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MATERIALS DEPARTMENT

THERMOCHROMIC DISPLAY MATERIALS FOR USE UNDER WIDE VARIATIONS IN AMBIENT ILLUMINATION LEVELS

CONTRACT NAS 12-89

Second Annual Progress Report
by

Dr. Raymond P. Borkowski
Dr. Marvin J. Kornblau
Dr. Daniel Grafstein
Mr. William L. Flint

Prepared for

National Aeronautics & Space Administration
Electronic Research Center
GC/Control and Information Systems Laboratory
575 Technology Square
Cambridge, Massachusetts

31 January 1968

AEROSPACE RESEARCH CENTER
GENERAL PRECISION SYSTEMS INC.
KEARFOTT GROUP
LITTLE FALLS, NEW JERSEY

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Approved: Daniel Grafstein
Dr. Daniel Grafstein
Principal Staff Scientist
Manager, Materials Department

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ABSTRACT

This report documents the results of the second year of research under Contract NAS 12-89. The objective of this research was to develop useful thermochromic materials and to study their applications in display devices. A major portion of the effort was concerned with the synthesis and evaluation of ternary halides and chalcogenides, these being inorganic crystals which exhibit pronounced and reversible color changes with change in temperature. Each material can exist in either of two distinct thermodynamic states depending on the temperature. In general, the color change occurs at a sharp transition temperature and is accompanied by a dramatic change in electrical conductivity and by discontinuities in heat capacity. These changes in properties suggest a number of useful applications, for example, in the display and computer input fields. At the display device level, effort during the past year has concentrated on the utilization of thermochromic materials either by themselves or in combination with standard phosphors as screen materials in cathode ray tubes (CRT's).

A reduction to practice was achieved which demonstrated the ability of an electron beam in a demountable CRT system to induce thermochromic transitions in a variety of materials. Several substrate materials for the thermochromic material Ag_2HgI_4 were utilized to intercept the CRT electron beam. This served to prevent decomposition of the thermochromic. The most useful substrates examined include .003-.005" thick conducting glass and nickel foils. In addition, the use of a sandwich structure consisting of magnesium oxide, Ag_2HgI_4, and thin conducting glass also has shown promise. In this latter configuration, the electron beam is allowed to strike the magnesium oxide layer. It should be noted that Ag_2HgI_4 has been utilized to date because of its ready availability, but it must be considered primarily as an interim material to be replaced by more thermally stable materials now being synthesized. Some mixtures of thermochromic materials and conventional CRT phosphors appear to be compatible and demonstrate both thermochromic and luminescent properties under electron bombardment.

A variety of new materials have been synthesized and examined for thermochromic activity. Those with useful thermochromic properties are a series of derivatives of Ag_2HgI_4 and Cu_2HgI_4 in which Cd has been substituted for Hg. Cadmium contents up to 0.70 atomic percent in Ag_2HgI_4 give materials with yellow to red thermochromic transitions whose transition temperatures increase with increasing amounts of cadmium. Higher cadmium-content compositions are poorly thermochromic. Four solid solutions of AgI and PbI_2 that were prepared show significant thermochromic activity. The transition temperatures are between 99 and 137°C and the compounds are stable at 150°C as well as to vacuum.

Thermal conductivity experiments on the low- and high-temperature forms of Ag_2HgI_4 indicate that the thermal conductivity of the low-temperature form is slightly greater than the high-temperature form.

A number of problems concerning the application of thermochromics to CRT use are described:

> Ag_2HgI_4 is not an ideal material for the CRT application due to its tendency to decompose. The material could be made more useful if an encapsulation method suitable for CRT application can be developed.
>
> In the configuration considered, the rise time and decay time are both dependent on the mass and properties of the substrate and are long if a good deep color change is induced in the material. These decay times are of the order of seconds. This is the right order of magnitude for applications where moderate image persistence is required. Depending on the substrate, a tendency for spreading of the written line has been observed. This is, of course, intimately related to the decay time and is due to lateral diffusion of heat through the substrate and thermochromic.

ADMINISTRATIVE INFORMATION

This 24-month program was sponsored by the NASA-Electronics Research Center, Cambridge, Massachusetts under Contract NAS 12-89. The NASA monitoring scientist was Mr. E. H. Hilborn. The Project Supervisor at the General Precision Aerospace Research Center was Dr. Daniel Grafstein. The Principal investigators were Dr. Marvin Kornblau and Dr. Raymond P. Borkowski. Mr. William Flint has been primarily responsible for the CRT test phase of the program. He has been assisted by Mr. Alfred Brauer.

TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

FIGURES

TABLES

1. INTRODUCTION

This study is directed towards the design and evaluation of displays suitable for use under wide variations in ambient illumination levels. These displays should be useful in aircraft, space vehicles, and other situations in which high ambient illumination conditions occur due either to sunlight or artificial light. Those conventional displays which incorporate mechanically coupled moving parts are usable under most light levels but they have the potentialities for failure common to all systems containing moving parts. Most other display devices make use of materials that emit light. Depending on the material, various methods of excitation have been employed in the past. Electroluminescent, fluorescent, and incandescent devices are excited by electric fields and/or an electric current. Cathodoluminescent materials are excited by an electron beam. All of these devices tend to saturate at emission brightness levels that are too low to be seen clearly in conditions of high ambient background light. In addition, the power requirements needed to maintain a high emission brightness are often excessive and sometimes reduce the life expentancy of the device.

It is the objective of this program to consider the device application of materials that undergo changes in reflectivity or color as a function of temperature. These changes can easily be seen under conditions of high ambient illumination. It is expected that these materials should be capable of being used in display devices which contain no moving parts. Combinations of such materials with systems of the light-emissive type could also lead to displays readable at all ambient illumination levels with approximately constant contrast.

The study is specifically concerned with the application and evaluation of thermochromic materials in display devices and with the preparation of new thermochromic materials. A device based on such materials would have no moving parts and should operate best under high ambient light levels.

1.1 Thermochromism

Thermochromism can be defined as a change in the color of a material brought about by a change in the temperature of the material. This color change can be of varying sorts depending upon the particular underlying mechanism responsible. The color response to changing temperature can be slow or fast, sharp or gradual for a given energy throughout. In some cases, for example, the thermochromism of some organic materials, chemical bonds must be broken and new ones formed. Such a system would tend to show a relatively slow thermochromic transition. In addition, such a system would tend to show a gradual color change as the relative amounts of reactants and products, that is the relative amounts of the two colored forms, is a function of temperature. This and other objections for display purposes apply to the various other types of thermochromics that exist with the exception of those inorganics whose thermochromism depend upon an order-disorder solid-state phase transition.

The change in color in these materials involves the moving of certain small cations in an otherwise rigid lattice of closely packed anions. The transition in these material's is rapid with respect to temperature. A major difficulty is that very few such materials are known and that they are expected to be relatively unstable thermally.

1.2 Properties of Previously Known Materials

Prior to the start of this program several thermochromic ternary iodides were known that exhibited thermochromism due to an order-disorder phase transformation. Details of their properties were given in the First Annual Progress Report. They will be briefly summarized here.

The low-temperature form of silver mercuric iodide (Ag_2HgI_4) is a bright yellow that changes reversibly to a red-orange high-temperature form at 50.5°C. The low-temperature tetragonal form is a cubic close packed array of iodide ions with a regular disposition of the silver and mercury ions in holes in the lattice. The cubic high-temperature form is similar except that the cations are arranged randomly in the iodine anion lattice. The specific heat rises to three times its normal value at 50°C and falls to a normal value once the transition temperature is passed. The electrical conductivity shows a pronounced increase on passing through the transition region. Ag_2HgI_4 is one of the best known solid ionic conductors in the temperature range 51 - 140°C.

Copper mercuric iodide, Cu_2HgI_4, undergoes a color change from a red low-temperature form to a black high-temperature form at 69.5°C. The mechanism appears to be the same as for Ag_2HgI_4. A eutectic solid solution of Ag_2HgI_4 and Cu_2HgI_4 having the composition $Ag_{1.14}Cu_{0.86}HgI_4$ undergoes a thermochromic change from orange to red at 34°C. The mechanism is presumed to be the same as in Ag_2HgI_4. This eutectic is of limited value due to its low transition temperature. It would change color on a hot day. Thallium mercuric iodide Tl_2HgI_4 undergoes a change from orange to red at 116.5°C. Unfortunately it decomposes fairly rapidly at 130°C which is too close to its transition temperature.

1.3 Summary of First Year's Results

The purpose of the first year's work was to prepare new thermochromic materials and evaluate their use for display devices. A prototype numeric display device was fabricated. Many new thermochromic compositions were prepared.

1.3.1 Materials

An analysis of the mechanism for thermochromism in silver and copper mercuric iodide, the disordering of cations in an essentially unchanged iodide anion lattice, gave rise to the idea that partial substitution of other ions in the lattice could bring about a change in properties. The following materials were prepared:

$Ag_2HgI_{4-x}Br_x$	($x = 0.17$ to 1.40)
$Ag_2Hg_{1-x}Cd_xI_4$	($x = 0$ to 0.25 in steps of 0.05)
$Ag_2Hg_{1-x}Cd_xI_{3.84}Br_{0.16}$	"
$Cu_2Hg_{1-x}Cd_xI_4$	"
$Ag_2HgI_{3.75}Cl_{0.25}$	
$Cu_2HgI_{3.75}Br_{0.25}$	

1.3.2 Devices

Prototype display devices utilizing resistance heating of segments of a thermochromic panel were fabricated using both Ag_2HgI_4 and Cu_2HgI_4 as the active materials. However, only the former material was satisfactory. By the use of a switching circuit any number from 0 to 9 could be selected for display by electrically heating appropriate resistance wires placed under a smooth layer of thermochromic embedded in plastic. No attempt was made to optimize this device and its response was slow both in the writing and in the erasing modes.

1.4 The Situation at Start of Present Year

As indicated in the preceding section, a prototype display device based on resistance heating of thermochromics was developed to demonstrate the principle of a display device using thermochromic materials. Further, calculations indicated the possibility of using thermochromics as the display material in a cathode ray tube. This device would make use of the heating effect of the electron beam to induce a thermochromic change in the target. Experimental work was therefore needed to prove the feasibility of the concept.

A group of new thermochromic compounds having a wide range of transition temperatures was prepared in the first year's program. All but one of them, however, contained mercury and iodine and would, on the basis of the available data, be expected to be thermally unstable. One of the new materials, $CdIn_2S_4$, has good thermal stability, but its thermochromic change has poor visual contrast and is fairly gradual with respect to temperature change.

A possible solution to this problem of thermal instability is to consider materials not based on mercury iodides. Accordingly a variety of possible candidate materials were suggested for the present program.

The major emphasis of the program, however, was to be placed upon the experimental development of the use of thermochromic materials in display devices, particularly in a cathode ray tube. This would involve the construction of a demountable cathode ray tube apparatus and experimentation on various thermochromic substrate combinations. Parameters, such as accelerating voltage, beam current, substrate material and thickness, and thermochromic thickness, were to be evaluated experimentally.

2. PRELIMINARY APPLICATIONS EXPERIMENTS

Prior to obtaining a demountable cathode ray tube needed for the evaluation of thermochromics as target materials, preliminary experiments were performed using the electron beam available in the electron microscope. In addition, experiments on the ultraviolet induced fluorescence of mixtures of thermochromics and CRT phosphors were performed in order to gain some indication of their compatibility.

2.1 Electron Microscope Equipment Used

The electron microscope used in the experiments was an Hitachi, Type HU-11. The instrument is capable of operating at fixed voltages of 50, 75, and 100 KV. Focusing and deflecting are done magnetically. The only position available in the electron beam path is in the vicinity of the fluorescent screen normally used for visual observation during use as a microscope. The instrument has a microammeter in the cathode circuit but due to the low vacuum (10^{-4} Torr) in the instrument the indicated reading is probably not a good measure of the beam striking the screen. The focused beam size was on the order of several millimeters in diameter. Deflection of the beam was accomplished by normal use of the instrument controls and was no faster than a centimeter in 3 or 4 seconds.

2.2 Target Materials Preparation

In order to have an electron beam strike and induce an effect in a powdered material such as a phosphor or a thermochromic, it is useful to have the powder coat and adhere to some rigid substrate. For example, in a conventional cathode ray tube the cathodoluminescent phosphor is deposited from a fine suspension along with a small amount of binder onto the faceplate of the tube. Two methods of coating glass or other solid substrates with thermochromics or phosphors were used. The simplest was to prepare a slurry of the solid powder in a suitable volatile liquid such as acetone or methyl alcohol and paint the slurry onto the surface with a suitable brush. The material was usually freed from excess solvent by placing it under vacuum for a short time. This brushing technique gave a very non-uniform coating that often showed a tendency to flake off in use.

A method that gave better results was to mill a mixture of the powder and xylene in a jar with ceramic mill balls for about 24 hours. The resulting suspension showed only a slight tendency to settle and could be applied uniformly to the substrate by means of a standard artist's air brush. The sprayed material was then subjected to a vacuum for removal of the last traces of solvent. The surface density of the sprayed material could be obtained by weighing the substrate before spraying and then reweighing after spraying and drying. As long as the material was not subjected to mechanical impact the layer of powder was reasonably adherent. Nonetheless, it may be beneficial to employ a binder similar to those used with conventional phosphors.

2.3 Results on Pure Iodides in the Electron Microscope

In the first preliminary experiments in the electron microscope, a 1/8" thick conducting glass plate was coated with each of the thermochromics, Ag_2HgI_4 and Cu_2HgI_4. The coating was prepared by painting from an acetone slurry of the powders. The thermochromic layer was on the conducting surface of the glass, which in turn was electrically grounded to the chassis of the instrument in order to avoid arcing and random deflections of the beam.

The thermochromic was then exposed to a stationary, focused beam at 75 KV electrons at an indicated beam current of 30 μamp. It was not possible to measure the size of the spot but it was estimated at a few millimeters in diameter. Both materials underwent their characteristic color change with difficulty: Ag_2HgI_4 went from yellow to orange, Cu_2HgI_4 went from red to black. The transition to the low-temperature form took several seconds upon removal of the beam.

It was decided that the extreme slowness of the color change was due to the large mass of material that had to be heated when the thermochromic was mounted on a thick(1/8") glass plate. The experiment was repeated in much the same way except that a sheet of very thin conducting glass (0.003 - 0.005") was used. Thermal contact with the microscope was minimized by raising the plate off the surface of the chassis with alumina thimbles. Electrical contact to the chassis was made by a thin metal clip. Under these conditions the thermochromic transition was more rapidly induced and it was possible to write on the thermochromic target with a moving beam. The transition back to the low-temperature form was much slower than in the previous experiment. This is most likely due to the smaller mass of the thin plate and to its relative thermal isolation. This experiment using thin glass coated with Ag_2HgI_4 was also repeated with the glass surface facing the beam. Good reversible changes were observed with a moving focused beam.

2.4 Mixtures of Iodides and CRT Phosphors

Early in the program, before any work using an electron beam was begun, some experiments were performed to determine if the ternary iodides, Ag_2HgI_4 and Cu_2HgI_4, would poison CRT phosphorous with respect to their flourescence properties under ultraviolet irradiation.

Fifty percent mixtures of each of the two thermochromics and the cathodoluminescent phosphors P-1, P-2, P-7, P-14 and Red Sylvania 1120 were subjected to long-wavelength ultraviolet radiation. All samples fluoresced with a shift in the color of the emitted light when compared with the emission of the undiluted phosphor. The shift was towards the yellow when Ag_2HgI_4 (a yellow powder) was the diluent and towards the red when Cu_2HgI_4 (a red powder) was the diluent.

Each of the mixtures was also shown to be thermochromic with an observed transition temperature at least within 2 degrees of that of the parent thermochromic component. Generally, the apparent contrast change was diminished by the phosphor which acts as a diluent for the color. However, in one case, that of Ag_2HgI_4 and P-14 (a lemon-yellow color phosphor), the apparent contrast was comparable to the undiluted thermochromic. This is because the color of this phosphor is similar to the color of the low-temperature phase of the thermochromic and the filtering evidently does not appreciably change the observed color shift of the thermochromic material. It is evident that considerable care must be used in selecting a mixture of thermochromic and phosphor if good contrast is to be obtained.

When the electron microscope became available for use, experiments were performed in it on mixtures of phorphors and thermochromics.

Experiments were conducted of fifty percent mixtures of the two thermochromics, Ag_2HgI_4 and Cu_2HgI_4, and the CRT phosphor P-14. The mixtures were painted onto the very thin conducting glass plates. These were thermally isolated from the chassis as described above. At 75 KV and an indicated current of 30 μamp and with a stationary focused beam it was possible to induce the thermochromic color change in the Ag_2HgI_4 mixture but not in the Cu_2HgI_4 mixture. Both showed cathodoluminescence but at a lower output intensity than the pure P-14 phosphor which was also examined under the same conditions. In addition, the color of the light emission was different from the yellow emitting P-14. With the Ag_2HgI_4:P-14 mixture the light was orange, and with the Cu_2HgI_4:P-14 mixture the light was red. This is most likely due to filtering of the phosphor light output by the colored thermochromics.

Another series of experiments was performed on mixtures of thermochromics and CRT phosphors: mixtures containing 50, 25 and 10 percent of the green emitting phosphor P-2 with Ag_2HgI_4 were painted onto a 1/8 inch conducting glass plate from an alcohol slurry. Experiments were performed at both 50 and 75 KV with currents nominally at 30 μamp. All of the mixture fluoresced with a blue-green light and the fluorescence could be observed in both room light levels and in the dark. Comparison with the pure phosphor emission indicated a slight shift towards the blue. The intensity of the emission decreased with increasing Ag_2HgI_4 content. Reversible thermochromic color changes with a stationary beam were observed only in the 10 percent P-2 mixture when viewed in a normal room ambient. The viewer is conscious of seeing both the thermochromic and phosphor transition together but with the thermochromic transition having less visual impact. With the other mixtures either decomposition or no thermochromic transition was noted depending on the current level.

Experiments on mixtures of the red emitting Sylvania phosphor No. 1120 and Ag_2HgI_4 were also performed in the electron microscope. Mixtures containing 50 and 25 percent by weight of the phosphor were prepared as in the above experiment. The red fluorescence was quite weak in both the mixtures and in the pure phosphor at 50 KV and 20 μamps. At 75 KV and 30 μamps the fluorescence was much stronger and no color shift of the emitted light was noted as compared to the pure phosphor. Due to the red color of this phosphor it was extremely difficult to determine if a thermochromic transition had occurred. In one case, however, that of the 25 percent phosphor mixture in the 75KV beam, some faint reversible color shifts were noticed. The use of a strong red phosphor is not recommended with Ag_2HgI_4. It might be more useful with Cu_2HgI_4.

3. DEVELOPMENT OF DEMOUNTABLE CATHODE RAY TUBE SYSTEM

Earlier calculations have shown that writing on a thermochromic material with an electron beam was feasible, provided that proper values of the beam energy and scanning speeds were selected. On this basis it was first decided to mount an electron gun in an evacuated bell jar and direct the electron beam from the gun onto a moving substrate coated with thermochromic material. Initially this design suggested the use of an electron gun modified with a tungsten cathode instead of the more conventional alkaline earth oxide coated cathodes. The latter are rendered inactive on contact with the moisture and carbon dioxide present in the air. Such contact with the air appeared to be inevitable since the bell jar housing the gun target had to be opened in order to modify the experimental conditions. As a result of these considerations electron guns (type SE-3R) modified with tungsten cathodes were ordered. Also, this particular electrostatic focusing and deflection gun was selected because the necessary driving electronics were available in our laboratory. Subsequent discussions with a representative of a commercial supplier of cathode ray tubes indicated that the above scheme would not be too satisfactory. It was pointed out that tungsten filaments will not produce usable electron beams of sufficient energy. In addition, electrostatic tubes are also inherently very wasteful of beam energy. This is all further compounded by the fact that at 2×10^{-6} Torr, the maximum vacuum available in our systems, the beam losses are further increased due to scattering. In order to avoid these difficulties, our initial plans were modified in order to obtain a more versatile experimental system.

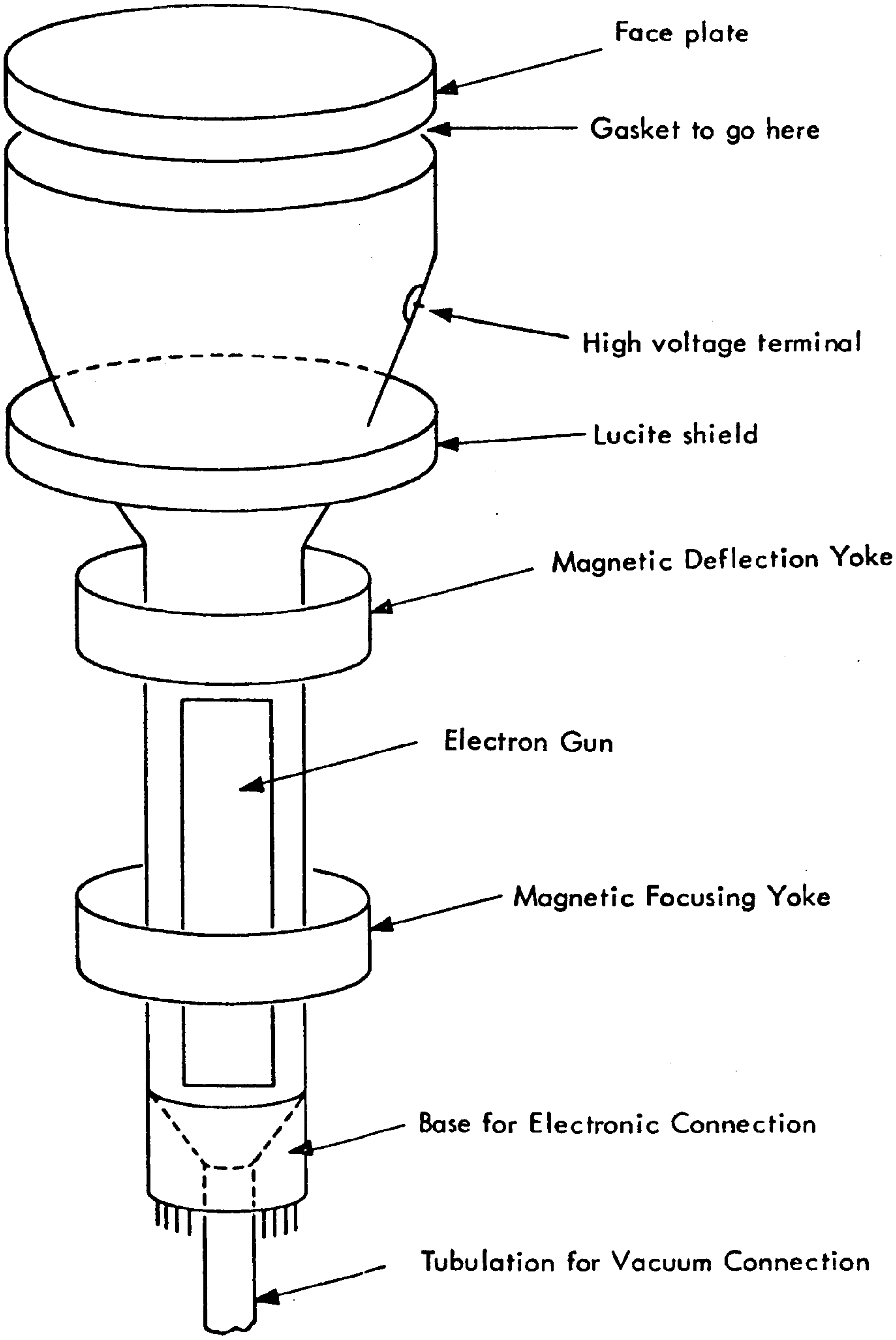
3.1 Initial Equipment

It was decided to use a magnetic focus, magnetic deflection cathode ray tube. The face plate of the tube removed in such a way as to allow it to be replaced, with the help of a Viton A gasket, onto the body of the tube. The CRT was also obtained with the tubulation used for the final evacuation of the tube left in place. It was then possible to connect the demountable CRT to an appropriate pumping system through the tubulation and make electronic connections through the usual lead-in wires. A schematic diagram is shown in Figure 1. At this stage the Lucite shield was not yet installed on the tube.

The three tubes actually purchased were Thomas Electronic 5FP-A demountable cathode ray tubes. They are described by the manufacturer as magnetic focus and magnetic deflection tubes suitable for radar application. The following are the maximum operating conditions specified by the vendor:

Heater voltage	6.3 volts
Heater current @6.3 volts	0.6±10% ampere
Accelerator voltage	8,800 volts dc
Accelerator input	6 max. watts
Grid No. 2 voltage	770 max.volts dc
Grid No. 1 voltage	
Negative bias value	180 max. volts dc
positive bias value	0 max. volts dc
positive peak value	2 max. volts

Additional specifications are described in the Appendix. In addition, a normal sealed tube of the same design was also received. It was used to check out the various power supplies and control circuitry needed to operate the demountable. This was completed, and no further use was made of this tube.



SCHEMATIC OF DEMOUNTABLE CRT

FIGURE 1

The demountable CRT's were attached to a Veeco, Type C Quick Connect coupling through a flange in an MRC vacuum collar which is located on the baseplate of a Veeco vacuum system. A vacuum gauge is present in the bell jar of the vacuum system. Due to the presence of relatively long narrow-diameter tubing between the bell jar and the CRT, the indicated pressure of about 2×10^{-6} Torr is probably about an order of magnitude higher than in the CRT.

3.2 Cathode Activation Problem

Attempts to obtain electron emission from one tube was unsuccessful using the cathode activation scheme suggested by the vendor and with no bake-out. The cathode activation scheme suggested was as follows:

"When vacuum has reached best level of the system, preferably in 10^{-6} Torr scale, bring filament voltage up to 6 volts AC. Hold there for several minutes, then raise to 9 volts AC again letting it remain at this voltage several minutes.

Raise the filament to 10 volts and hold for 30 seconds, then raise it to 11 volts and let it remain for 30 seconds. Bring it up to 12 volts for 30 seconds, then to 13 volts for 15 seconds and start lowering voltage in one volt steps leaving the voltage on each level for 30 seconds until 9 volts is reached. The cathode should be ready to operate.

During the activation cycle the vacuum will drop off once or twice but should come back to its original value in a short time."

It was then decided to use another tube and to bake it out at about 190°C under vacuum for 3 days. After baking, the system was opened to a dry nitrogen atmosphere, and a glass slide coated with P-14 phosphor was placed in the tube. After evacuation to a pressure of 2×10^{-6} Torr, as measured by the ionization gauge in the bell jar, the above activation procedure was followed with negative results. A modified activation scheme based on data in the "Superior Electronics" Electron Gun catalogue was then followed. The filament voltages and times at a particular voltage used in this scheme were: 5.5 volts, 5 minutes; 7.5 volts, 5 minutes; 9.0 volts, 5 minutes; 12.5 volts, 1 1/2 minutes; and 7.5 volts, 5 minutes. This scheme was successful and it was possible to obtain "beam currents" in excess of 50 μ amps. The "beam current" was measured with a microammeter in series with the high voltage lead to the Aquadag tube coating. It is not an accurate measure of absolute beam current. It later turned out that if this activation scheme were followed it was not necessary to bake out the tube to achieve activation.

Each time a sample was removed, the tube was kept under a heavy stream of dry nitrogen in order to prevent deactivation of the cathode. It was possible in this way to get very long life from the tube. For example, one tube was opened about 15 times before the emission became too poor for satisfactory operation.

3.3 High Voltage Problems

For reasons that are explained in Section 5 of this report, it was decided to modify this demountable CRT for use at voltage as high as 30 KV. At that voltage and even as low as 20 KV, arcing occurred between the high voltage lead on the side of the tube and the metal parts of the magnetic deflection yoke. This was solved by fastening a lucite ring around the tube with an epoxy cement. The ring is placed between the high voltage lead and the yoke. This shielding ring is shown in the schematic in Figure 1.

3.4 Beam Current Measurements

Early in the experimental work on the demountable CRT it was learned that the beam current as measured in the high voltage circuit was not the actual current striking the screen. It was finally decided to make use of a Faraday cup(1) as a collector for the electron beam in the vicinity of the screen. A thin-walled copper can, 7 mm in height and 15 mm in diameter, with a 5 mm hole was fabricated. A sheet of copper foil was soldered to the back end of the can so that the foil could pass out of the demountable tube between the Viton gasket and the glass shell to permit electrical contact. A glass slide with the cup attached was cemented to the wire gauze that was used as a sample support in the CRT. The microammeter was connected between the high voltage source and the copper foil coming from the Faraday cup.

With the Faraday cup installed as described, it was possible to measure beam currents of about 1.5 microamperes. The beam current behaved properly when biasing voltages were applied at the first anode. This behavior was not always noted when the other beam current measuring methods were tried.

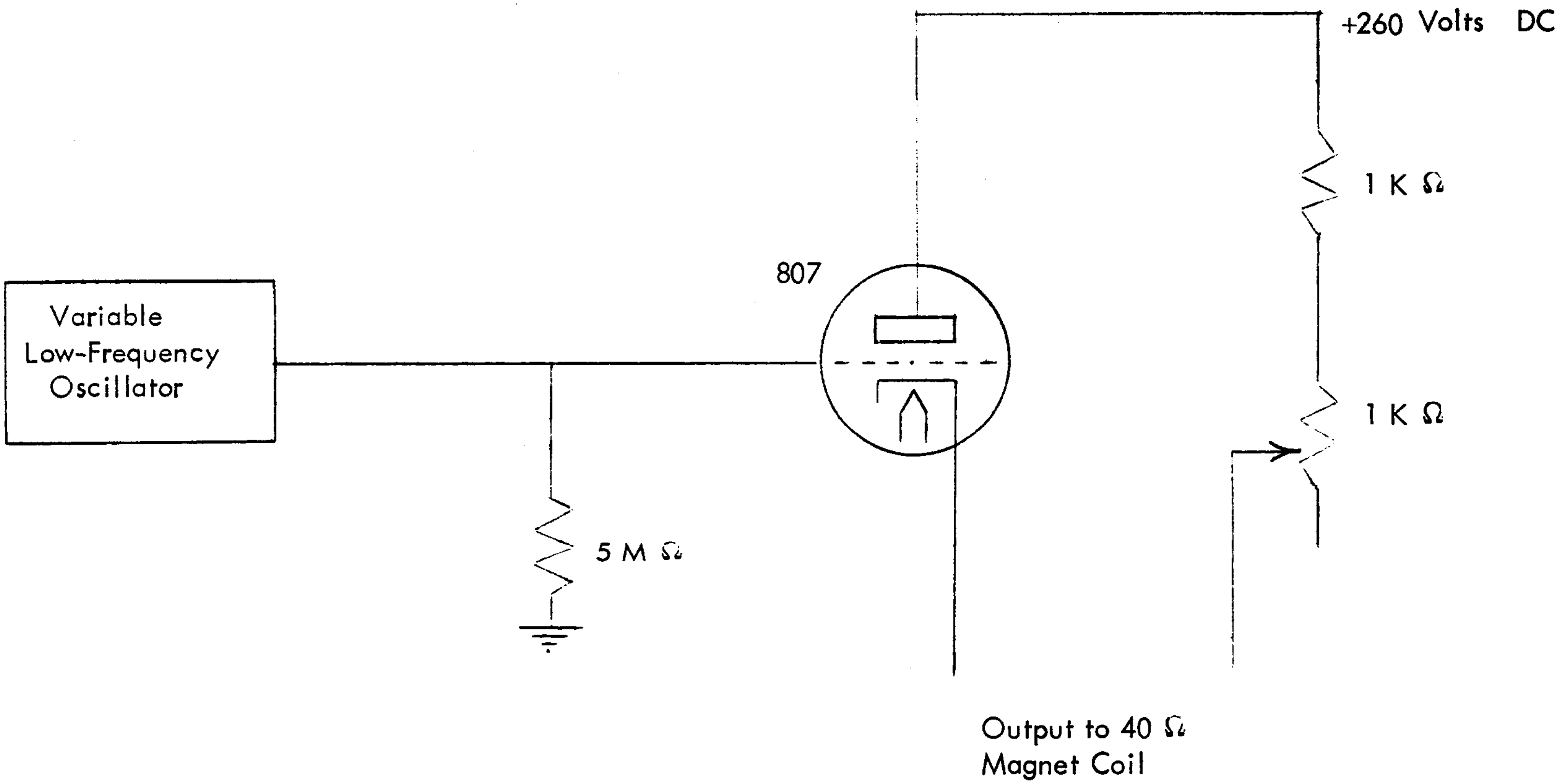
3.5 Beam Scanning Arrangements

Most of the work in the demountable CRT involved the use of a manual scanning arrangement. That is, a variable resistance was used to control the current to the deflection coils from a bank of batteries. It was later decided that more reproducible results could be obtained with an electronically driven scanning system . A power amplifier was used in conjunction with a variable frequency oscillator. The circuit diagram is shown in Figure 2. It is possible with this arrangement to achieve a total scan of about 2.5cm. The scan rate is reasonably linear except at the extreme ends of its travel.

3.6 Method for Mounting Thermochromics in the CRT

The target materials were, as described previously, applied to various glass or metal substrates. The substrates were then joined to a wire gauze by painting the gauze and the edge of the substrate with a viscous solution of Apiezon "W" vacuum wax in benzene. The solvent was evaporated by pumping. The wire gauze used in this mount was bent into a configuration that would give a solid support of the substrate in the CRT and insure contact to the Aquadag coating. Sections of the wire gauze were cut out to allow the electron beam to strike the substrate and Faraday cup.

In the following section the detailed results of all experimental work in the demountable CRT are described. This includes the use of thermochromics in a variety of configurations using various materials as substrates.



Schematic of Electronic Scanning Power Supply
FIGURE 2

4. EXPERIMENTS IN THE CATHODE RAY TUBE

In this chapter all of the experimental work done using the demountable cathode ray tube in conjunction with thermochromic materials is described. Each experiment is given a number in order to facilitate cross referencing.

4.1 Exposure of Ag_2HgI_4 Directly to the Electron Beam

The first group of experiments was designed to achieve reversible thermochromic changes with Ag_2HgI_4 directly facing the electron beam. This would be the best configuration if it were desired to use mixtures of Ag_2HgI_4 and cathodoluminescent phosphors in which both would be excited directly by the electron beam. Many modifications were made in the experimental set up as the results appeared to indicate that variations such as higher voltages, measurement of beam current and beam area, and measurement of thermochromic thickness, were needed.

4.1.1 Initial Experiments

The initial experiments with Ag_2HgI_4 were performed with the demountable CRT in a vertical position with the face plate up. This was later changed to a horizontal position due to a tendency of phosphor and thermochromic powder to fall into the electron beam with resulting arcing and erratic behavior of the beam current. The Ag_2HgI_4 was applied to glass substrates that were in turn supported on a wire gauze which was located below the face plate inside the tube. The thin coatings of Ag_2HgI_4 used in EXP I were applied to thin conducting glass (0.003 - 0.005") by spraying on an alcohol slurry of previously sieved thermochromic (400 mesh) with an air brush. Later, slurries of thermochromic were applied using other liquids.

In EXP I, a well focused beam was moved across the surface of the thermochromic in the CRT at rates up to a few centimeters per second. This approximate rate was used in all experiments unless otherwise indicated. At voltages between about 3 KV and 10 KV it was possible to induce irreversible color changes in both samples. There was some evidence for reversible color changes along the edges of the trace. Evidently enough heat travelled laterally to induce a slight color change but not decomposition. There did not seem to be any setting of the tube using voltages between 0 and 10 KV and current between 0 and 70 μamp (Aquadag current reading) that caused a good reversible transition in the main trace. The Aquadag-coating current is the current flowing in the high voltage circuit. Similar results were observed (EXP II) on samples sprayed on a 1/8 inch conducting glass substrate.

Since these results did not seem to be consistent with the good reversible color changes that were observed at 50 - 75 KV in the electron microscope, the experiments were repeated in the electron microscope. Reversible changes were again observed. There are two differences between the electron microscope experiments and the demountable CRT experiments that may be significant. First, the thermochromic change in the microscope was observed on the same side that the electron beam strikes the material. This enabled the viewer to move the beam once the transition occurred and thereby avoid overheating. In the CRT, it is possible that overheating may have occurred in some of the thermochromic before a significant color change had occurred on the side facing the viewer.

The second difference is the much higher voltage used in the electron microscope. The penetration limit of the electrons is directly proportional to the square of the voltage in the range from 10^3 to 10^5 volts and inversely proportional to the density as given by Terrill's equation :(2)

$$X_e = 2.5 \times 10^{-12} \sigma^{-1} V_o^2 \mathrm{cm}$$

where X_e represents the penetration limit, σ the density, and V the voltage. The penetration limit for the electrons at 75KV as used in the electron microscope experiment is estimated to be 23.5 microns for Ag_2HgI_4.

The penetration limits for electrons at 5 and 10 KV are estimated to be 0.10 and 0.42 microns respectively. If it can be assumed that the last 25 percent of the material receives 50 percent of the beam energy,(3) it is likely in the electron microscope experiments that a large part of the energy is given up to the glass which, in turn, heats the thermochromic. Since the penetration is so small at the voltages used in the CRT, at similar power levels the chance of overheating the thermochromic is much greater in the CRT than in the electron microscope. The thermal conductivity of Ag_2HgI_4, a powdered salt, is probably sufficiently low so that the energy deposited by the electrons would be slowly dissipated allowing for temperature build up. Precise calculations of the heat transfer involved are difficult. Therefore, these statements are only qualitative.

Another factor that may also be important is the anomalous specific heat behavior of Ag_2HgI_4. Both above and below the transition temperature the specific heat is about 0.05-0.06 cal/g -°C; however, as the transition temperature is approached from low temperatures the heat capacity rises to about three times these values(4). This would tend to lead one to use higher power levels to achieve the transition. These high power levels subsequently could lead to overheating above the transition temperature.

It was decided, for the reasons cited above, to modify the CRT so that voltages up to 35 KV could be obtained. In EXP III reversible thermochromic transitions were observed at 35 KV. The other experimental conditions were similar to those in EXP I. Experimental difficulties prevented the beam current measurement.

It was also decided at this time that a better method for measuring the beam current was needed. The current that was being measured on the Aquadag coating included the beam current and any scattering of electrons to the G-2 focusing anode or to the Aquadag coating. There could be appreciable scattering in the demountable system because of the relatively poor vacuum and the possibility of non-optimum alignment of the magnetic focusing coils. A Faraday cup was then used as a collector for the electron beam. A meter having a sensitivity of 100 μ amperes full scale was used in measuring the current in the cup.

In EXP IV, which was performed on the same target as used in EXP III and using the Faraday cup, very slight reversible color changes were observed at 10 KV and a beam current of 1.5 μ amp. This corresponds to a power of 1.5×10^{-2} watts. Much more distinct reversible color changes were observed at 20KV and 1.5μ amp a power of 3×10^{-2} watts.

4.1.2 Refined Experiments

It was decided that more refinements in experimental procedure were needed in order to optimize the conditions for obtaining good reversible thermochromic changes in the CRT. A cathetometer was used for the measurement of the diameter of the electron beam as seen on an area of the target coated with the cathodoluminescent phosphor P-14. A more sensitive meter (0-16μamp, full scale) was used for measuring beam current. The conducting glass surface was sprayed very evenly and the thermochromic was weighed by difference using an analytical balance.

In a series of experiments, EXP V - EXP VII, Ag_2HgI_4 was sprayed onto the conducting side of a 1/8" thick conducting glass plate to form a uniform-looking coating with an average surface density of 18.7 mg/cm^2. This corresponds to a thickness of 30 microns if the theoretical density is used in the calculation. The results, as shown in Table 1, are all negative; that is at all voltages from 10 - 20 KV and at an approximately constant power density of 4 watts/cm there was a great tendency towards decomposition. It may be desirable to repeat these experiments at other power densities and possibly with much thinner layers of thermochromic powder. Higher voltages do not seem desirable for most applications.

In another series of experiments (EXP VII- EXP XV) Ag_2HgI_4 was sprayed onto the conducting side of 0.0044" thick conducting glass. The surface density was 4.1 mg/cm^2 which corresponds to a layer approximately 7 microns thick. In a general way, an approximately constant power density was maintained through many of these experiments. In all cases there was a great tendency towards decomposition of the thermochromic although some reversible color changes

TABLE 1

Results of Experiments V - VII Ag_2HgI_4 on Thick Glass

EXP #	Anode Current (μa)	Faraday Cup Current (μa)	Voltage(KV)	Power (Watts)	Beam Diameter(cm)	Power Density (watts/cm^2)	Comments
V	3	1.5	20	$3x10^{-2}$	0.10	3.8	Reversible & Irreversible changes
VI	6	3.0	15	$4.5x10^{-2}$	0.12	4.1	Irreversible changes only
VII	30	~4.2	10	$4.2x10^{-2}$	0.12	3.8	Reversible & Irreversible changes

TABLE 2

Results of Experiments VII - XV Ag_2HgI_4 on Thin Glass

EXP #	Anode Current (μa)	Faraday Cup Current (μa)	Voltage(KV)	Power (Watts)	Beam Diameter(cm)	Power Density (watts/cm^2)	Comments
VIII	2	1.5	20	$3x10^{-2}$	0.10	3.8	Reversible & Irreversible changes
IX	2	1.0	20	$2x10^{-2}$	0.10	2.5	Reversible & Irreversible changes
X	3	3.0	15	$4.5x10^{-2}$	0.10	5.7	Reversible & Irreversible changes
XI	3	1.7	15	$2.6x10^{-2}$	0.10	3.2	Reversible & Irreversible changes
XII	2	1.0	15	$1.5x10^{-2}$	0.10	1.9	More reversible changes & some irreversible
XIII	3	2.5	10	$2.5x10^{-2}$	0.10	3.2	Reversible & Irreversible
XIV	3	1.0	10	$1.0x10^{-2}$	0.10	1.2	Little - if any change
XV		0.5	20	$1.0x10^{-2}$	0.10	1.2	Brighter than EXP XIV slight reversible changes

were noted. It would appear, however, that it is going to be fairly difficult to get good color changes with the thermochromic powder facing the beam. The results are shown in Table 2.

4.2 Ag_2HgI_4 Experiments with the Beam Incident On a Backing Material

4.2.1 Glass Substrates

Since reversible thermochromic transitions had been observed in the electron microscope with the beam striking the very thin glass substrates, it was decided to try this configuration in the CRT. Since the thin glass used is much thicker than the penetration limit of the electrons used, it is evident that the beam is heating the glass, and that the heat then diffuses through the remaining glass, across the interface, and through the thermochromic. It should, therefore, be possible to protect the thermochromic from overheating more easily in this configuration than with the beam incident upon the thermochromic directly.

In a first experiment, EXP XVI, a reversible thermochromic transition in Ag_2HgI_4 was observed above 5 KV and with unknown beam currents.

Later experiments, EXP XVII, showed reversible changes at 20 KV and 10 KV and a nominal current of 4 μamp. The Faraday cup was then placed in the system to measure the beam current and the beam diameter was measured with a cathetometer. Reversible thermochromic changes were now observed at 20KV and at 1.5 and 2 μamps. These correspond to power-density levels of 3.8 and 5.1 watts/cm^2, The thermochromic change produced is fairly broad due to lateral diffusion of heat. However, reversible thermochromic changes were easily produced in this configuration. It was much easier to avoid overheating the thermochromic then in the configuration in which the beam strikes the material directly.

4.2.2 Copper Substrate

Glass is a poor conductor of heat. Its thermal conductivity(5) is in the range from 1.7 x 10^{-3} to 3 x 10^{-3} cal cm^{-1} sec^{-1} $^{o}C^{-1}$ and its specific heat is about 0.2 cal g^{-1} $^{o}C^{-1}$. It was decided to see what effect a material of high thermal conductivity would have on the ease of inducing a thermochromic change with the electron beam. Copper (5) has the high thermal conductivity of 0.94 cal $cm^{-1}$$sec^{-1}$ $^{o}C^{-1}$ and a specific heat of 0.092 cal g^{-1} $^{o}C^{-1}$.

A 0.0015" thick sheet of copper was used in the preliminary experiment, EXP XVIII. A coating of Ag_2HgI_4 was painted onto the copper foil. Exposure to a 20 KV electron beam at the relatively high power density levels of 8.2 - 12.3 watts/cm produced no color change at all. The power density was higher than that which gave good color changes with a substrate of thin conducting glass and yet no color change was observed with the Cu base. Since the thermal conductivity of copper is very high relative to Ag_2HgI_4 and to glass, the heat energy is spreading excessively and therefore rapidly dissipating laterally into the copper with very little heating of the Ag_2HgI_4. No further work with this substrate is indicated.

4.2.3 Nickel Substrate

Nickel has a thermal conductivity(5) of 0.22 cal cm^{-1} sec^{-1} $°C^{-1}$ and a specific heat of 0.10 cal g^{-1} $°C^{-1}$. Its thermal conductivity is considerably less than copper but still much higher than glass. EXP XIX was performed by spraying Ag_2HgI_4 onto a 0.00035" thick nickel foil. The coating was very fragile and tended to flake off very easily when the foil was bent. In an application using this foil it would be important to use it in a taut configuration to avoid flexing. The nickel was exposed to a 20 KV electron beam at a power density of 7.6 watts/cm^2. The current was 3 μamp . Successful reversible thermochromic changes were observed at this power level.

In EXP XX the same nickel foil used in EXP XIX was spray coated alongside a piece of thin conducting glass. In this way the coating thickness of the two materials would be about the same. At 20 KV it was possible to achieve good thermochromic transitions with the glass substrate at slightly lower power levels than with the nickel substrate. On the other hand, the rate of fading of the thermochromic color change was slightly faster with the nickel than with the glass. Nonetheless, the fading times were of the order of 10 seconds. Since it is possible to obtain relatively strong nickel foils as thin as 0.0001" it seems reasonable to attempt other experiments using thinner foils.

4.2.4 Magnesium Oxide-Thermochromic-Glass Sandwich

It is difficult to obtain glass substrates of any desired thickness when working at thicknesses of the order of thousands of an inch. It was decided to use a sprayable ceramic substrate as a substitute in order to be able to vary the thickness. This,however, presents another problem : the sprayable ceramic would not be sufficiently rigid to form a mechanically stable structure. It is necessary to introduce a rigid transparent third member into the configuration. The obvious choice is the thin glass used in previous experiments. Magnesium oxide, MgO, was chosen as the sprayable ceramic as it is readily available at a very fine powder. The thermal conductivity(6) of compressed MgO is about 0.001 cal cm^{-1} $°C^{-1}$, which is comparable to that of glass. The maximum penetration of electrons in a solid layer of MgO at 20 KV would be about 2.8 microns as calculated by Terrill's equation. Therefore, the thickness of the MgO should be greater than this in order to reduce the likelihood of overheating the thermochromic.

In EXP XXI Ag_2HgI_4 was sprayed onto thin conducting glass to obtain a surface density of 5.0 mg/cm^2 and a thickness of 8.3 microns as calculated from the density and surface weights. MgO was sprayed onto the thermochromic layer in a manner similar to that used to spray the thermochromic. Its surface density was 72 mg/cm^2. From the density of $3.58/cm^3$ and the surface density, the film thickness is calculated to be 20 microns.

The MgO was allowed to be struck by the electron beam. Color changes in the middle thermochromic layer could be observed through the outer glass layer. At both 10 and 20 KV, and at power levels ranging from 1 - 2.5 $watts/cm^2$ only irreversible changes were observed in the thermochromic. Close examination of the MgO coating revealed the presence of numerous small cracks. It is likely that the electrons were striking the Ag_2HgI_4 directly. This is also indicated by the fact that the decomposition marks on the thermochromic were irregular in shape and not straight as usually happens. Evidently this application technique for MgO was not a good one.

It was then decided to form a coating of MgO by burning magnesium metal and allowing the smoke to impinge upon the thermochromic. A denser, more opaque coating of MgO might be achieved by this method since this is the procedure used in spectrophotometric work for reflectance standards.

In EXP XXII a coating of Ag_2HgI_4 having a surface density of 2.8mg/cm^2 and a calculated thickness of 4.6 microns was sprayed onto thin conducting glass. The sample was then exposed to MgO smoke from a burning magnesium ribbon. The calculated thickness of the MgO is 2.2 microns (0.0001"). The coating was very opaque and had no visible cracks. The MgO surface was exposed to a 20 KV electron beam at a beam current of 0.8 μamp which at the usual spot size of 1 mm corresponds to a power density of 2.0 watts/cm^2. Further experiments could not be performed due to failure of the tube. The color change produced was not as intense as when the glass faced the beam in EXP XVI and EXP XVII, but the line thickness was thinner and the color faded more rapidly. A fluorescent glow produced by the beam could be seen through the MgO and Ag_2HgI_4 coatings. The source of the glow has not been determined; however, it suggests the possibility of using a CRT phosphor in place of the ceramic if it is desired to fabricate a combined thermochromic cathodoluminescent device.

4.3 Initial Results with Electronic Scanning

Due to the fact that the scanning mechanism was installed late in the report period, relatively few experiments were performed using it. It is premature therefore, to draw any conclusions from the experiments. Future work should make consistent use of this type of apparatus. Nonetheless, the two experiments performed will be described.

In EXP XVII, in which the electrons were allowed to strike thin conducting glass coated with Ag_2HgI_4, a maximum scan rate was determined to be 1 cm/sec for a good color change. At 20 KV and 5 watts/cm^2 the energy deposited on a 1 cm^2 area was 0.25 cal.

4.4 Experiments with Other Materials

4.4.1 Cu_2HgI_4

Only qualitative observations were made in the performance of this material in a CRT. In EXP XXIII, Cu_2HgI_4 was sprayed onto the thin conducting glass and placed in the CRT with the thermochromic facing the beam. Bombardment of the Cu_2HgI_4 at voltages between 3 KV and 10 KV and nominal currents between zero and 70 microamperes produced irreversible changes in this configuration. The current readings at this time were measured at the Aquadag coating. No beam size measurements were made, but they are estimated to have been about 0.1 cm in diameter.

With the beam striking the glass in EXP XXIV, reversible color changes were achieved at 5 KV and 30 μ amp (Aquadag reading). It was important not to allow the color change to proceed to a very deep black color. If this occurred, there was partial decomposition along with some reversibility.

4.4.2 AgI

Silver iodide, AgI, was considered as a candidate material in the CRT since it is probably a more stable material than Ag_2HgI_4. The AgI thermochromic transition temperature (147°C) is much higher than the ternary iodides. It changes from yellow to red. This color change is not as dramatic as Ag_2HgI_4, but it has good visual contrast.

A AgI slurry was painted on thin conducting glass with an artist's brush. In these experiments, EXP XXVIII, the AgI was struck directly by the electron beam. The results are given in Table 3. In the experiment the AgI seemed to decompose as evidenced by lack of reversibility and the formation of an off color to a greater extent under the impact of the beam than did the Ag_2HgI_4. In EXP XXVII, at just twice as much power only severe decomposition was observed. No explanation is available for this sudden change.

Experiments were also performed with AgI in which the electron beam was allowed to strike the conducting side of the thin conducting glass substrate upon which AgI was sprayed from a butyl alcohol slurry. In EXP XXIX the surface density was 5.5 mg/cm^2. At a voltage of 20 KV, the whole silver iodide surface suddenly became badly discolored as the beam current was increased to 6 or 7 microamperes. A second sample with a surface density of 3.6 mg/cm^2 was prepared and placed under vacuum overnight in EXP XXX. The voltage was then adjusted to 20 KV and a small current of less than 1 microampere was applied with no apparent color change. An increase to 7 microamperes produced the same sudden discoloration described above. No explanation is available at present. Experiments should probably be performed at other levels.

4.4.3 Mixture of Ag_2HgI_4 and P-14 Phosphor

In EXP XXXI, a 50 percent mixture of P-14 phosphor and Ag_2HgI_4 on a thin conducting glass substrate was placed into the horizontally mounted CRT with the phosphor mixture facing the beam. Between 10 and 20 KV no reversible thermochromic transition was observed.

TABLE 3

SILVER IODIDE IN A CRT

Expt. No.	Amode Current (μa)	Faraday Cup Current (μa)	Voltage (kv)	Beam Diameter (cm)	Comments
EXP XXV	2.0	1.0	20	0.10	Irreversible color change
EXP XXVI	2.0	0.5	20	0.10	Irreversible color change
EXP XXVII	2.0	2.0	10	0.10	Irreversible color change
EXP XXVIII	-	1.0	10	0.10	No color change

Beam currents were nominally 10 microamperes as measured by the Aquadag current. The target material decomposed as evidenced by a permanent dark trace on the thin conducting glass supporting the mixture. Reduction of the beam current from 10 μ amps to inhibit decomposition produced little or no change in the color of the thermochromic. Thus employed, the effect was either decomposition or no color change at all. In all cases yellow cathodoluminescence was clearly visible.

5. MATERIALS SYNTHESIS AND PROPERTIES

Materials Synthesis and Properties

A variety of materials were prepared in this program in an attempt to generate new thermochromic materials. The details of the syntheses will be found in the Appendix.

5.1 Cadmium Substitution in Ag_2HgI_4

Firings of mixtures of AgI, CdI_2, and HgI_2 leading to the compositions $Ag_2Hg_{1-x}Cd_xI_4$, where x goes from 0.30 to 0.70 in steps of 0.05 were completed. All materials showed thermochromic activity, the color going from a yellowish low-temperature form to an orange high-temperature form. The transition ranges of the first three members of this series were determined on a variable temperature-gradient stage. These results along with those obtained from earlier studies in which x was varied from 0.0 to 0.25 are given in Table 4. The results are consistent with the previously prepared formulations. The transition temperature increases with increasing cadmium content and the broad temperature range over which the transition occurs is still present.

5.2 Other New Materials

Mixed crystal compositions(7) prepared from AgI and PbI_2 in the following mole ratios were prepared by heating at 450°C: 3:1, 2:1, 1:1 and 2:3. All resulting materials were thermochromic. The analysis of their thermochromic properties are given in Table 5. A mechanical mixture of AgI and PbI_2 in a 2:1 mole ratio was also prepared and examined for thermochromicity alongside the fired composition. There was a color change in the mechanical mixture but it was very slight as compared to the materials prepared.

TABLE 4

Transition Temperature of $Ag_2Hg_{1-x}Cd_xI_4$ As a Function of X

X	Transition Temperature Range (°C)
0	47° - 51°
0.05	48° - 55°
0.10	48° - 58°
0.15	52° - 63°
0.20	51° - 65°
0.25	56° - 67°
0.30	62° - 77°
0.35	64° - 82°
0.40	68° - 88°

TABLE 5

Thermochromic Behavior of AgI-PbI_2 Compositions

$3AgI:PbI_2$ - broad transition, yellow to red, 99-137°C pronounced change at 124°C

$2AgI:PbI_2$ - broad transition, lemon yellow to reddish-orange 110-137°C

$AgI:PbI_2$ - broad transition, yellow to orange-red, 99-135°C

$2AgI:3PbI_2$ - broad transition, yellow to red-orange, 97-137°C

$T\ell I:CdI_2$

Toxicity data on compounds of thallium have been reviewed(8). In general it can be concluded that thallium and its compounds present no worse and probably less of a hazard than mercury compounds.

Four formulations, $3T\ell I:CdI_2$, $2T\ell I:CdI_2$, $T\ell I:CdI_2$, and $2T\ell I:3CdI_2$ were prepared in the same manner as the $AgI:PbI_2$ compositions. None were thermochromic.

$2CuI:PbI_2$

A composition of the formula $2CuI:PbI_2$ was prepared. The product did not display significant thermochromism.

$AgI:SnI_2$

Compositions $AgI:SnI_2$ in 2:3, 1:1, 2:1, and 3:1 molar proportions were prepared. The materials were all yellow to yellow-orange and had the odor of iodine . The materials darkened with decomposition as they were heated to 230°C where they decompose rapidly. No significant thermochromic activity was observed.

$CuI:SnI_2$

Compositions of CuI and SnI_2 2:3, 1:1, 2:1, and 2:1 proportions were prepared. They all had the odor and color of iodine and decomposed and darkened rapidly on heating. No useful thermochromism was observed for these unstable compositions.

$AgI:CdI_2$ and $CuI:CdI_2$

Six mixtures leading to the three molar compositions 2:1, 1:1, and 1:2

have been fired for each of the above systems. Both 2:1 systems decomposed after showing a gradual yellow to yellow-orange thermochromic change. All the others did show some thermochromic activity, but it was of low contrast and very gradual. None looked promising.

$CaIn_2S_4$

$CaIn_2S_4$ was prepared from an equimolar mixture of CaS and In_2S_3 according to the method of Hahn and Klinger(10). There was a slight darkening of the light orange material at about 170°C. This material does not appear to be a useful thermochromic.

5.3 Thermal and Vacuum Stability Studies

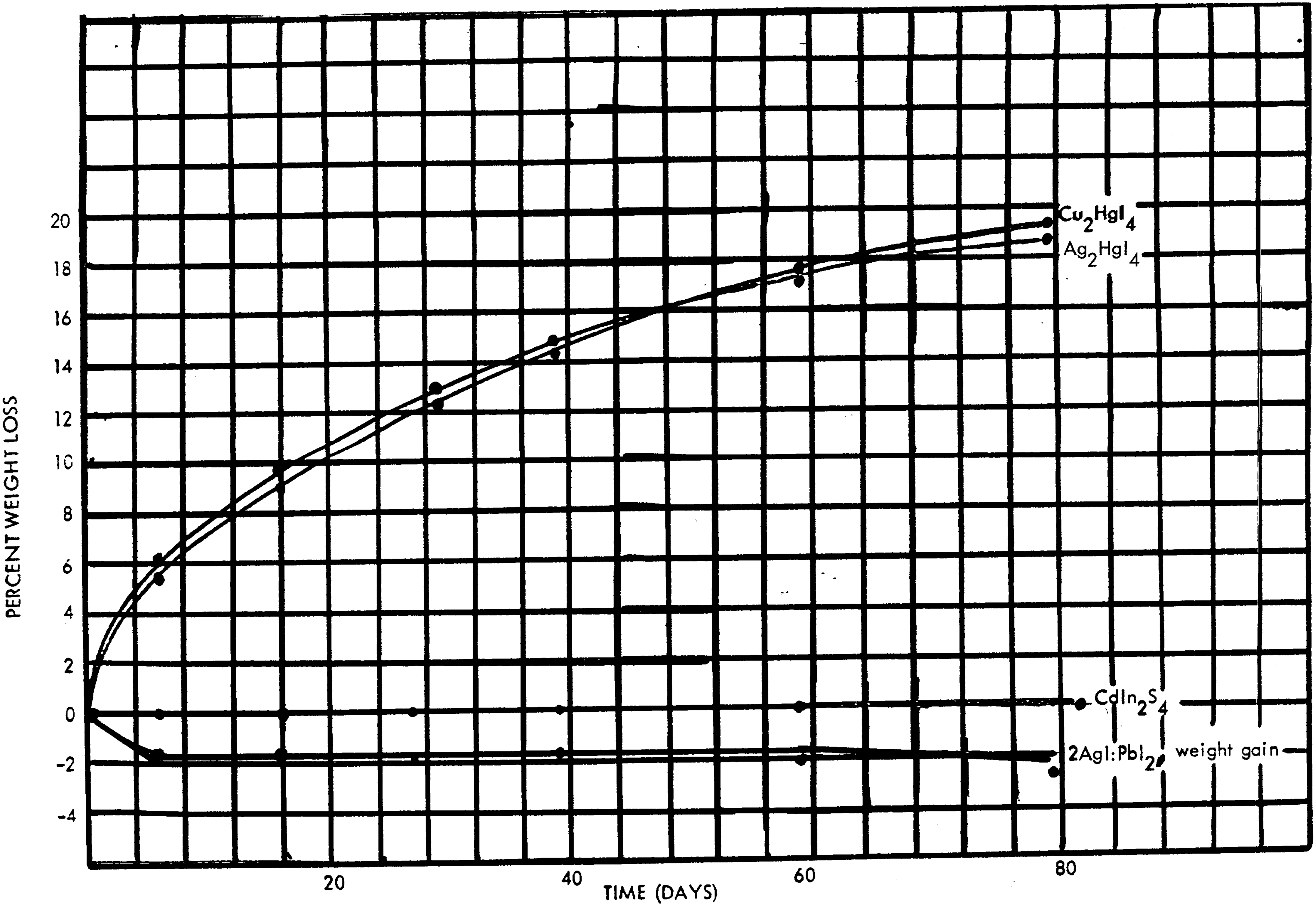
5.3.1 Thermal Stability Tests

Since the use of thermochromic materials involves, by definition, heating them above their transition temperature, it is important to know how stable they are above the transition temperature. In the First Annual Progress Report, weight loss data are presented as a function of time for both Ag_2HgI_4 and Cu_2HgI_4 held at 10°C above their respective transition temperatures. Both tended to decompose in a matter of months.

The composition $2Ag:PbI_2$ was maintained at a temperature of 150°C at atmospheric pressure for a period of two months. No significant change in weight was observed in that time. This material is more thermally stable than either silver or copper mercuric iodide.

5.3.2 Vacuum Stability Tests

Since a major projected application of thermochromics is in a CRT environment, it is important to know how well these materials will hold up to exposure to vacuum for a long time. Samples of Ag_2HgI_4, Cu_2HgI_4, $CdIn_2S_4$, and $2AgI:PbI_2$ were subjected to a vacuum stability test. They were maintained at room temperature in vials at a vacuum of about 10^{-7} Torr for 79 days under conditions of continuous pumping. The samples were weighed periodically. Figure 3 is a graph showing the percentage of weight loss (referred to the original weight) as a function of vacuum exposure time. The two mercury containing ternary iodides showed the greatest weight loss. They were still losing weight, at a decreasing rate, however,



WEIGHT LOSS OF THERMOCHROMICS AT ROOM TEMPERATURE AND 10^{-7} TORR (CONTINUOUSLY PUMPED)

FIGURE 3

at the end of the test. $CdIn_2S_4$ was stable in this test environment. The lead containing material showed a rapid weight gain of about 2 percent followed by a long period with little additional change. The initial gain could be an experimental artifact. This material, however, does show an undesirable property. It exhibits severe surface discoloration after a short exposure to this environment. It is not a good candidate material for the CRT application.

5.4 Specific Heat Measurements and Electrical Conductivity Measurement

It is useful to know the specific heat of materials intended for use in an application requiring heating. The specific heat and the thermal conductivity are important parameters in determining how great a rise in temperature will occur under a given set of heating conditions.

Specific heat measurements at several temperatures for $Ag_2HgI_{3.84}Br_{0.16}$ and $CdIn_2S_4$ were determined. Both of these materials were prepared in the first year's work under this program.

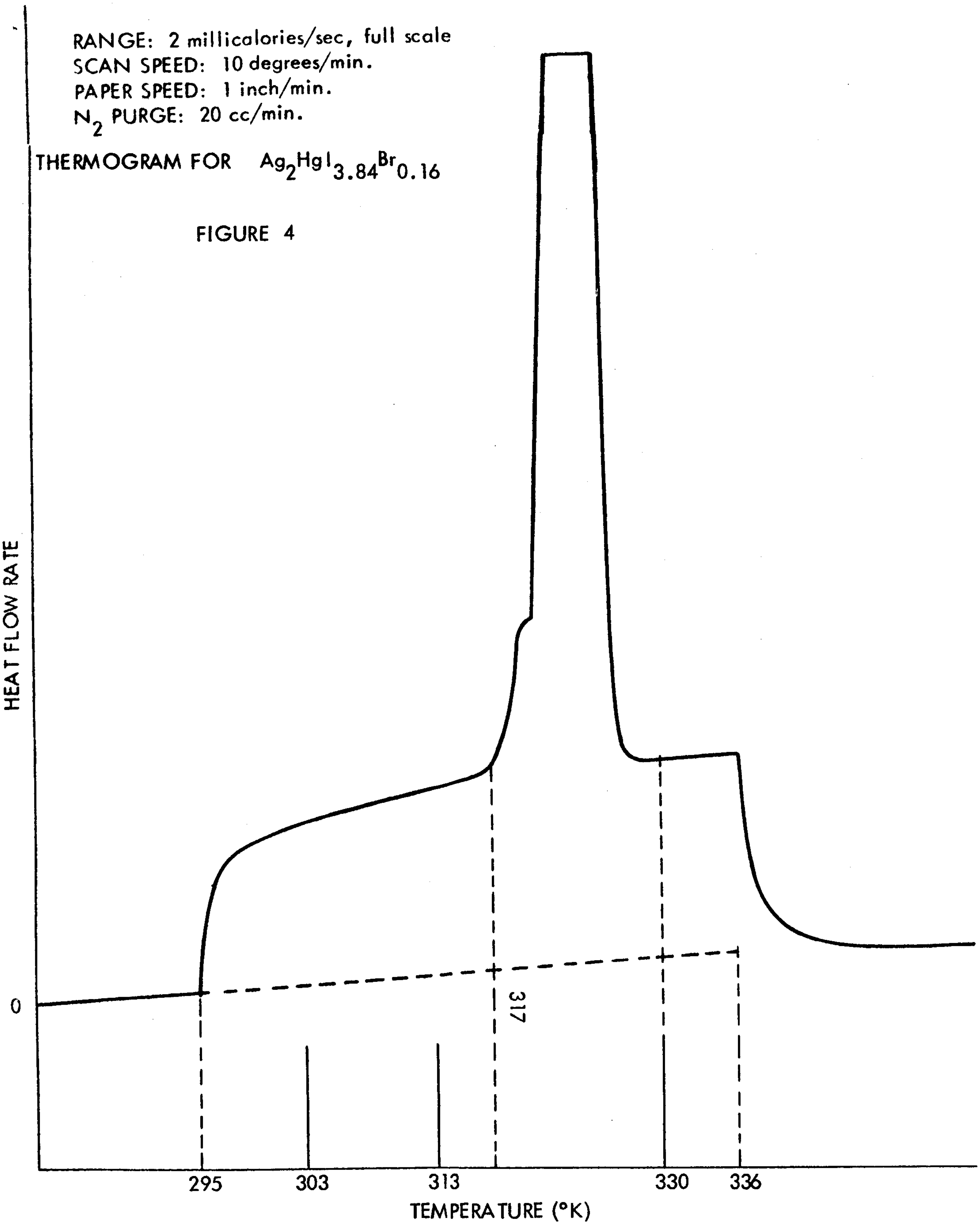
We are indebted to the Perkin Elmer Corporation, Norwalk, Connecticut for these measurements which were performed on their differential scanning calorimeter. The results are given in Table 6. Specific heat data for Ag_2HgI_4 reported by Ketelaar(4) are presented for comparison.

A large endothermic behavior was observed for the solid-solid transformation of $Ag_2HgI_{3.84}Br_{0.16}$ but no such behavior was apparent for $CdIn_2S_4$ over the temperature range 17°C - 158°C. This latter observation indicates

TABLE 6

Specific Heat Of Three Thermochromic Materials As A Function Of Temperature

Temperature (°C)	Cp (cal/g-deg)		
	$Ag_2HgI_{3.84}Br_{0.16}$	Ag_2HgI_4	$CdIn_2S_4$
30	0.051_7	0.0526	
40	0.058_6	0.0550	
57	0.061_8	0.0624	
75	-----	-----	0.103_8
95	-----	-----	0.104_3
120	-----	-----	0.104_4

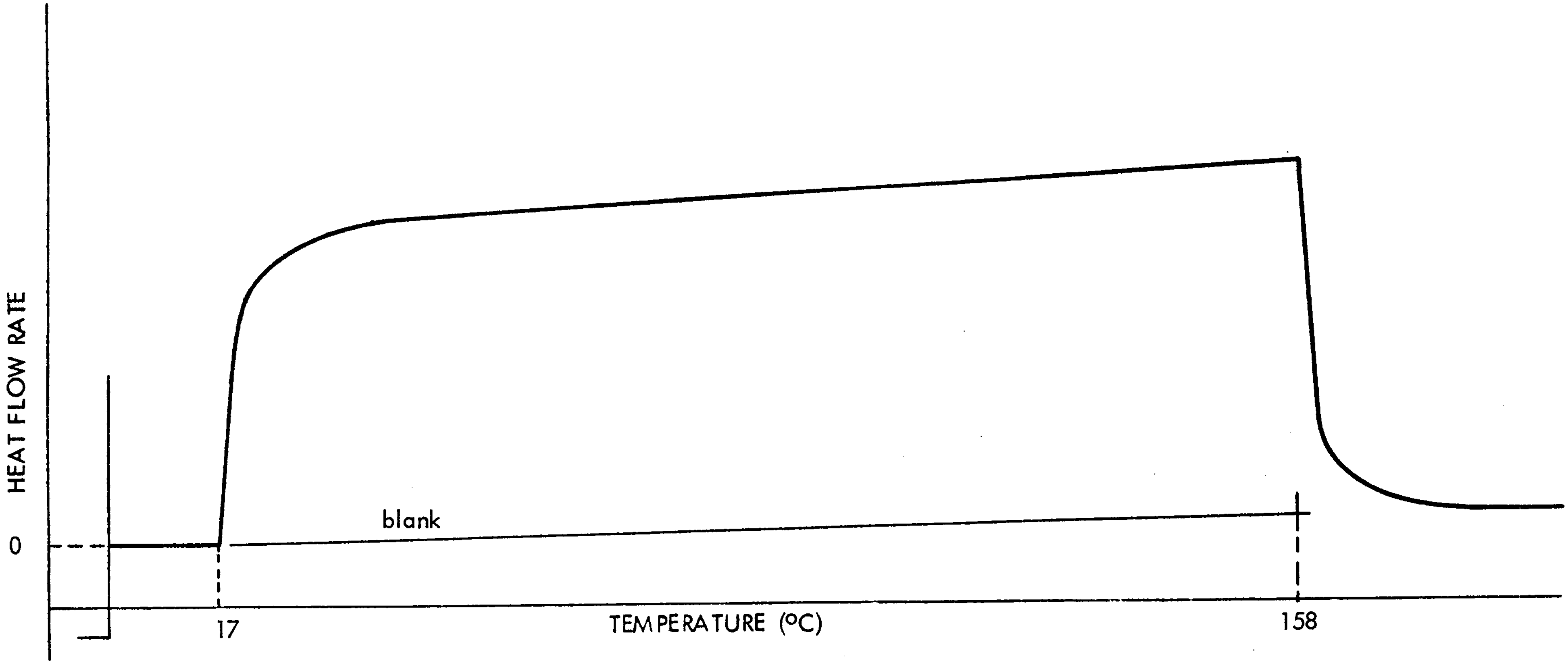


RANGE: 2 millicalories/sec, full scale
SCAN SPEED: 10 degrees/min.
PAPER SPEED: 1 inch/min.
N_2 PURGE: 20 cc/min.

THERMOGRAM FOR $Ag_2HgI_{3.84}Br_{0.16}$

FIGURE 4

RANGE: 2 millicalories/sec, full scale
SCAN SPEED: 10 degrees/min.
PAPER SPEED: 1 inch/min.
N_2 PURGE: 20 cc/min.



THERMOGRAM FOR $CdIn_2S_4$

FIGURE 5

that the change in color observed for $CdIn_2S_4$ which takes place over the temperature range 95°C - 100°C is not due to an order-disorder transformation of the type that occurs in Ag_2HgI_4 but is probably attributable to a lattice expansion or some other type of phase transition. Thermograms for silver mercuric iodide bromide, $Ag_2HgI_{3.84}Br_{0.16}$ and cadmium indium sulphide, $CdIn_2S_4$, are shown in Figure 4 and 5.

5.5 Thermal Conductivity Measurements

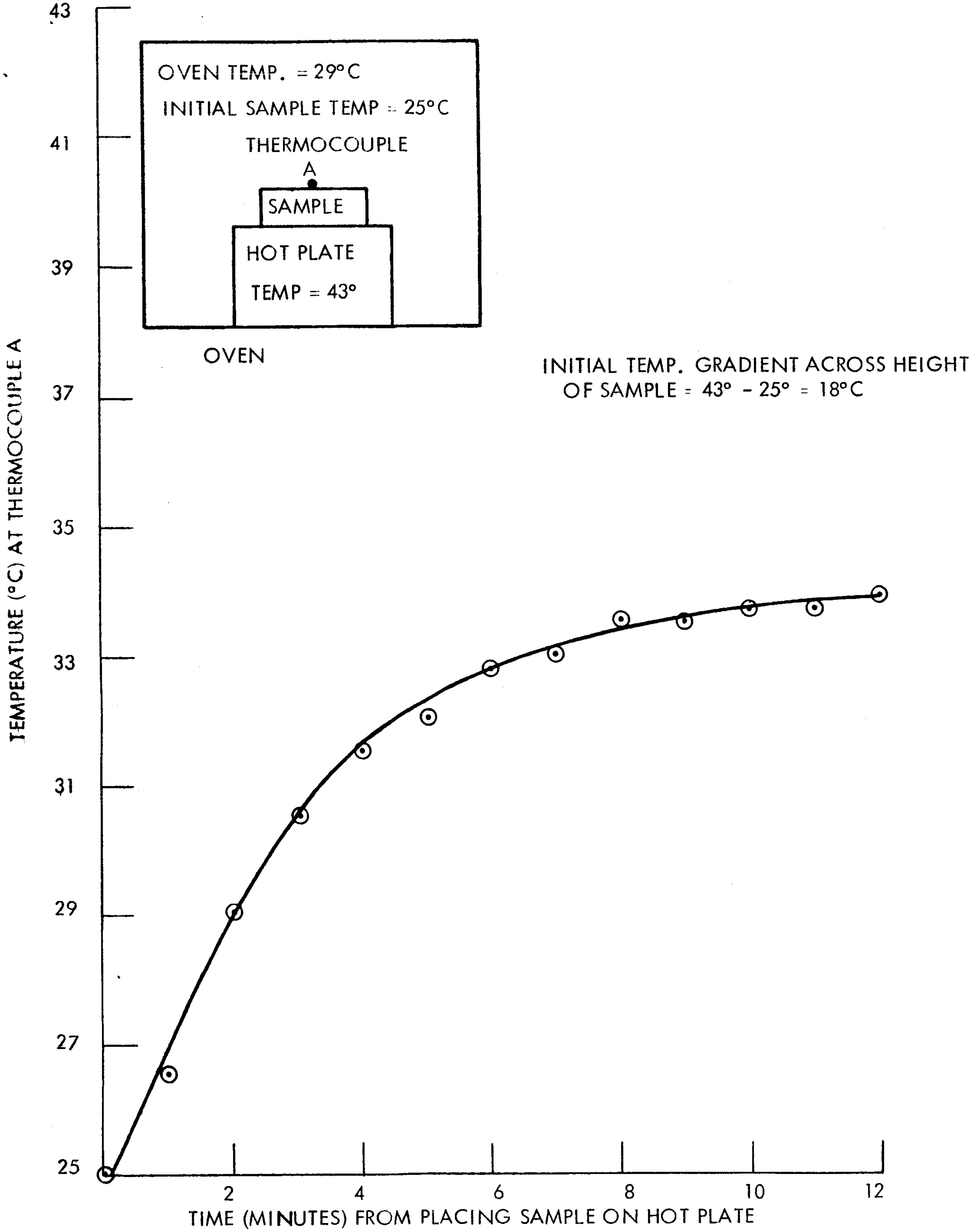
Experiments were conducted on Ag_2HgI_4 in order to determine if there is a substantial change in thermal conductivity on exceeding the transition temperature, corresponding to the change in electrical conductivity previously noted. This type of information is important in the design of an apparatus using the material. A discontinuity or other dramatic change in thermal conductivity would have to be taken into account when estimates are made of the amount of heating power needed to achieve a final temperature.

The pellet was prepared by placing 30g of Ag_2HgI_4 in a one inch diameter die. The load on the die was increased gradually over a period of about an hour. When the pressure was increased rapidly there was a tendency for the material to turn orange at the bottom of the die and to crack in directions approximately normal to the die length. The final cylindrical pellet measured 2.54 cm diameter and 1.10 cm thick. This gives a density of 5.92 g/cc which is 98.4 percent of the value (6.02 g/cc) given in the Handbook of Chemistry and Physics for single crystal material.

A shallow radial groove was cut into the aluminum surface of a small electric hot plate. A chromel-alumel thermocouple with its bead at the center of the hot plate was epoxied into the groove. The top of the bead was flush with the hot plate surface. A 0.001" thick sheet of gold was taped on the hot plate in order to insure good thermal contact with the Ag_2HgI_4 and to avoid chemical reaction with the aluminum.

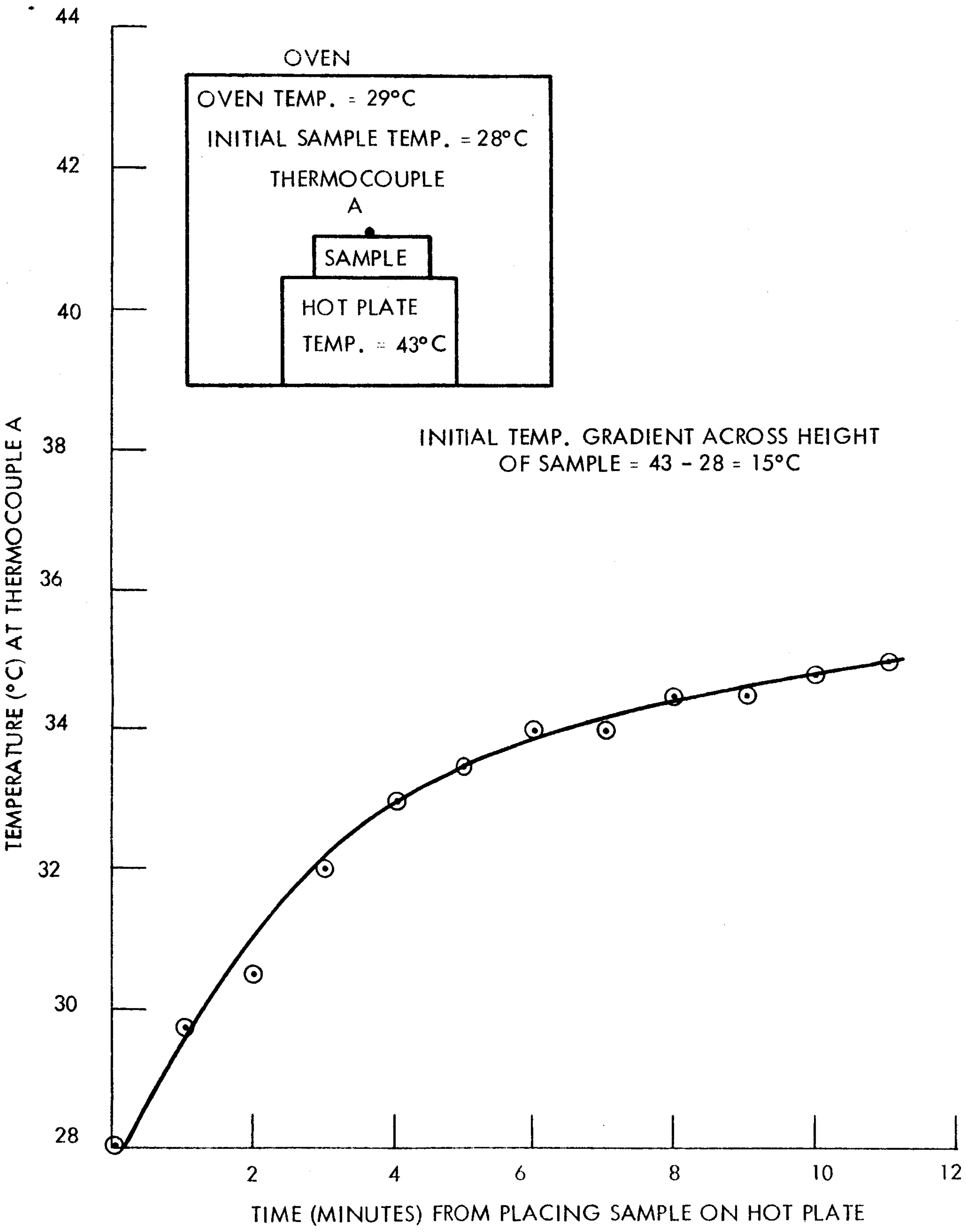
A small hole was scratched in the center of one of the flat surfaces of the pellet and another chromel-alumel thermocouple was taped to the pellet with its bead in the hole. The pellet, with the thermocouple attached was then covered with asbestos sheet on all sides except the flat side opposite to the one with the thermocouple attached. This uncovered surface was the one placed in contact with the hot plate during the experiment. The hot plate itself was enclosed in an asbestos shroud except for the exposed gold foil which was used to heat the thermochromic pellet. The whole apparatus was placed in an oven so that the overall test temperature could be controlled.

Figures 6 and 7 show the results of experiments below the transition temperature. The temperature plotted as the oridinate is that measured by the thermocouple on the pellet. A slightly faster temperature rise is indicated in experiment I as compared with experiment II. This is probably due to the higher initial temperature gradient in I than in II. Figures 8 and 9 show the results at temperatures above the transition temperature. The temperature rise in these experiments is about half of that in the low-temperature studies. Even if the somewhat higher specific heat of the high-temperature form is taken into account, it is probable that there is no order of magnitude change in the thermal conductivity. It appears that the thermal conductivity of the high-temperature form is less than that of the low-temperature form.



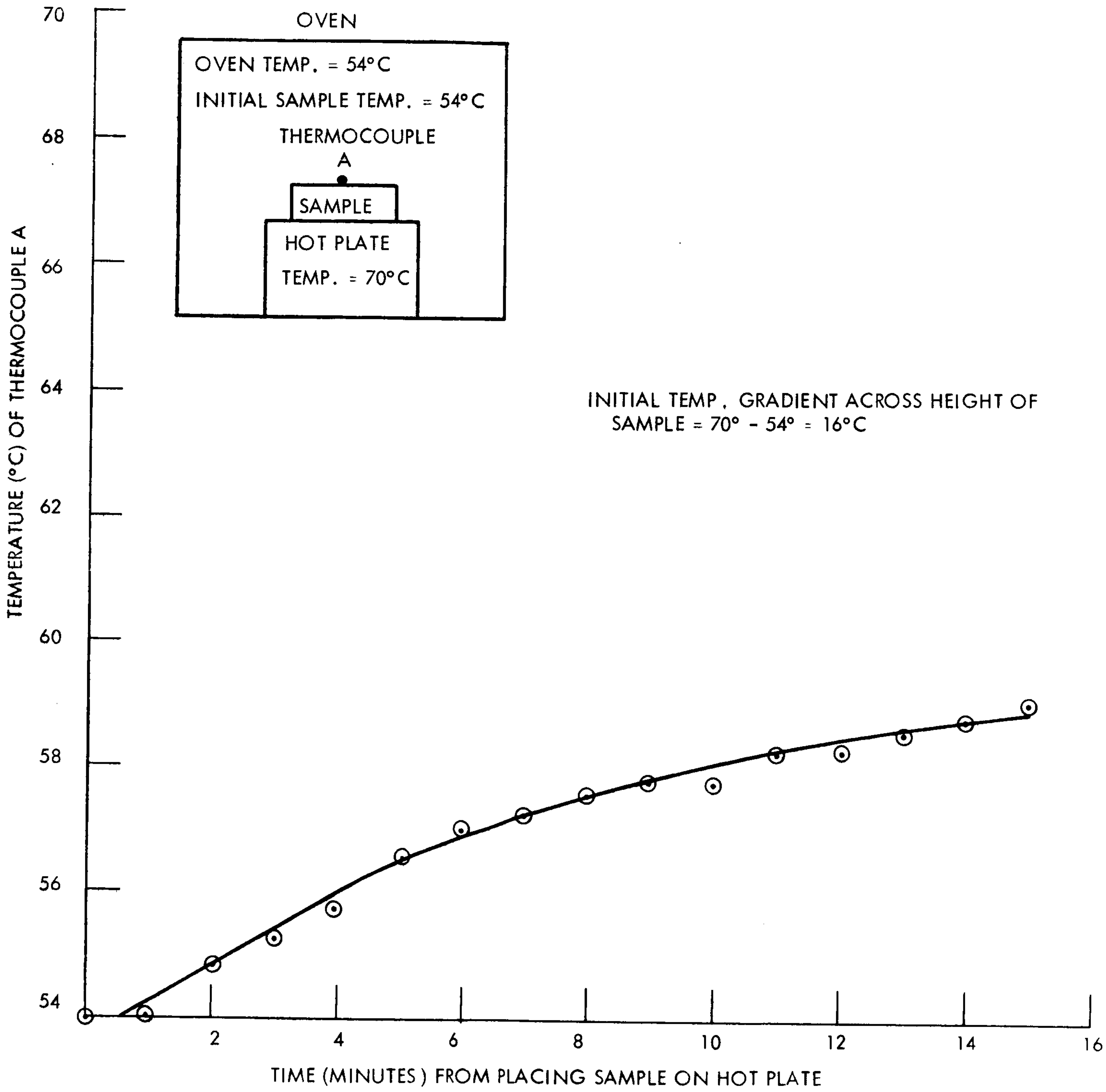
THERMAL CONDUCTIVITY (EXPERIMENT I) OF LOW TEMPERATURE FORM OF Ag_2HgI_4

FIGURE 6



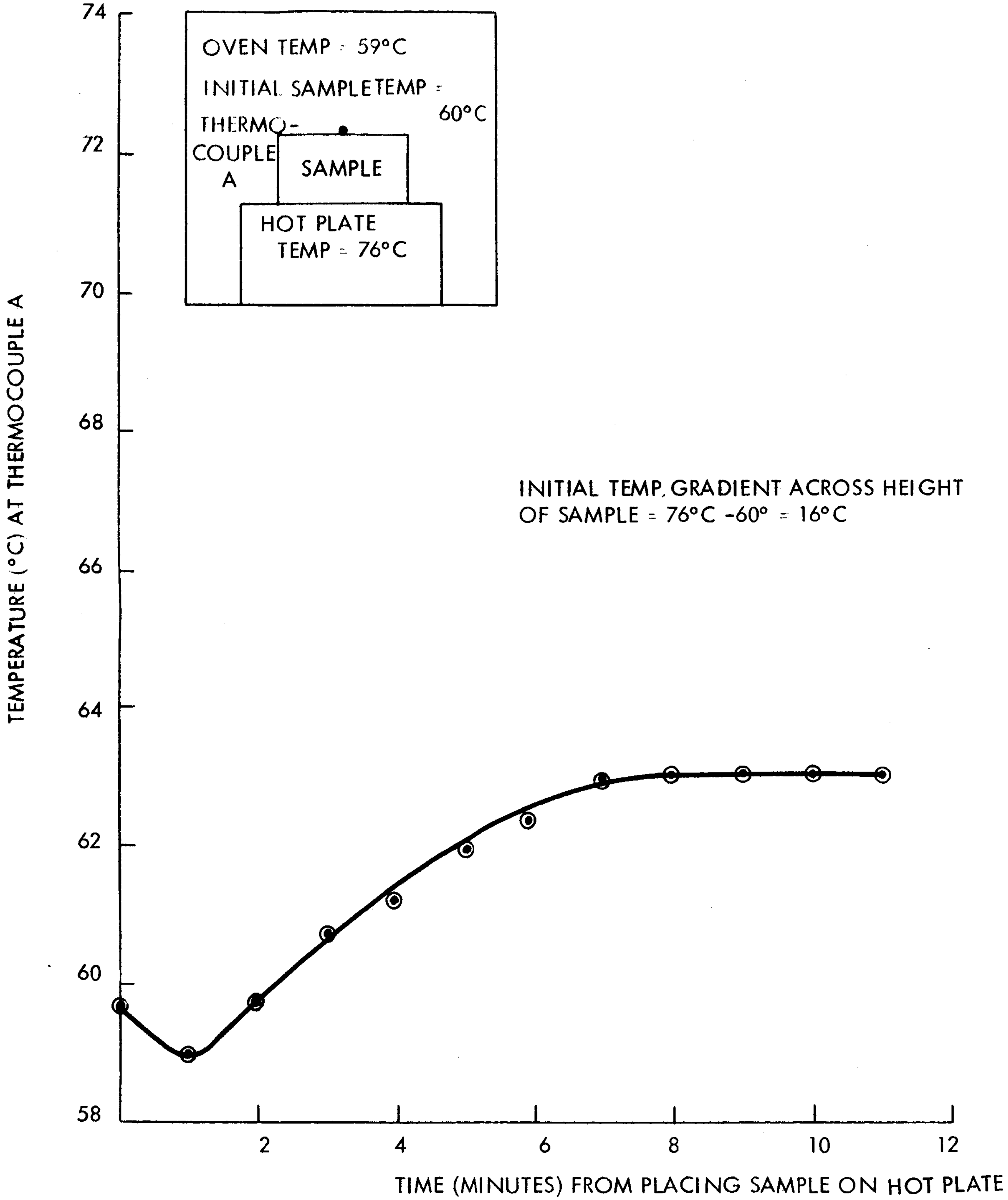
THERMAL CONDUCTIVITY (EXPERIMENT II) OF LOW TEMPERATURE FORM OF Ag_2HgI_4

FIGURE 7



THERMAL CONDUCTIVITY (EXPERIMENT III) OF HIGH TEMPERATURE FORM Ag_2HgI_4

FIGURE 8



THERMAL CONDUCTIVITY (EXPERIMENT IV) OF HIGH TEMPERATURE FORM OF Ag_2HgI_4

FIGURE 9

Electrical Conductivity

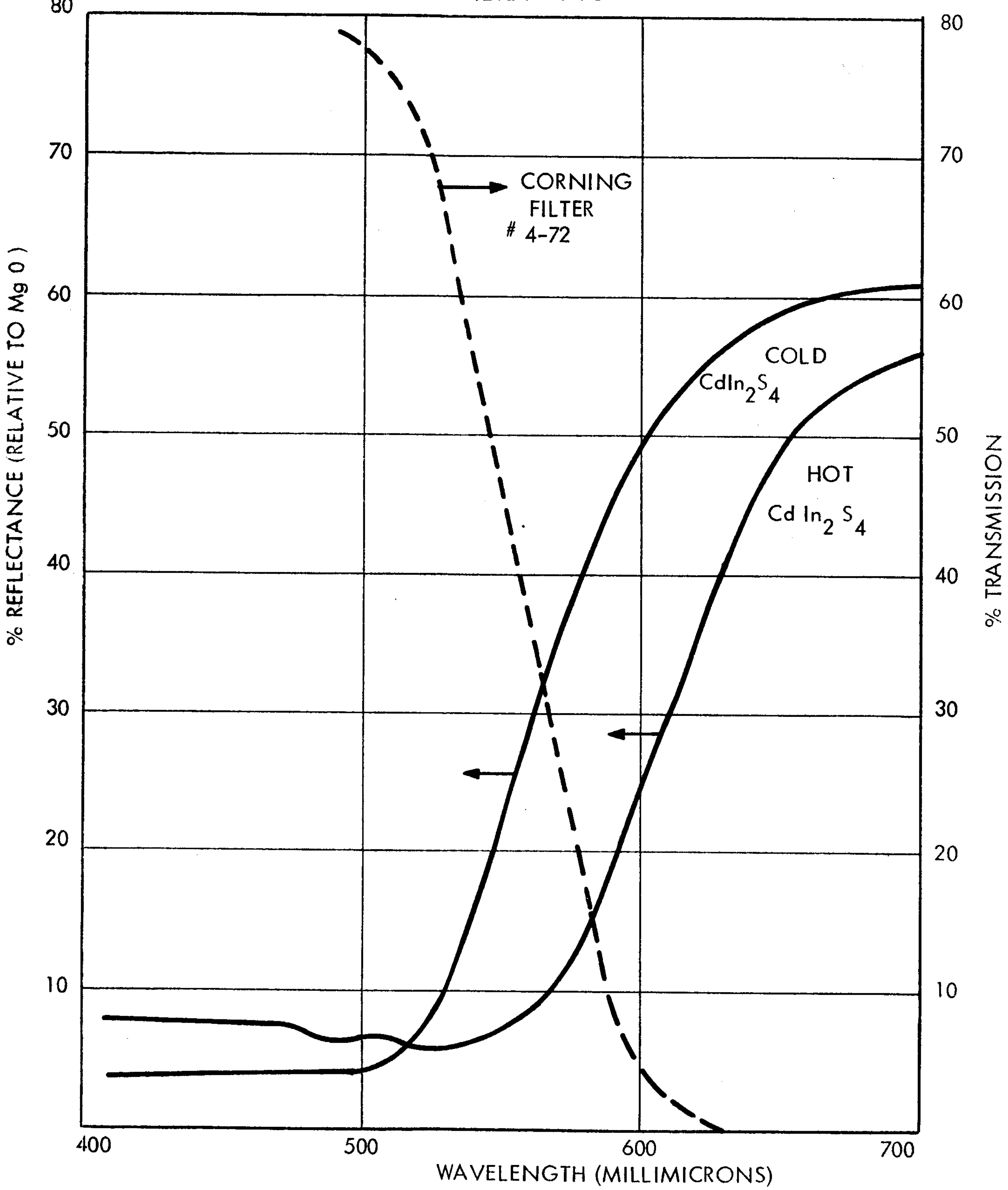
In order to further characterize the material and determine if it has an electrical conductivity change accompanying its color change, efforts were made to measure the electrical conductivity of pelletized $CdIn_2S_4$. This was not successful as the material would not form a satisfactorily adherent pellet. It may be possible to improve the pellet forming ability of $CdIn_2S_4$ by grinding the material to a very fine particle size in a jar rolling mill. This would, however, require very much larger amounts of material as there is normally significant loss of material in using mills. This does not seem worthwhile as the specific heat data mentioned above does not show any significant change in passing from the low- to high-temperature forms. It is likely, therefore, that there will be no dramatic difference in electrical conductivity between the two forms.

5.6 Optical Enhancement of Thermochromic of $CdIn_2S_4$

Filter catalogues of several different manufacturers have been examined with an eye to finding a filter capable of enhancing the optical contrast of $CdIn_2S_4$. The best of these appears to be a blue-green filter manufactured by Corning Glass Works. The catalogue number is 4-72. A plot of the transmission characteristics of this filter along with the reflectance spectra of the hot and cold forms of $CdIn_2S_4$ is shown in Figure 10.

FIGURE 1 0

REFLECTANCE SPECTRA OF HOT AND COLD $CdIn_2S_4$ AND TRANSMISSION SPECTRUM OF CORNING FILTER # 4-72



6. PRELIMINARY DESIGN STUDIES FOR A SEALED - OFF CRT ASSEMBLY

At the present time the most useful thermochromics that are available are the materials based on the ternary iodides Ag_2HgI_4 and Cu_2HgI_4 and the iodides themselves. These materials all suffer from a fairly high degree of thermal instability and as a result conventional methods of constructing a CRT, which use high temperatures for bakeout, cannot be used if these materials are to be included in the tube. The preliminary approach to a sealed-off tube presented here is predicated upon the use of these materials in the tube.

A tube will be obtained in essentially the same configuration as given in Figure 1. All parts including any needed internal-mounting hardware for supporting the thermochromic and its substrate will be subjected to thorough outgassing at elevated temperatures. After this has been done the parts will be stored in an entirely inert environment. This could be either highly purified nitrogen, helium, or argon. The spraying of the thermochromic onto its substrate will also be conducted in a similar environment. All solvents will be carefully purified of deleterious contaminants for spraying purposes.

The faceplate of the tube will finally be fastened to the body by means of a very thin layer of a suitable adhesive. Possibilities include epoxies or Eastman 910. If an epoxy is used it will be carefully selected in order to minimize any outgassing problems. This will, for example, require the use of a solvent-free,ultra-pure epoxy and curing agent. The manufacturer of Eastman 910 states that it is suitable for use in a vacuum environment. The configuration selected was chosen so as to minimize the surface area of the adhesive that is exposed to vacuum, hence the outgassing from the adhesive will be minimized.

The activation of the cathode will be performed prior to final seal-off of the tube at the vacuum tubulation. The heating required will occur fairly remote from the area containing the thermochromic and so should not affect it. It is also expected that a long-lived gettering material can be selected that will minimize the possible deleterious effect of any volatiles escaping into the tube. If this is not possible, consideration will be given to the use of a tungsten cathode providing sufficient beam current can be obtained.

7. SUMMARY AND CONCLUSION

(a) A magnetic focus, magnetic deflection, automatic scan, demountable cathode ray tube apparatus was assembled. It was possible to remove the faceplate as many as fifteen times, exposing the cathode to an inert atmosphere, and still generate a useful beam current after evacuation.

(b) A proof of principle, demonstrating the heating effect of an electron beam to induce thermochromic changes in a variety of materials, was obtained.

(c) A variety of substrate materials for Ag_2HgI_4 were utilized to intercept the electron beam. This served to prevent decomposition of the thermochromic. The most useful substrates examined include .003 - .005" thick conducting glass and nickel foils. In addition, the use of a sandwich consisting of magnesium oxide, Ag_2HgI_4, and thin conducting glass also has shown promise. The electron beam is allowed to strike the magnesium oxide layer.

(d) It is difficult to induce reversible thermochromic transitions in Ag_2HgI_4 exposed directly to the electron beam of a CRT without also developing irreversible decomposition reactions.

(e) Some mixtures of thermochromic materials and conventional CRT phosphors appear to be compatible and demonstrate both thermochromic and cathodoluminescent properties under electron bombardment.

(f) The following problems are noted:

(1) Ag_2HgI_4 is not an ideal material for the CRT application due to its tendency to decompose. The material could be made more useful if an encapsulation method suitable for CRT application can be developed.

(2) In the configuration considered the rise time and decay time are both dependent on the mass and properties of the substrate and are long if a good deep color change is induced in the material. These decay times are of the order of seconds. These might be improved by other design techniques or by cooling. This latter course would have the disadvantage of requiring larger beam powers for writing.

(3) Depending on the substrate, a tendency for spreading of the written line has been observed. This is, of course, intimately related to the decay time and is due to lateral diffusion of heat through the substrate and thermochromic. It may be minimized by the use of a substrate having anisotropy of its thermal conductivity. An anisotropic substrate would also tend to reduce the power requirements.

(g) A variety of materials have been synthesized and examined for thermochromic activity. Those with useful thermochromic properties are a series of derivatives of Ag_2HgI_4 in which Cd has been substituted for Hg in an amount as large as .70 atomic percent. These materials are probably thermally unstable and have higher transition temperatures than Ag_2HgI_4 and so would probably not be as suitable for CRT application.

Four solid solutions of AgI and PbI_2 that were prepared show significant thermochromic activity. The transition temperatures are between 99 and 137°C and the materials are stable at 150°C. However, they undergo a severe surface discoloration on exposure to vacuum and require a protective coating or sandwich configuration if they are to be useful in a CRT.

(h) Thermal conductivity experiments on the low- and high-temperature forms of Ag_2HgI_4 indicate that the thermal conductivity of the low-temperature form is slightly greater than that of the high-temperature form.

Further work on the CRT application should be concentrated on new and more stable thermochromics and the development of techniques for encapsulating available thermochromics.

A detailed engineering study of the problems associated with the rise and decay times should be begun in order to suggest the optimum method of handling the materials. This study could be undertaken immediately using the available data for the known thermochromics and assuming that they may be protected for use. Such a study might reveal the need for other kinds of data or could suggest maximum operating characteristics.

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9. APPENDICES

9.1 Methods of Preparing New Materials

The System $Ag_2Hg_{1-x}Cd_xI_4$

The reactants used for these materials were Ag_2I, HgI_2, and CdI_2. Carefully weighed amounts of the starting materials were fired at about 400°C for a day or two in evacuated, sealed pyrex tubes. All samples were yellow and all were thermochromic. The transition temperatures were measured on the temperature gradient stage. This device was described in the First Annual Progress Report.

X-ray diffraction analysis of the materials where x=0.0, 0.05, 0.10, 0.15, 0.20 and 0.25 indicated the absence of starting materials. The materials are most likely solid solutions or mixtures of solid solutions.

Other Ternary Iodides

All of these materials were prepared by sealing carefully weighed amounts of the corresponding binary iodides into evacuated pyrex tubes and heating for a day or two at 400 - 450°C. All compositions were liquid at this temperature. Initial screening tests for thermochromics were done on a hot plate using temperatures up to about 400°C. Further tests, if needed, were performed on a temperature gradient stage.

$CaIn_2S_4$

An equimolar mixture of CaS and In_2S_3 were mixed in a dry box and sealed into a quartz tube under 0.5 Torr pressure. The firing schedule was as follows: 600°C, 12 hours; 750°C, 17 hours; 900°C, 48 hours;

cooling to 600°C during 8 hours; 600°C, 87 hours; cooling to room temperature during 24 hours. The very slight thermochromic activity of this material was determined using a hot plate.

9.2 Thermal and Vacuum Stability Studies

9.2.1 Thermal Stability Studies

This test was conducted in an "Abderhalden" drying apparatus. A liquid of suitable boiling point is placed in the flask and maintained at its boiling point. The condensing vapors surround the sample chamber and keep it at a constant temperature approximately equal to the boiling liquid chosen was n-pentyl acetate which has a boiling point of 150°C. The material was weighed periodically for a period of two months with no observed change in weight. The sample weight was about 1/2 gram and weighings were done to the nearest 0.1 mg.

9.2.2 Vacuum Stability Studies

The materials were placed in preweighed vials and placed into a Varian vac-ion vacuum system. This system is capable of maintaining a vacuum of 10^{-7} Torr by continuous pumping. Each of the test samples were weighed periodically in order to determine if there were any weight change.

It should be noted that this technique is not strictly analogous to the situation in a CRT. This is due to the continuous pumping used here.