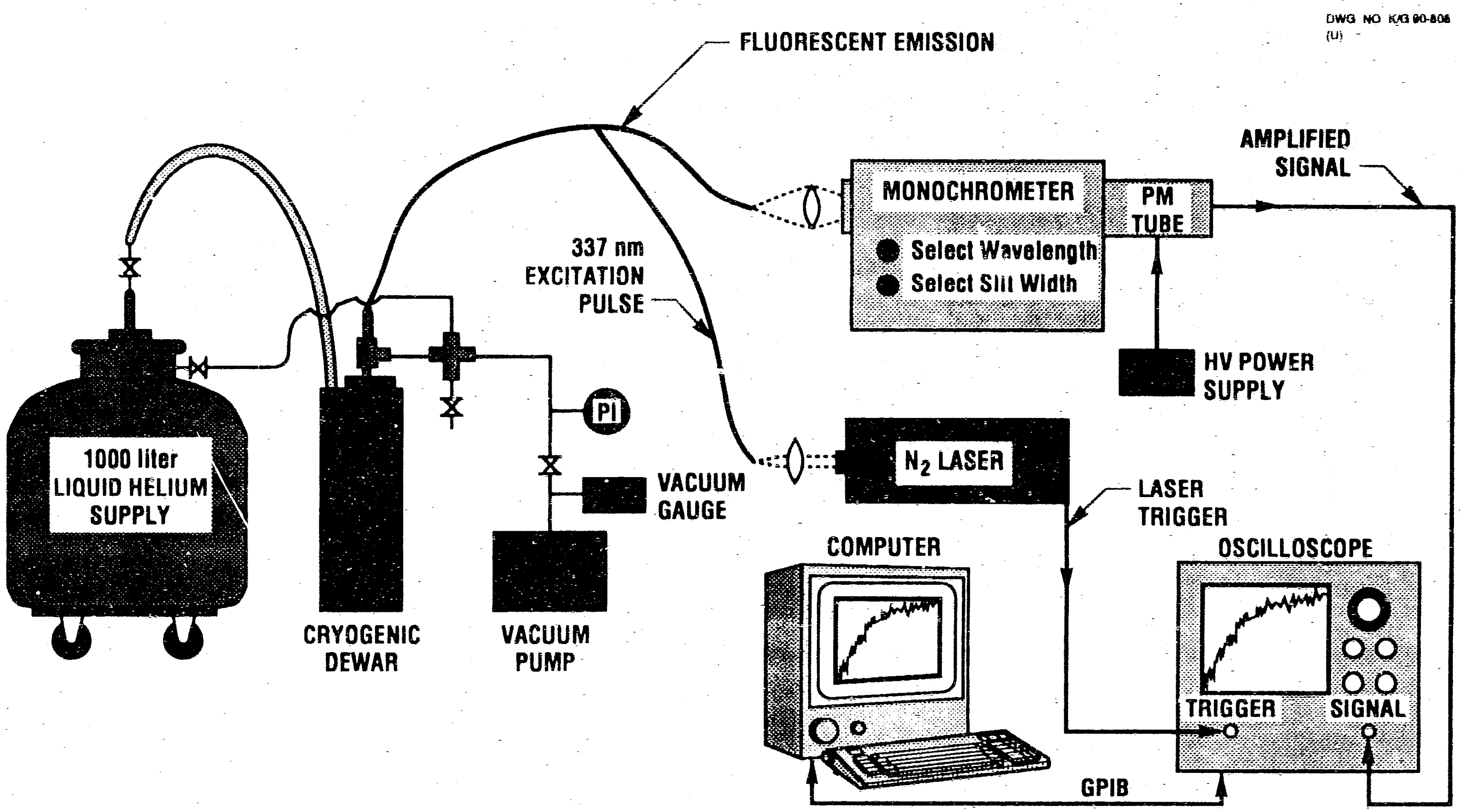

Fig. 8. Cryogenic temperature calibration setup.

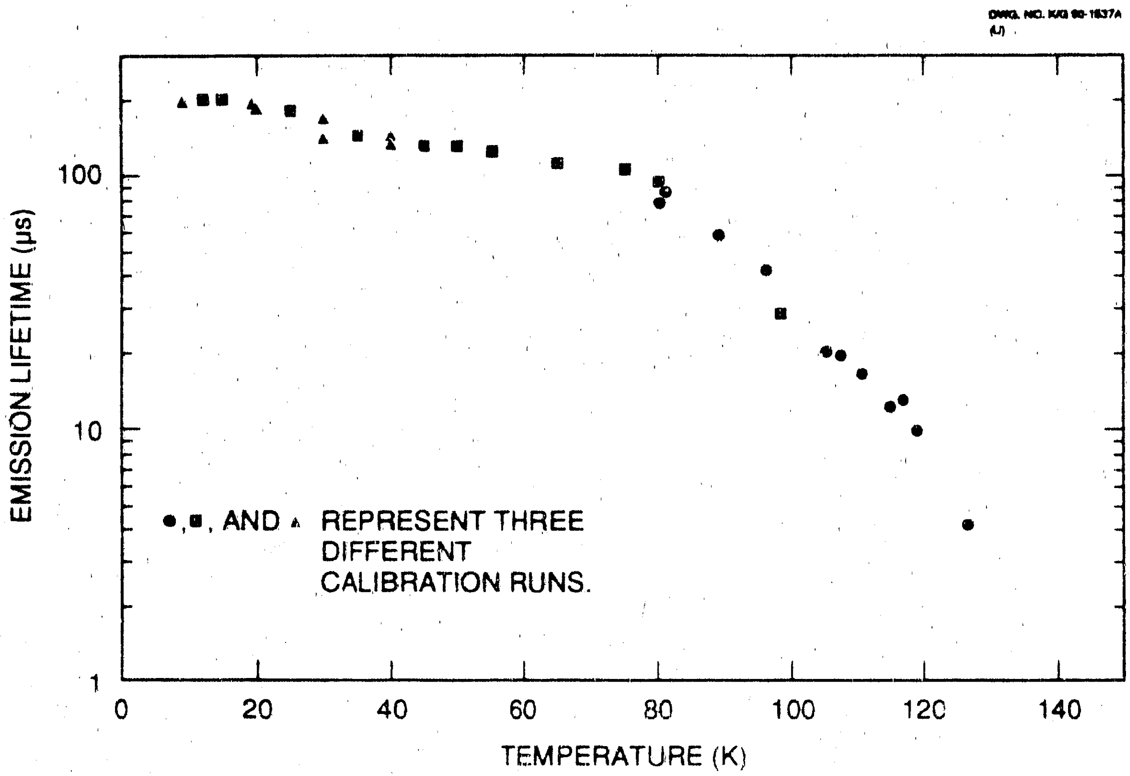

Fig. 9. La_2O_2S:Eu phosphor calibration.

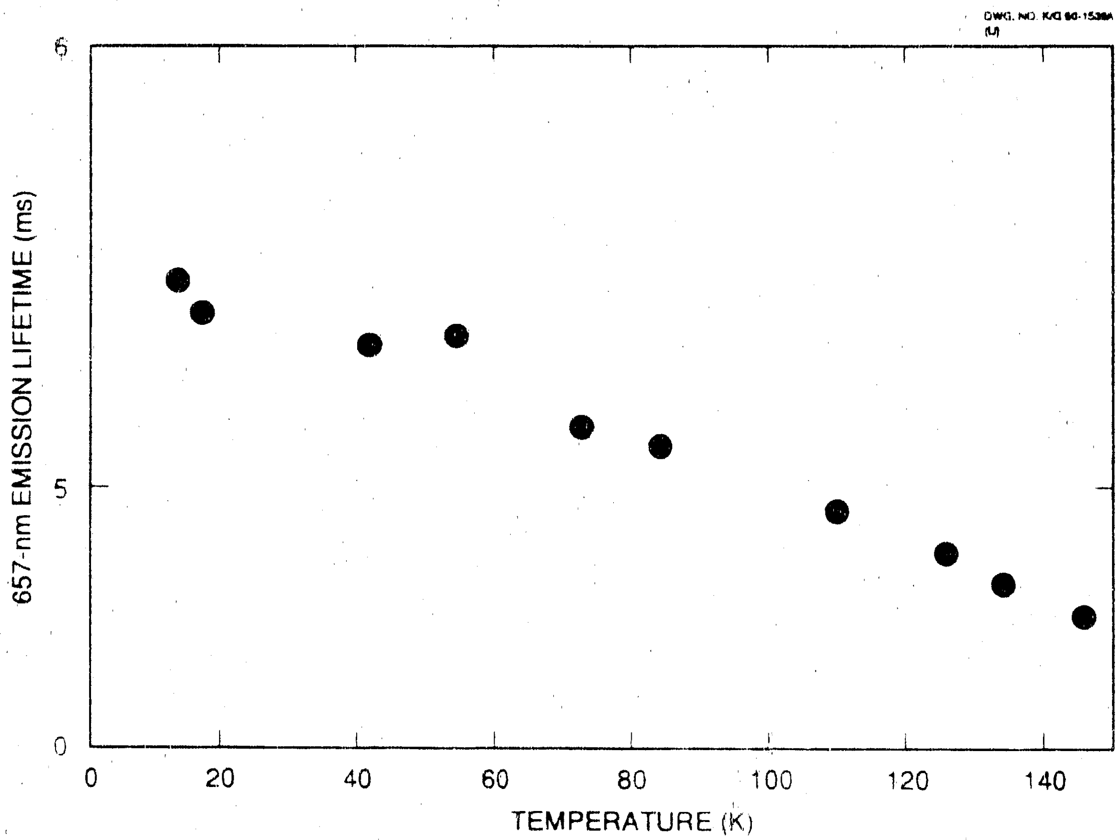

Fig. 10. $Mg_4(F)GeO_6$:Mn phosphor calibration.

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