POLYTECHNIC INSTITUTE OF BROOKLYN

FINAL REPORT

ORGANIC LUMINESCENT MATERIALS FOR OPTICAL MASERS

by Gerald Oster

(with the collaboration of N. Geacintov, T. Cassen, G. Gabor, A. Baczynski, and M. Yamamoto)

Report date: December 13, 1965

Contract No. Nonr 839(36)

ARPA order No. 306-36

Contract NR 017801

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This research is part of Project DEFENDER under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research and the Department of Defense.

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Members of Project Nonr-839(36)

Principal Investigator:

Dr. Gerald Oster, Professor of Polymer Chemistry
Polytechnic Institute of Brooklyn

Postdoctorals (Research Associates):

Dr. Andrej Baczynski, Present address:
Department of Physics, Nicolas Copernicus University
Torun, Poland.

Dr. Nicholas Geacintov, Present address:
Solid State and Radiation Laboratory
New York University, N.Y. 3, N.Y.

Dr. Gavriella Gabor, Present address:
Dept. of Biochemistry, Stanford University
Palo Alto, California

Graduate Students

Masahide Yamamoto (Received Ph.D. degree from the project research).
Present address:
Department of Polymer Chemistry, Kyoto University
Kyoto, Japan

Thomas Cassen, P.I.B. (expected to receive Ph.D. on work from project in approximately ½ year)

Ann Zelechow, P.I.B. (expected to receive Ph.D. in approx. two years).

The principal investigator was directing U.S.Atomic Energy Commission project AT(30-1)2206 which overlapped in some aspects with the present project.

ABSTRACT

The luminescence properties of aromatic hydrocarbons in plastic matrices were examined.

The relation between luminescence and photoconductivity of zinc oxide and its dependence on environmental factors was established.

A fluorescein plastic having properties indicative of induced emission was made and tested.

A new method for determining the degree of coherence of non-monochromatic light sources was devised.

CONTENTS

I. Introduction and Summary

The original purpose of the project was to investigate the possibility that fluorescent organic substances in high polymeric matrices might exhibit stimulated emission. Early findings in our laboratory showed that aromatic hydrocarbons dissolved in plastics exhibit at room temperature a phosphorescence with a lifetime of the order of one second (Oster, Geacintov and Khan, Nature, 196, 1089 (1962)). It was subsequently found that the details of the emission (spectra, lifetime, order of decay) were dependent on the nature of the polymeric matrix and other factors (paper No. 1). Ultraviolet excitation of such systems produces not only phosphorescence but also thermoluminescence (paper No. 2). The thermoluminescent species is a distinct chemical species and has a characteristic electron spin resonance signal.

Some effort was devoted to the details of sample fabrication. We have developed a differential heating technique for the polymerization of methyl methacrylate whereby the resulting plastic is free of strains (as shown by the absence of birefringence) and free of refractive index gradients (as shown by the absence of schlieren). The method for obtaining plastic samples free of optical inhomogeneities consists of polymerizing the monomer in a thermal gradient with gradual extension of the tube (containing the oxygen-free monomer) into the hotter portion of the gradient, the system being driven by a slow clock mechanism.

We also were able to make homogeneous boric oxide glasses. The method consists of careful control (temperature and time) of the heating of boric oxide being cognizant of the various hydrates which are transformed. The samples also do not crystallize (and thereby become opaque) as do the samples heretofore described in the literature. Incidentally, this material also makes a convenient matrix for inorganic ions as well as for organic dyes and metal chelates. The material is as hard as silica glass yet requires only 200°C for the firing temperature.

Dibenzanthracene, as well as several other fused-ring aromatic substances, in plastic matrices exhibit strong triplet-triplet spectra in the visible range with a lifetime of one second. When such samples in the form of rods are placed in a helical xenon flash lamp the visible light emission from the lamp has a lifetime far shorter than the decay time of the xenon lamp (i.e. much shorter than 10^{-3} sec.). Apparently due to the formation of the triplet species (which we estimate to occur in less than 10^{-12} sec.) there is a filtering effect which acts as a shutter. Due to the long duration of the triplet species the shutter is closed for about one second. By the proper choice of aromatic compound (e.g. picene which has a deep red absorbing triplet-triplet spectrum) this should also work for the ruby laser.

One obvious drawback of the aromatic hydrocarbons as possible laser materials is that their triplet-triplet absorption bands seriously overlap with the phosphorescence emission band (beta phosphorescence). This problem does not appear to be the

case with fluorescein, at least in the manner in which we employed this substance (paper No. 3). Our samples are in the form of rods (but not silvered ends) and are excited by a helical xenon lamp. Fluorescein (in the unionized form) in polymethyl methacrylate gives off a strong burst of light of several milliseconds duration after the exciting flash has decayed. The natural lifetime of emission is shorter than the lifetime of the pumping flash lamp. The opposite is the case with ruby and hence results in shortened lifetime when threshold is exceeded. Doubling the length of the fluorescein rod increases the intensity of emission by a factor of one hundred. Our system bears some resemblance in performance at room temperature to that of the europium chelates at low temperatures where stimulated emission seems to occur (Lempicki and Samelson, Appl. Phys. Letters 2, 159 (1963)). Thus, we are convinced that we have demonstrated induced emission in the fluorescein organic system but we do not have a narrowing of spectrum of emission as is the case with the ruby laser.

We noticed that zinc oxide phosphorescence at low temperatures is excited by red light from a ruby laser or from a helium-neon laser. In order to follow this through we undertook a detailed study of the luminescence and photoconductivity of zinc oxide (paper No. 4). Although this work may not have immediate application to laser technology it does, however, point out a neglected area, namely, environmental factors, in the physics of solids.

Since the emission spectra from the fluorescein plastic are broad we felt the need for a method whereby coherence as a function of wavelength could be determined. Our method

was tried with a tungsten source and consists of the examination of the spectra of the central portion of the interference pattern from a Michelson Interferometer (paper No. 5). The method proved to be sensitive and coherence of one part in a thousand seems to be feasible to detect. Our work shows that interference can occur at path differences a hundred times greater than the calculated coherence length.

PHOSPHORESCENCE OF AROMATIC HYDROCARBONS IN POLYMERIC MATRICES *

By Gerald Oster, Nicholas Geacintov ** and Thomas Cassen

Polytechnic Institute of Brooklyn, Brooklyn 1, NY, USA

The advantages of plastics as matrices for the study of phosphorescence of organic compounds are outlined. The luminescence of 1,2,5,6-dibenzanthracene in various plastics is given as an example. The effect of chemical composition of the matrix, temperature, and oxygen pressure, on the phosphorescence is described.

1. Plastics as matrices

It is well-known that many aromatic substances in rigid media exhibit a phosphorescence. Indeed, this observation was made as early as 1888 by Wiedermann [1]. In more recent years such workers as Jabłonski [2], Terenin [3], Lewis and Kasha [4] and McClure [5], have examined in detail the phosphorescence of organic compounds in rigid glasses. Boric oxide glass and EPA glass (ether-isopentane-alcohol mixture at low temperatures [3]) have been widely used as a matrix. Another matrix which is particularly convenient for water-soluble luminescent substances is glucose glass which we have extensively utilized [6, 7]. All of these matrices suffer from one disadvantage or another. For example, boric oxide glass has not been obtained free of trace impurities (notably ferric salts) which absorb strongly in the near ultraviolet region. EPA glass is useful only at very low temperatures (–196°C). Glucose glass is very hard at room temperature but is extremely hygroscopic.

We have shown [8] (compare [8a]) that many plastics provide excellent matrices for the study of phosphorescence of organic compounds. The luminescent substances may easily be introduced by melting, *via* solvents, or by *in situ* polymerization. Among the many advantages of plastics is their optical clarity and their ability to form strong thin self-supporting films. This latter feature

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** Present address: Radiation and Solid State Laboratory, New York University.

is particularly important when gases or vapors are to be introduced or removed for a particular experiment. The wide variety of plastics available allows the study of the influence of chemical constitution of the matrix on the phosphorescence of organic compounds. Plastics provide a convenient matrix for the study of phosphorescence as a function of temperature. For example, we have observed the phosphorescence of some aromatic hydrocarbons in polycarbonate (melting point 260°C) at temperatures ranging from 100°C to liquid nitrogen temperature, a range of three hundred degrees.

Independently of us, polymethylmethacrylate has been used as a matrix in the study by Melhuish and Hardwick [9] of triplet-triplet spectra of anthracene and in the study by El-Sayed [10] of the polarization of phenanthrene.

We have examined the luminescence characteristics of some aromatic fused-ring hydrocarbons in a variety of plastics. These studies include the effect of type of polymer, temperature, and oxygen content on phosphorescence. The aromatic compounds examined include 1,2,5,6-dibenzanthracene, chrysene, 1,2-benzanthracene, picene, perylene, dibenzpyrene, fluoranthene, phenanthrene, and naphthacene. All of these substances in degassed plastics at room temperature show a strong phosphorescence with a lifetime of the order of one second. Our most detailed studies have been with 1,2,5,6-dibenzanthracene (hereafter abbreviated as DBA), the results of which we will now summarize. A more extensive account will be presented elsewhere. The experimental techniques, based largely on the use of the Cary 14 spectrophotometer for determination of emission spectra and the Tektronix 535 oscilloscope for lifetimes, have been reviewed [11]. Throughout we have used thin plastic films 20 microns in thickness prepared by the solvent film casting technique [8] with concentrations of DBA varying from 0.2 to 1.0%.

2. *Spectral features of DBA*

Like other fused-ring aromatic compounds DBA has a complex ultraviolet absorption spectrum. Between 280 and 400 mμ there are three band regions each of which has three major peaks. Of particular interest for us are the peaks at 374, 384, and 394 mμ which correspond to transitions to the first excited singlet state. On excitation with the 365 mμ line of mercury (from a 1 KW Hg-Xe Hanovia lamp) one observes (see Fig. 1) a blue fluorescence (principal maxima at 398, 420, and 440 mμ) and a greenish-orange phosphorescence with maxima at about 550 mμ (the *G* band) and about 600 mμ (the *O* band). The phosphorescence is entirely of the beta type, *i.e.* radiation transition from the metastable state directly to the ground state (see [2]). The fluorescence, which is very strong, has a quantum yield roughly ten times that of the phosphorescence. The polarization of fluorescence is small and positive and the polarization of phosphorescence is negative and large, about

25% at room temperature (*i.e.* nearly the maximum value expected for perpendicular emission [12]).

For comparison we examined DBA in EPA glass at −196°C. Here the spectrum of phosphorescence (lifetime 1.4 sec) shows more fine structure than for the plastics at this same temperature and the peaks lie at somewhat shorter wavelengths. In EPA glass the ratio of maxima of the *O* to *G* bands is 0.6 whereas in plastics it is usually more than twice this value (see below).

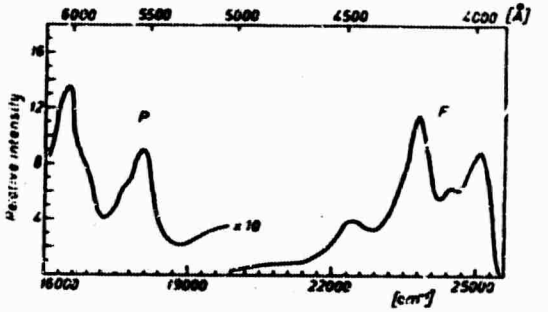

Fig. 1. Total luminescence of 1,2,5,6-dibenzanthracene in polycarbonate at 25°C

3. *Effect of polymer matrix*

The lifetime of phosphorescence of DBA in degassed plastic samples at room temperature is noticeably dependent on the chemical nature of the polymeric matrix. For example, in polyvinyl acetate the lifetime is 1.1 sec whereas in polymethyl methacrylate it is 0.8 sec and a still shorter lifetime is observed in polyvinyl chloride (0.7 sec). It should be noted that at room temperature polyvinyl acetate is considerably softer than the other polymers. Obviously the macroscopically determined rigidity is not a determining factor in the lifetime of phosphorescence [13]. The half width of the *G* band (750 cm^{-1} to 1000 cm^{-1}) in different polymers is roughly inversely proportional to the lifetime but for the *O* band this relation does not apply. Incidentally, the greatest *O* to *G* ratios in different plastics coincide with the longest lifetimes. For example, $O/G = 1.5$ for polystyrene, polycarbonate, and polyvinyl acetate (all with lifetime 1.1 sec), $O/G = 1.2$ for polymethyl methacrylate (0.8 sec), and $O/G = 1.1$ for polyvinyl chloride (0.7 sec).

The relative quantum yields of phosphorescence to fluorescence (φ_P/φ_F) is lowest for polymethyl methacrylate (0.03) and is about 0.07 for the other plastics. Polyvinyl chloride is peculiar in that φ_P/φ_F is concentration dependent, being 0.07 for 0.2% DBA and 0.16 for 1.0% DBA, whereas for the other plastics there is no concentration dependence in this concentration range. Apparently

the interactions between the phosphorescent metastable species is greatest for polyvinyl chloride since the band widths of the phosphorescence is greatest (1000 cm^{-1} for both the *G* and *O* bands) yet absorption and fluorescent band widths are practically identical with those of the other polymers. Furthermore, the *G* and *O* bands show a small red shift relative to those for the other plastics. Presumably these phenomena are manifestations of the influence of heavy atoms, such as chlorine, on the triplet state [5].

For all cases, the degassed samples exhibit a strictly exponential decay of phosphorescence over at least six lifetimes (*i.e.* down to e^{-6} of its initial value). When, however, the solvent is not completely removed in the usual manner (namely, by heating at 60°C *in vacuo* for 16 hours) the phosphorescence decay is non-exponential. Furthermore, the lifetime is of much shorter duration than for the essentially solvent-free plastic and the *O*/*G* ratio is considerably smaller. These results demonstrate that the solvent reduces the macroscopic viscosity [13] and that the solvent is not uniformly distributed. As a consequence there is a distribution of lifetimes (*cf.* [14]).

4. *Effect of temperature*

For polycarbonate the intensity and the spectrum of fluorescence is practically unchanged between −196°C and 62°C. On the other hand, the intensity of phosphorescence decreases with increasing temperature and the *O* and *G* bands are broadened especially above room temperature. In a similar fashion, the polarization of fluorescence is practically independent of temperature while the polarization of phosphorescence changes with temperature being −0.28, −0.26, −0.20 at −196°C, 25°C, and 62°C, respectively. The lifetime of phosphorescence as a function of temperature follows an Arrhenius plot from 25°C to 97°C with an activation energy of only 0.08 eV and the activation energy is still lower at lower temperatures (lifetimes of 1.1, 1.3, 1.3 sec at 25°C, −73°C and −196°C, respectively). Polystyrene has the same temperature dependence of lifetime up to 72°C above which this plastic softens and the lifetime drops precipitously. In polyvinyl chloride the lifetime of phosphorescence is independent of temperature between −196°C and 65°C above which temperature the plastic softens.

5. *Effect of oxygen*

Oxygen quenches the phosphorescence of DBA in plastics. The phosphorescence gradually appears as air is pumped out of the thin film. At the same time, we noticed that the fluorescence intensity decreased by roughly the same number of quanta appearing as phosphorescence. Typically, after complete evacuation (6 min for polystyrene) the fluorescence peak at 420 mμ has decrease (relative to that in air) by 15% and φ_P/φ_F is 7%. In the reverse experiment, namely introducing oxygen to a fully degassed sample, the fluorescence is enhanced and the phosphorescence is suppressed. This cycle of degassing and admission of oxygen can be repeated many times with the same results. In the absence of oxygen the lifetime of phosphorescence is so great that even with moderate exciting intensities, the concentration of ground state molecules can be depleted in proportion to the number of molecules in the metastable state, and hence the fluorescence will decrease. Since oxygen quenches the metastable state, the concentration of these species in oxygen-containing samples is very low and hence the fluorescence intensity will be higher than for the degassed samples. This argument is based, of course, on the assumption that oxygen does not affect the probability of transition from the excited singlet state to the metastable state.

The phosphorescence decay and intensity of DBA in polystyrene films in equilibrium with oxygen has been studied as a function of oxygen pressure in the range of 0–100 microns of mercury. The decay which is more rapid the greater the oxygen pressure is non-exponential in the first 0.4 sec after the exciting light is removed but is thereafter strictly exponential up to at least six lifetimes. The initial portion of the decay curve corresponds to a distribution of shorter lifetimes than in the later exponential portion of the curve. Those oxygen molecules which happen to be in the immediate vicinity of a metastable species will quench it more readily than one would expect from the steady-state diffusional encounter theory of Smoluchowski [15] and Sveshnikov [16] (for review see Förster [17]).

The lifetimes determined from the exponential portions of the decay curves decrease with increasing oxygen pressure in the same manner in which the intensity decreases. For low oxygen pressures (0–20 microns) the curves follow the Stern-Volmer expression. From the measured quenching constant we calculate from the theory of diffusional encounters the constant of diffusion for oxygen into plastics which is in reasonable agreement with the values obtained by direct measurements (for review see [18] and [19]). At low temperatures where diffusion is suppressed, the presence of oxygen does not influence the lifetime but does affect the decay during the first 0.1 sec, in which region it deviates from exponentiality.

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ORGANIC PHOSPHORESCENT MATERIALS*

Gerald Oster and Gavriella Gabor
Polytechnic Institute of Brooklyn

ABSTRACT

Irradiation by X-rays or by ultraviolet light produces an enhanced phosphorescence in plastics containing dibenzanthracene. Samples which have been irradiated exhibit a thermoluminescence when heated above room temperature.

The phosphorescence enhancement is accompanied by an increase of the absorption at 450 mμ and by a free radical e s r signal. On allowing the irradiated material to stand for long periods of time at room temperature all these three characteristics decay.

Introduction

Fused-ring aromatic hydrocarbons dissolved in plastics exhibit phosphorescence at room temperature.[1] The phosphorescence is of a duration of about one second. On the other hand, the fluorescence has a lifetime of a few nanoseconds. For the aromatic hydrocarbons-the phosphorescence is of the beta type, that is, it is of longer wavelength than the fluorescence. Hence, by the simple expedient of introducing a cut-off filter for the fluorescence, one observes only the phosphorescence. The beta emission is associated with the transition from the long-lived metastable state to the singlet ground state. The situation is more complicated, however, since in the case of 1, 2, 5, 6 dibenzanthacene, for example, two phosphorence bands change their relative intensities under different conditions (different plastic matrices, different temperature, etc.[2]). Oxygen quenches the phosphorescence. The effort is reversible in that on removal of oxygen the phosphorescence is completely restored.

The present work is based on the observation that samples of dibenzanthracene in plastics and in the presence of air increase their phosphorescence with increasing dosage of either ionizing radiation or of ultraviolet light. We have also observed a thermoluminescence on heating these samples which had previously been irradiated.

The effect of ionizing radiation seems to be of the same character as that observed with irradiation by ultraviolet light. For convenience we have employed in the present studies mainly ultraviolet light. We have confined most of the work to 1, 2, 7, 8 dibenzanthracene, since this substance gives a more pronounced effect than does 1, 2, 5, 6 dibenzanthracene or, for that matter, any of the other available hydrocarbons.

Experimental

In the present studies we confined our attention to only two matrices, namely polyvinyl chloride and polymethyl methacrylate. Polyvinyl chloride was found to be a more effective matrix for the production of increased phosphorescence. The fused-ring aromatic hydrocarbon 1, 2, 7, 8 dibenzanthracene (hereafter abbreviated as DBA) was mixed and ground with the powdered polymer. The mixture was subjected to pressure (18,000 p.s.i.) and heat (150° C for polyvinyl chloride and 180° C for polymethyl methacrylate), in a heated hydraulic press.

The absorption spectra of the clear plastic films were measured in a Cary 14 spectrophotometer. The absorption spectra of DBA in the films are identical with those in ordinary organic solvents.[3] The absorption spectra above 280mμ consists of many peaks grouped into three bands. The first region which corresponds to the transition to the first excited singlet state is between 365 and 400 mμ while the

second excited singlet transition is between 320 to 365 mμ

The emission spectra were determined with Perkin-Elmer monochrometer and the intensity was recorded photometrically. The exciting light was a mercury arc (point source Osram HBO-100) where the mercury lines were isolated with a Bausch and Lomb grating monochrometer.

On irradiation of the sample with a 100 watt mercury lamp (GE type AH4) at a distance of 30 cm. the phosphorescence (as observed by excitation with a 4 watt GE Black lamp emitting mainly 365 mμ) increases with time of irradiation (Fig. 1). Elimination of irradiation wavelengths below 330 mμ (using appropriate cut-off filters) did not influence the effect. Elimination of 365 mμ from the irradiation source, however, practically eliminated the effect. Irradiation with a mercury resonance lamp (emitting mainly 254 mμ) resulted in decomposition of the aromatic hydrocarbon. This destruction of the hydrocarbon was not, however, apparent when irradiation was carried out using X-rays since the effective dosages were quite small. In the case of ionizing radiation the source was a tungsten target Machlett tube operating at 50 KV and 10 milliamps.

On irradiation the absorption spectrum of DBA is modified. In particular a new peak is produced at 450 mμ (Fig. 2). Both the absorption and the phosphorescence increase in parallel manner (Fig. 1, Table I). In the phosphorescence spectrum of unirradiated polymer (in the absence of oxygen), the ratio of the orange to green peaks is nearly unity. With irradiated polymer, the orange to green ratio progressively increases (Table I).

Plastic films which are thin show a greater sensitivity to irradiation than those which are thick. Thus, for the production of the same degree of phosphorescence and of the 450 mμ absorption peaks a dosage of forty times more is required for a 0.46 mm. sample than for a 0.16 mm. sample. The 450 mμ absorption peak decays slowly with time at room temperature and the decay (first order) is more rapid for the thin sample than for the thick sample (decay times of 1.0×10^2 sec. and 1.1×10^3 sec., respectively). The decay in the intensity of phosphorescence follows that of the decay in the absorption at 450 mμ. The decay is slower <u>in vacuo</u> than in the presence of oxygen.

On rapid heating (about 80-90° C) of the irradiated sample the loss of the 450 mμ peak is immediate and a thermoluminescence is observed. This effect should not be confused with the low-temperature thermoluminescence. The plastic containing DBA, whether or not it had been previously been irradiated, will show a thermoluminescence when it is excited with weak ultraviolet light at liquid nitrogen temperature and then warmed up. At liquid nitrogen temperature the sample exhibits a very long lived phosphorescence which is independent of whether or not the sample had been

irradiated. After the phosphorescence is allowed to decay at -196° C the sample is warmed up and a strong thermoluminescence appeared with its greatest intensity at about -130° C. Here again, the effect is independent of the previous irradiation. The plastic alone (i.e. DBA absent) likewise exhibits a low-temperature thermoluminescence[4] but this effect is several orders of magnitude weaker than when DBA is present.

Electron spin resonance of the samples were measured[5] in a Varian apparatus (Model). The unirradiated samples showed no signal nor did the irradiated polymer (free of DBA). The irradiated samples containing DBA showed a strong signal at a frequency of 9506 I 0.5 megacycles and H = 3,400 gauss with a signal width of about) gauss. This is a characteristic free radical signal[6]. The signal decays at room temperature; with time exactly parallel to the decay in the 450 mμ absorption peak (Fig. 3).

With X-rays the effect is linear with dosage at least down to 600 r, the lower detectible limit of the phenomenom.

Discussion

There are three related phenomena which occur when irradiating a sample of polymer containing DBA. There are the increases in the phosphorescence, the absorption at 450 mμ and the free-radical e.s.r. signal. All three phenomena decay at room temperature with the same rate.

The phosphorescence of the irradiation product is richer in green than in orange emission in contrast to the normal DBA[2] suggesting that the enhanced emission arises from a new chemical species. This species is free radical in nature (as shown by e.s.r. spectra) and might be a photo-ionized form of DBA. The ionization potential of DBA in polymeric matrices is not known and might be considerably lower than those calculated for aromatic hydrocarbons molecules in vacuo. The slow decay at room temperature of these species may be due to the slow diffusional encounters of the trapped photo-electrons and the ionized species. On warming the irradiated sample the plastic is softened and hence the recombination (accompanied by emiss.) is considerably accelerated. It is well known that free radicals are readily attacked by oxygen (to give peroxides) and hence the enhanced rate of disappearance of these species by oxygen is understandable. This also explains why the thinner samples in air show a greater rate of decay than the thicker samples since oxygen diffusion is the rate-controlling step. Oxygen also plays a role in the formation of the radical species since for a given dosage of absorbed ultraviolet light the effect is greater the thinner the sample.

We are now engaged in a study to find conditions which will increase the sensitivity of the phosphorescence enhancement effect. At the present time the effect is suitable for X-ray closimetry in the 1000 to 10,000r range.

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* Presented at the International Conference on Luminescence Dosimetry, Stanford University, June 21-23, 1965.
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Table I

1, 2, 7, 8 DBA in PVC 5% .31 mm thick.

	P_o/P_g	p/f	D
before irradiation	.546	.029	.025
1' "	.685	.260	.180
2' "	.720	.355	.335
after decay at room temp.	.800	.086	.080

FIGURES

Fig. 1 Parallel increase of optical density at 450 mμ (D) and phosphorescence as fluorescence ratio (p/f) on UV innoculation. Circled points represent the the decay of the effects.

Fig. 2 Production of emitting species as measured by production of new absorption b band.

Fig. 3 Decay of emitting species as measured by decrease of absorption at 450 mμ and decay of e.s.r. signal.

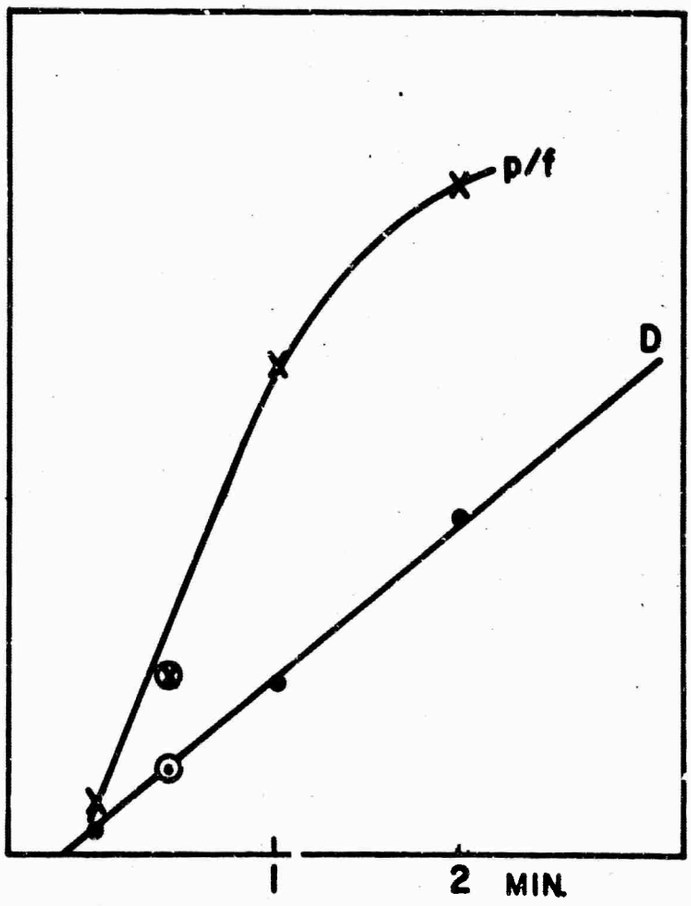

FIG. 1

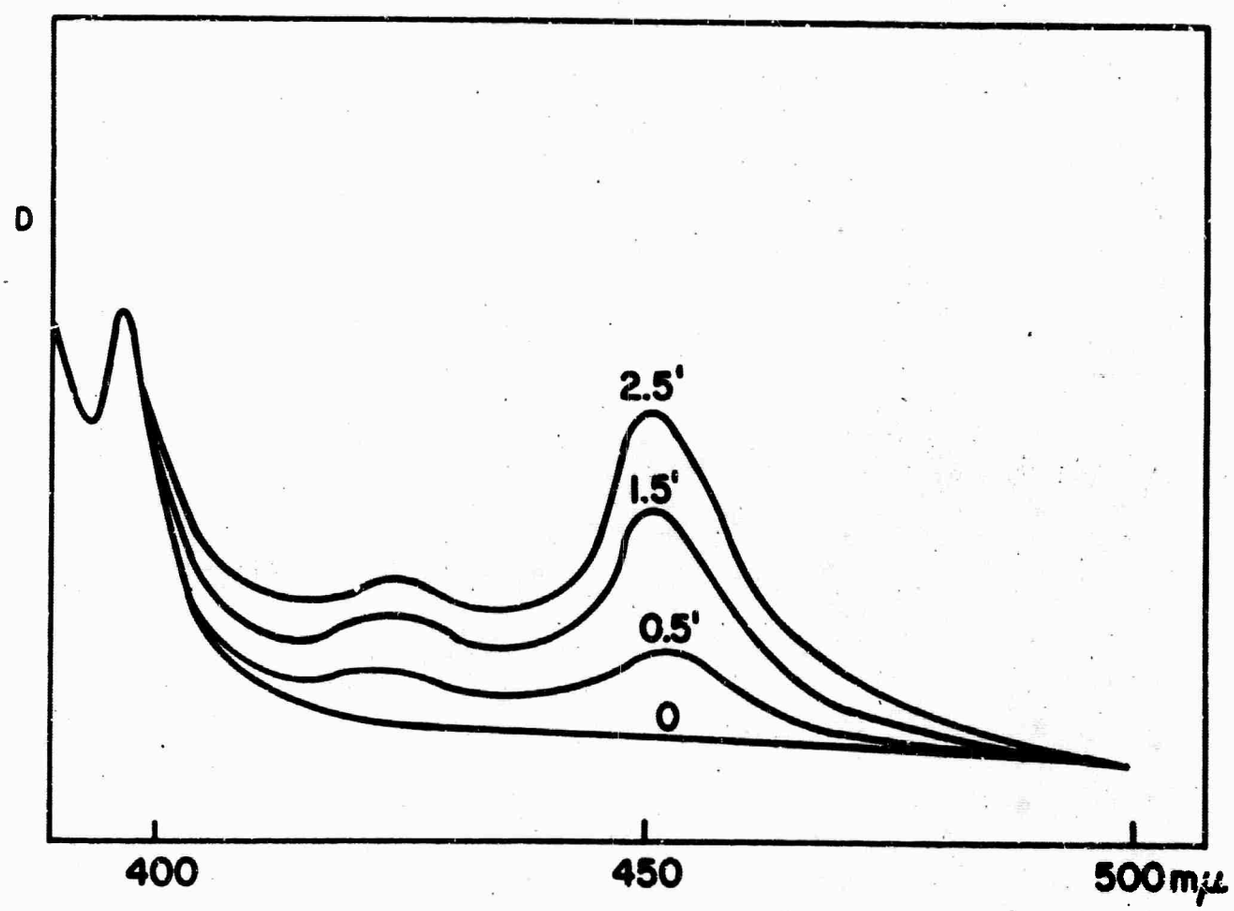

FIG. 2

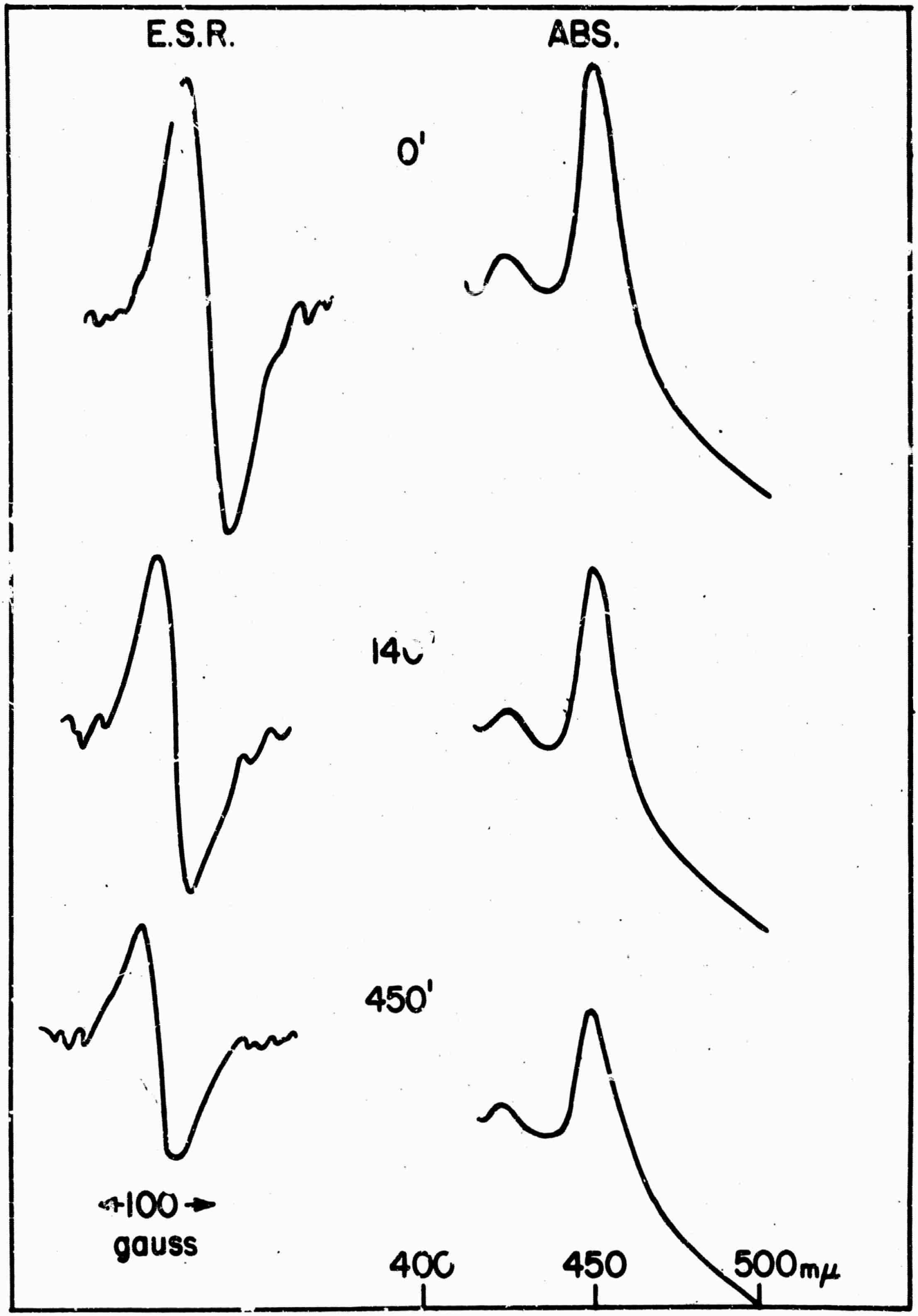

FIG. 3

FLASH-INDUCED EMISSION FROM A FLUORESCEIN PLASTIC*

Andrzej Kaczynski[+] and Gerald Oster
Polytechnic Institute of Brooklyn
Brooklyn, New York, 11201

When dyes are present during the free radical polymerisation of vinyl monomers the dye is incorporated into the polymer chain by virtue of chain transfer[1]. The luminescence properties of the resultant plastic may differ from those observed by merely dissolving the dye in a rigid glass or in a plastic matrix. We have observed that fluorescein chemically combined with polymethyl methacrylate plastic exhibits at room temperature unusual luminescence behavior when excited with a strong flash of light.

Fluorescein (acid-free) was dissolved in freshly distilled methyl methacrylate containing 0.1% benzoyl peroxide and the mixture was allowed to polymerize in 6 mm. diameter glass tubes sealed at both ends. In order to reduce optical inhomogeneities the polymerization was carried out in a thermal gradient. The resultant plastic rod was removed from the glass tube and its ends were cut and polished. Repeated selective solvent extraction of the material shows that fluorescein had been chemically combined with the polymer.

In the monomer fluorescein absorbs maximally at 320 mμ and at 450 mμ with a fluorescence emission band at 505 mμ the band width being about 100 mμ. The long wavelength absorption peak depends strongly on the concentration but the fluorescence emission spectrum remains practically unchanged.[2] On polymerization the absorption band at 320 mμ (which, by the way, corresponds to the strongly absorbing region of the polymer) shifts to 355 mμ with a marked increase in extinction coefficient but the luminescence spectrum is still maximally at 505 mμ.

On excitation of this rigid system with a low intensity flash the phosphorescence (alpha type) has a lifetime smaller than one millisec. With high intensity flash

excitation (achieved with a FX-42 flash lamp with the sample replacing the ruby rod of a type 3542 Maser Optics laser) the emission is prolonged and shows maxima several milliseconds after the flash is initiated. In Fig. 1 is shown a typical result which can be repeated several times for a given sample. The effect depends critically on the concentration of the dye and is best for concentrations between 10^{-4} and 10^{-5} gm. dye per gm. of original monomer. The high concentration limit may be due to reabsorption of the emission due to the long wavelength absorption band which for the polymer is also strongly dependent on dye concentration. Doubling of the length of the rod increases the intensity of emission by a factor of one hundred but in this case, after a few flashes, burnt-out specks appear along the core of the sample. There is a critical threshold of flash intensity (500 joules for a 2.5 cm sample but much lower for a 6 cm. sample) below which this unusual emission disappears.

The fact that the emission does not decay monotonically rules out the possibility of delayed emission due, for example, to the recombination of trapped electrons and holes. The effect is not due to thermoluminescence (evoked by heat production during the flash) since we observed a threshold energy and a critical dye concentration for the effect. The existence of a threshold and of the enhanced effect when the length of the rod is increased suggest the possibility of stimulated emission. Claims[3] of stimulated emission for aromatic compounds in low temperature glasses have not been substantiated[4,5]. Such compounds exhibit a beta phospherescence in plastics[6] and their triplet-triplet absorption[6,7] seriously overlaps with the emission. Indeed, we were unable to observe the fluorescein type emission with picene or with dibenzanthracene, both of which exhibit a beta phosphorescence[6]. The emission characteristics of our system are very similar to those observed[8] for europium chelates at low temperatures.

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+ Permanent Address: Dept. of Physics, Nicolas Copernicus University, Torun, Poland.

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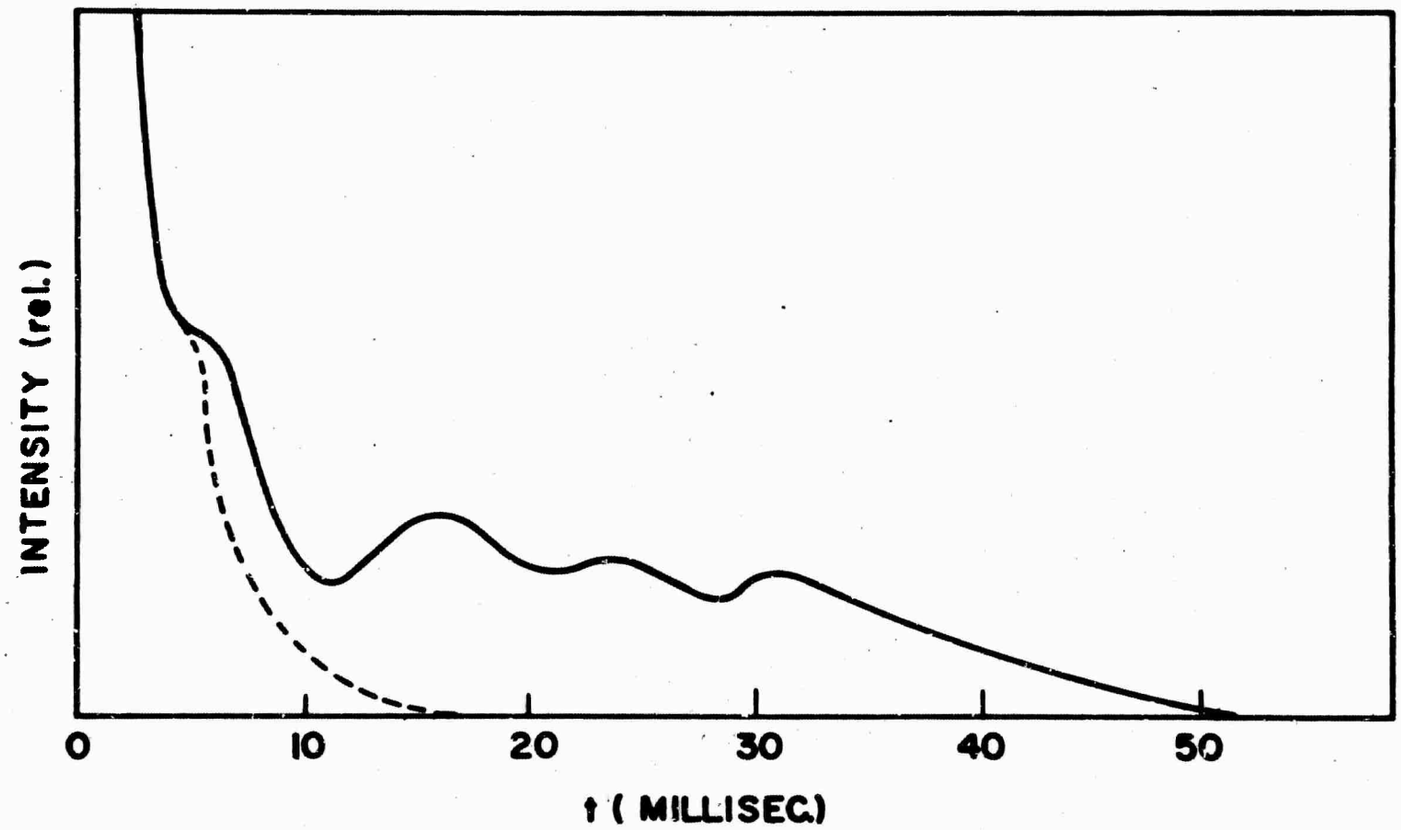
INTENSITY (rel.)
0
10
20
30
40
50
t (MILLISEC.)

Figure

Fig. 1 Time course of emission from a fluorescein plastic 2.5 cm. long (dye conc. 5×10^{-5} gm per gm of monomer). Input energy 600 joules. Dotted curve represents decay of flash tube. Light detector: RCA 7102 multiplier phototube.

ENVIRONMENTAL FACTORS IN THE LUMINESCENCE AND PHOTOCONDUCTIVITY OF ZINC OXIDE*

by

Gerald Oster and Masahide Yamamoto
Department of Chemistry
Polytechnic Institute of Brooklyn
Brooklyn, N. Y. 11201

ABSTRACT

Oxygen quenches the room temperature fluorescence of powder zinc oxide but enhances the low temperature phosphorescence and thermoluminescence. The low temperature ultraviolet emission (edge emission) is quenched by oxygen. Water in the presence of oxygen is particularly effective and this is ascribed to the production of hydrogen peroxide.

Parallel effects are observed for the photoconductivity but water is less effective due apparently to enhanced contact conductivity.

Flash desorption of oxygen shows a parallel behavior of room temperature luminescence and photoconductivity.

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Introduction

Zinc oxide is a photosensitizer for reduction or oxidation reactions[1]. For example, when zinc oxide is excited by ultraviolet light, in the presence of water and oxygen, hydrogen peroxide is produced. In recent years an electrostatic photographic process ("Elektrofax"[2]) has been developed which depends on the photoconducting properties of zinc oxide. Practice has shown that this process depends critically on ambient conditions. The role of oxygen in the photoconductivity of zinc oxide has been extensively studied[3]. A correlation of photoconductivity and luminescence of zinc oxide has not been established. Furthermore, the effect of water, which is important for the catalytic properties of zinc oxide, has not been heretofore examined.

In the present work the luminescence (fluorescence, phosphorescence and thermoluminescence) and photoconductivity of zinc oxide are studied under a variety of environmental conditions (oxygen and water pressure and at various temperatures) using a single type of zinc oxide powder. One result of this work is to separate intrinsic properties from properties associated with the surface of characteristics of the polycrystalline material. Our results help to establish a connection between these properties and the photocatalytic properties of zinc oxide.

Choice of Zinc Oxide and Sample Preparation

Zinc oxide is available in many forms but usually excess interstitial zinc is present and hence the material is an n-type semiconductor. For our studies we used the purest zinc oxide powder (diameter approx. 0.3 microns, specific surface area about 4 square meters per gram) commercially available, namely type SP-500 obtained from the New Jersey Zinc Company. This material contains one part per million of iron, copper, and manganese as impurities. It is made from the oxidation of zinc vapor and is pure white, unlike zinc oxide samples which have been sintered above 600° C which are yellowish.

For photoconductivity studies the powder was pressed into a pellet using a

hydraulic press (400 kilograms per cm^2) and the pellet (disc 1cm in diameter and 0.5 mm thick) was sintered at 400° C for one hour. This latter treatment is known to have no effect on the electrical properties of the material. Conducting electrodes were applied to the pellet using Silpaint (type 3043-01 from Handy and Harmon Co., New York), the distance between electrodes being 5 mm. The sample is mounted with its conducting wires on to a Lucite support which is inserted into a glass container which can be evacuated. For luminescence studies the zinc oxide powder was used directly in a flat container which is connected to the vacuum system.

Apparatus and Methods of Measurement

A variety of radiation sources were employed. For the 365 m μ radiation (approx. 4×10^{-10} einsteins per sec. falling on the sample) a 100 watt mercury lamp (GE-AH4) was used in conjunction with a Wood's glass filter. For visible light a 500 watt tungsten lamp was used in a 35 mm slide projector equipment with a heat filter and various filtered (Bausch and Lomb interference filters and Corning Glass cut-off filters) were employed. In one experiment a He-Ne laser (General Telephone) was used. The X-ray source was a 5 kilowatt tungsten target (Matchlett tube) installation whose voltage and current were varied. The dose-rate was determined by the current produced in a silicon P-N junction of known diffusion path length.[5]

For most of the studies of luminescence intensity the detecter is a RCA 931-A photomultiplier with an ultraviolet cut-off filter (Corning 3-71) used in conjunction with an Aminco stabilized voltage supply and current circuit[4] with the output recorded on a Varian G-10 recorder. For the spectral analysis of luminescence we used a Carey 14 spectrophotometer with the fluorescence attachment (medium pressure mercury lamp with Wood's glass filter).

Photoconductivity was measured under an applied voltage of 4.5 volts across the sample and the current across the load resistance (10,000 ohms) was determined

with a General Radio DC electrometer (type 1230-A) and the output was applied to a recorder.

The vacuum system is of the conventional design and pressures down to 5×10^{-6} Hg were obtainable when the sample was in the system. Purified oxygen (Matheson Research Grade) was used and the water was rendered free of oxygen by repeated freezing and thawing under vacuum.

For thermoluminescence studies the apparatus of Randall and Wilkins[6] was employed. The sample is attached to a cooling block which is surrounded by a heating coil. A thermocouple is inserted close to the sample. We modified their apparatus so that the sample could also be evacuated. The rate of heating of the system (0.1° C per sec.) was controlled with a variable transformer.

Luminescence at Room Temperature

Zinc oxide at room temperature has a feeble luminescence when excited with radiation below about 380 mμ the limit of edge absorption as shown by reflection measurements.[1] The emission is greenish-white (maximum at 500 mμ Fig. 1A) and, in addition, there is an ultraviolet emission peak at 372 mμ which at low temperatures exhibits a fine structure as shown in Fig. 1B (edge emission spectrum).

Oxygen depresses the luminescence in both the visible region and in the ultraviolet region as shown in Fig. 1A. Water has no effect on the visible luminescence at least up to a pressure of 24 mm Hg. But the combination of water and oxygen quenches the fluorescence. Thus if the intensity of fluorescence in vacuo is 100%, then with oxygen at 27 mm Hg the intensity is 84% but with 24 mm Hg of water vapor and 24 mm Hg of oxygen the luminescence is reduced to 31%. Allylhydroxyethylthiourea, a mild chemical reducing agent, increases the fluorescence of zinc oxide in the presence of air, the compound being applied in the form of an alcoholic solution to give a mull. The fluorescence after a short induction period increases with time of irradiation with 365 mμ (Fig. 2) indicating that the compound is being consumed

by active oxygen produced by the excited zinc oxide. A similar result is observed with X-ray excitation.

Photoconductivity at Room Temperature

Oxygen affects not only the photoconductivity of zinc oxide but also its dark conductivity. Oxygen decreases the dark conductivity[3] but on introduction of oxygen to an evacuated sample the behavior is complicated. A sample of zinc oxide was irradiated for a long period of time with ultraviolet light while being evacuated and left in the vacuum for two days. The dark current was measured at various oxygen pressures (Fig. 3). The temperature dependence of the dark conductivity showed an activation energy of 0.03 ev in agreement with that found by Harrison[9] who used the same sample of zinc oxide which we employed but with different sintering conditions. As seen by curve A-B the current decreases most rapidly as a function of oxygen pressure in the neighborhood of 10^{-2} mm Hg and thence is insensitive to oxygen pressure. If now the oxygen pressure is decreased (curve B-C') the dark current remains at the low level and only increases if the sample is allowed to stand for very long periods of time (24 hours for C'-C", 12 hours for C"-C"', 8 hours for C"'-D) at pressures below 10^{-3} mm. oxygen. Now on introduction of oxygen the curve (D-E) follows roughly the original curve (A-B) in that the greatest decrease in current occurs at about 10^{-2} mm Hg.

The photocurrent, as a function of oxygen pressure starting with the evacuated sample (curve F-G) has a similar form to curves A-B and D-E but the photoconductivity with decreasing oxygen pressures (curve H-I) actually shows a broad minimum in the neighborhood of 10^{-1} mm Hg.

In all cases the current measured at the various oxygen pressures is the reasonably steady value observed after ten minutes of current flow.

Water vapor whether alone or in the presence of oxygen slightly increases the dark conductivity. Oxygen considerably decreases the photoconductivity but addition

of moisture does not appreciably enhance this effect.

After removal of exciting light the decay in conductivity in vacuo is extremely slow but with moisture it is rapid and the decay is intermediate with oxygen (compare ref. 8). The fluorescence intensity at room temperature follows the conductivity as regards the effects with oxygen. This parallelism is illustrated in Fig. 4. The exciting light is a xenon photographic flash lamp which is activated momentarily (flash duration about 10^{-3} sec.) which is superposed on the weak steady illumination from a weak 365 mμ source. Oxygen decreases both the photoconductivity and the fluorescence under weak irradiation. The superposed fluorescence produced by the flash demonstrates the action of the flash in temporarily removing oxygen from the surface of the solid[10]. The slow decay of fluorescence in the absence of oxygen atmosphere is parallel with the slow decay of photocurrent.

Ionizing radiation also increases the conductivity of zinc oxide. The effect is very sensitive and the relative change in conductivity is directly proportional to the dosage as shown by electrom beam irradiation[11]. In Fig. 5 are shown our results for X-ray excitation as a function of dose rate. This system appears to be a practical dosimeter of ionizing radiation[12]. Incidentally, we found that the "Electrofax" process is also susceptible to X-rays. The zinc oxide paper was electrically charged with a Tesla coil and then exposed to X-rays through a lead mask. On subsequent dusting with an oppositely charged powder (the "toner") an image in the non-irradiated portion appears. This method is sensitive to dosages of about 5 roentgens.

Luminescence at Low Temperatures

The time response of photoconductivity of zinc oxide at low temperatures is too slow to be conveniently measured since the material has a very low conductivity when cooled. At low temperatures (e.g. liquid nitrogen (-196° C) zinc oxide exhibits a phosphorescence of duration of some minutes and on warming the sample

from the low temperature it shows thermoluminescence. The phosphorescence shows only visible emission (max. 500 mμ).

At -196° C the phosphorescence decays according to a second order recombination, i.e. the intensity follows closely the expression $I = I_o(1 + \sqrt{\alpha I_o}\, t)^{-2}$. We found that if t is expressed in seconds then with our light source (AH-4 lamp with Wood's glass filter) $\sqrt{\alpha I_o} = 2.57 \times 10^{-2}$ sec^{-1}. Thus the intensity decays to one half its initial value at t = 16.1 sec. Light above 430 mμ quenches the phosphoresce (also the thermoluminescence) and even a weak laser beam (632.8 mμ is effective.

Oxygen enhances the intensity of the low temperature visible emission, in contrast to its effect at room temperature. Thus the maximum in the visible peak is enhanced by 10% on addition of oxygen (60 mm Hg) to an evacuated sample. Water vapor also increases the effect (46% at 23 mm Hg) and the combination of water and oxygen is additive in their enhancement effect. On the other hand the intensity of the near ultraviolet fluorescence emission bands at low temperatures are quenched by oxygen (Fig. 1). Oxygen also extends the long wavelength portion of the visible emission of the phosphorescence.

The glow curve for zinc oxide, that is, the emission as a function of temperature for the material which had been irradiated at liquid nitrogen temperature is shown in Fig. 6. It was found that for short periods of illumination at (-196° C) the intensity of thermoluminescence increases with increasing time of irradiation but that for illumination times (with the AH-4 lamp) exceeding about one minute, the intensity of thermoluminescence is unchanged. As seen in Fig. 6 the glow curve has a strong maximum at -130° C and a shoulder at -110° C. Oxygen does not influence the form of the glow curve.

The total visible thermoluminescence, i.e., the integral of the glow curve is enhanced by oxygen by a factor of two over that in vacuo. A trace of moisture also has an enhancing effect. The combination of moisture and oxygen is particularly

effective in enhancing the total thermoluminescence.

Here, again the same results are obtained for X-ray excitation as for ultraviolet excitation.

DISCUSSION

Since the photoconductivity and luminescence require near ultraviolet light, the energy necessary to raise an electron to the conduction band is of the order of 3 ev. The midpoint of the absorption edge is about 380 mμ and hence the more precise value is 3.3 ev. It is known from the exciton theory of solids (for review see ref. 13) that excitation at an absorption edge can give fine structure in the emission spectrum. The origin of the fine structure of emission from zinc oxide[14] is not, however, unambiguous. The fact that oxygen quenches this luminescence strongly suggests that the fine structure may not arise entirely from the intrinsic properties of the material but the surface nature of the zinc oxide powder has some role in this phenomenon. The fact that treatment of single crystals of zinc oxide alters the edge absorption spectrum[7] supports our contention.

The luminescence presumably arises from a recombination of electrons and holes. The visible emission band (maximum at 500 mμ) corresponds to a transition from the conduction band to a luminescent center 2.5 ev below. The maximum in the glow curve, namely at -130° C, corresponds (see ref. 15) to an energy level of 0.27 ev which lies very close to the conduction band and on activation with heat is raised to the conduction band and thereby produces the thermoluminescence. These levels also correspond to traps for the low temperature phosphorescence. The luminescence is of long duration because of retrapping of electrons by these levels. Another somewhat deeper trap corresponding to -110° C lies at 0.32 ev below the conduction band. The quenching of thermoluminescence by visible light suggests the presence of intermediate energy levels corresponding to absorption by visible light. Another group of levels (shallow donor levels) are present since zinc oxide

serves as a sensitiser for the visible light photoreduction of silver ions[1].

At room temperature oxygen suppresses the luminescence presumably by trapping electrons from the conduction band. That is, these levels correspond to surface traps. At low temperatures these surface traps serve as storage centers and the electrons are promoted to the conduction band with accompanying phosphorescence or thermoluminescence. The surface traps suppress at room temperature the conductivity by combining with electrons. The mechanism of combination may involve the conversion of physically adsorbed oxygen into chemisorbed oxygen (possibly O_2^-). In addition, a depletion layer is produced which increases the resistance at the points of contact of the zinc oxide granules.

The unexpectantly large quenching of the room temperature luminescence by the combination of water and oxygen indicates an irreversible loss in electrons. This is further suggested from the fact that hydrogen peroxide is produced efficiently[1]. The enhancement of low temperature phosphorescence and of thermoluminescence by water could arise from the polarizing action of the molecules on preserving the storage centers. The combination of water and oxygen does not lower the room temperature photoconductivity appreciably below that for oxygen alone. Apparently water may compensate for irreversible losses in electrons by enhancing the electrical contacts between the grains of the powder.

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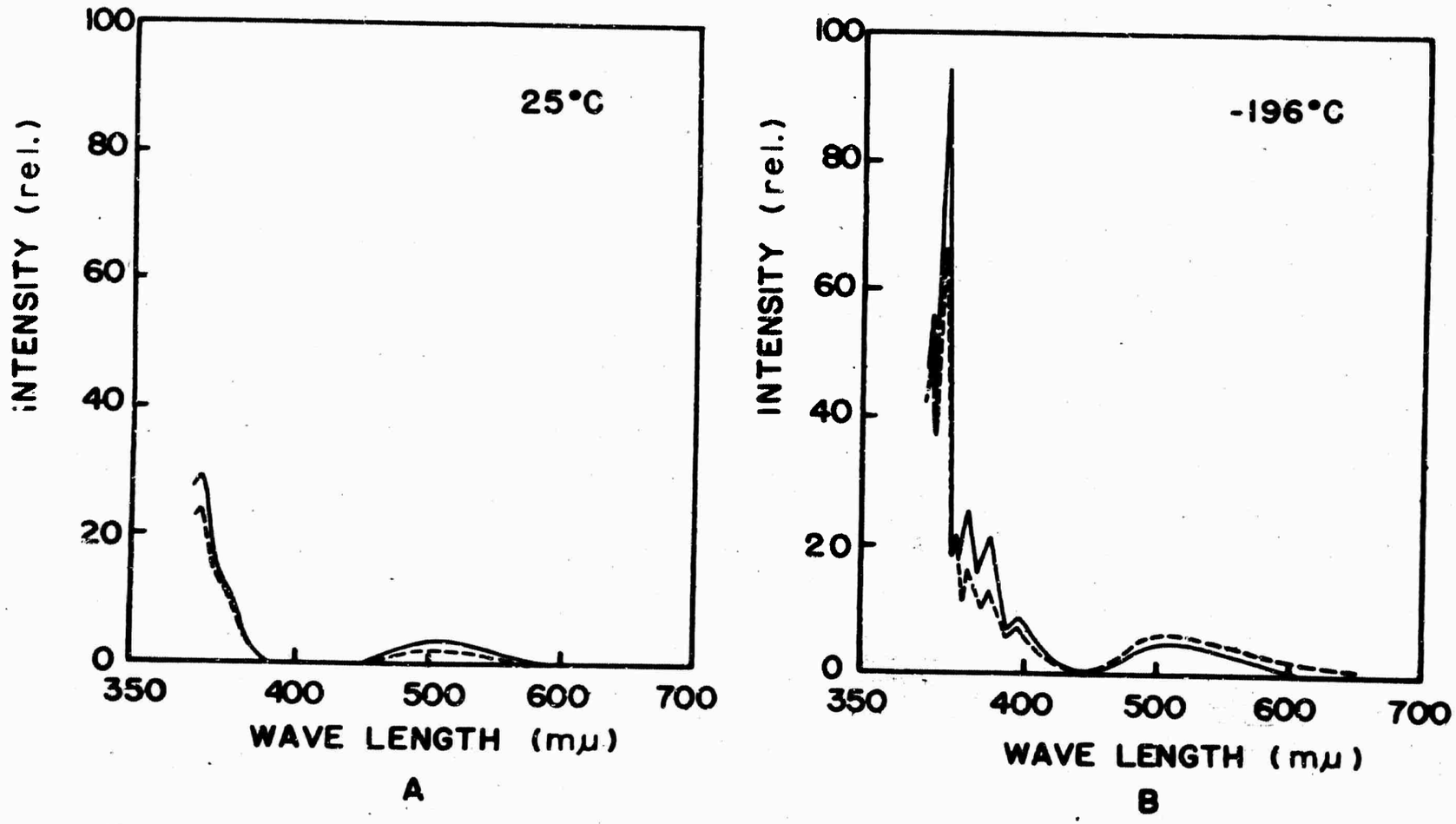
INTENSITY (rel.)
100
80
60
40
20
0
25°C
350
400
500
600
700
WAVE LENGTH (mμ)
A
INTENSITY (rel.)
100
80
60
40
20
0
-196°C
350
400
500
600
700
WAVE LENGTH (mμ)
B

Fig. 1

FIGURES

Fig. 1A. Luminescence spectra of zinc oxide at 25° C.
Solid line: in vacuo. Dotted line: in oxygen.

Fig. 1B. Luminescence spectra of zinc oxide at -196° C.
Solid line: in vacuo. Dotted line: in oxygen.

Fig. 2. Visible fluorescence increase in the presence of allylhydroxyethylthiour
Excitation wave length: 365mμ

Fig. 3. Oxygen pressure dependence of dark current and photocurrent.
Solid line: photocurrent. Dotted line: dark current.

Fig. 4. Comparison of the visible fluorescence and photocurrent after strong ultraviolet flash excitation.

Fig. 5. $\frac{1}{id}\left(\frac{di}{dt}\right)$ versus dose rate.

Fig. 6. Glow curve of thermoluminescence in vacuo.
Heating rate = 0.09° per second.

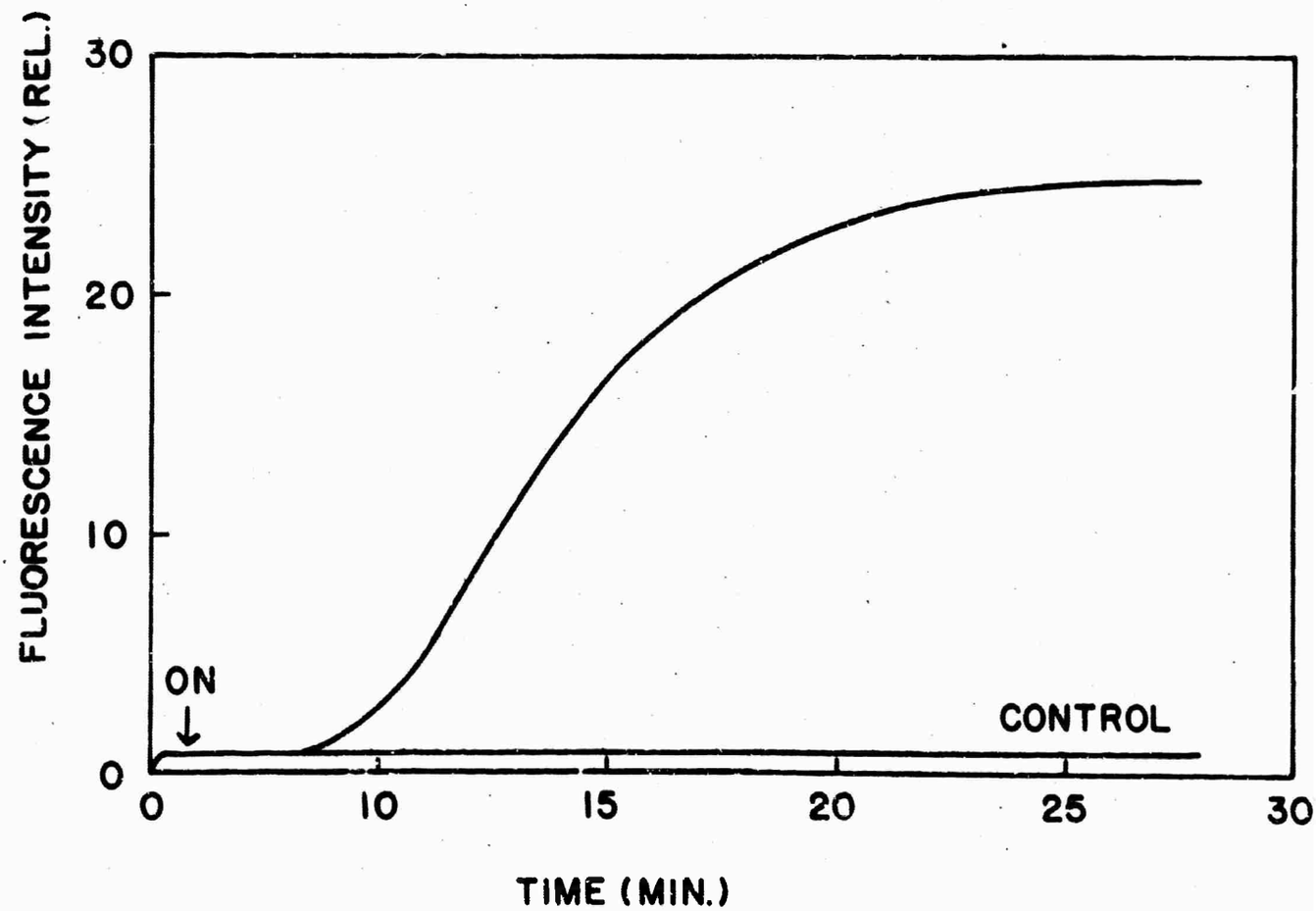
FLUORESCENCE INTENSITY (REL.)
30
20
10
0
ON
CONTROL
0
10
15
20
25
30
TIME (MIN.)

Fig. 2

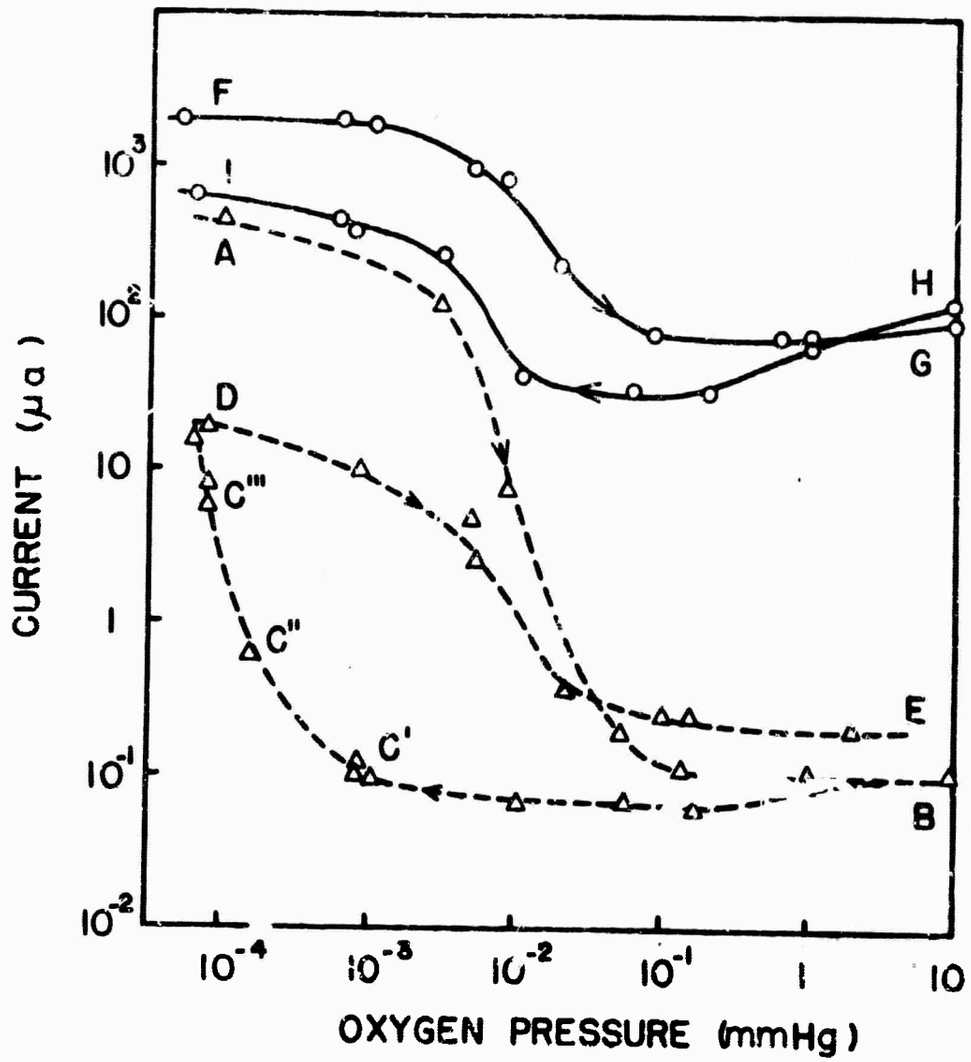
F
I
A
H
G
D
C'''
C''
C'
E
B
10^3
10^2
10
1
10^{-1}
10^{-2}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
1
10
CURRENT (μa)
OXYGEN PRESSURE (mmHg)

Fig. 3

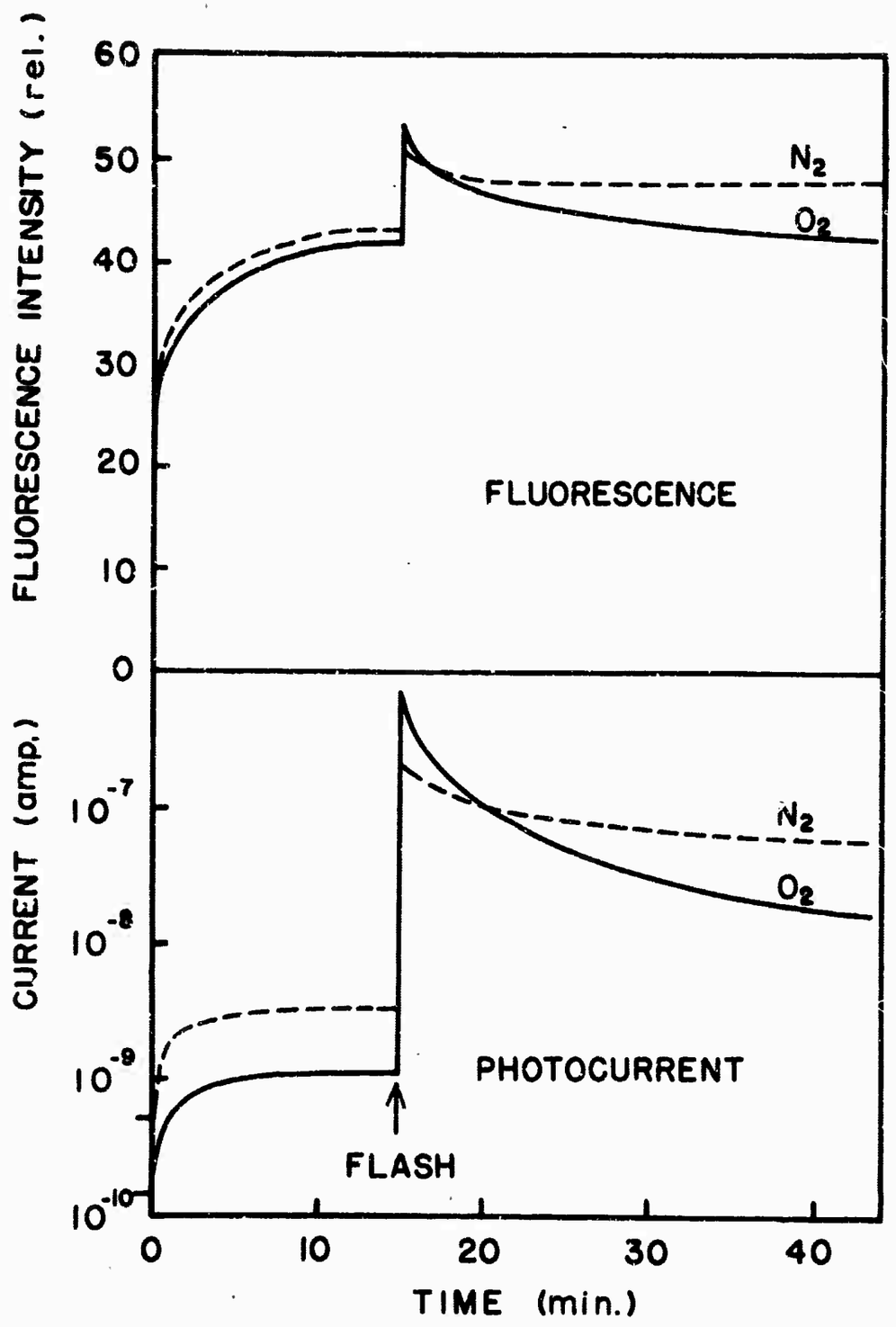
FLUORESCENCE INTENSITY (rel.)
60
50
40
30
20
10
0
N2
O2
FLUORESCENCE
CURRENT (amp.)
10-7
10-8
10-9
10-10
N2
O2
PHOTOCURRENT
FLASH
0
10
20
30
40
TIME (min.)

Fig. 4.

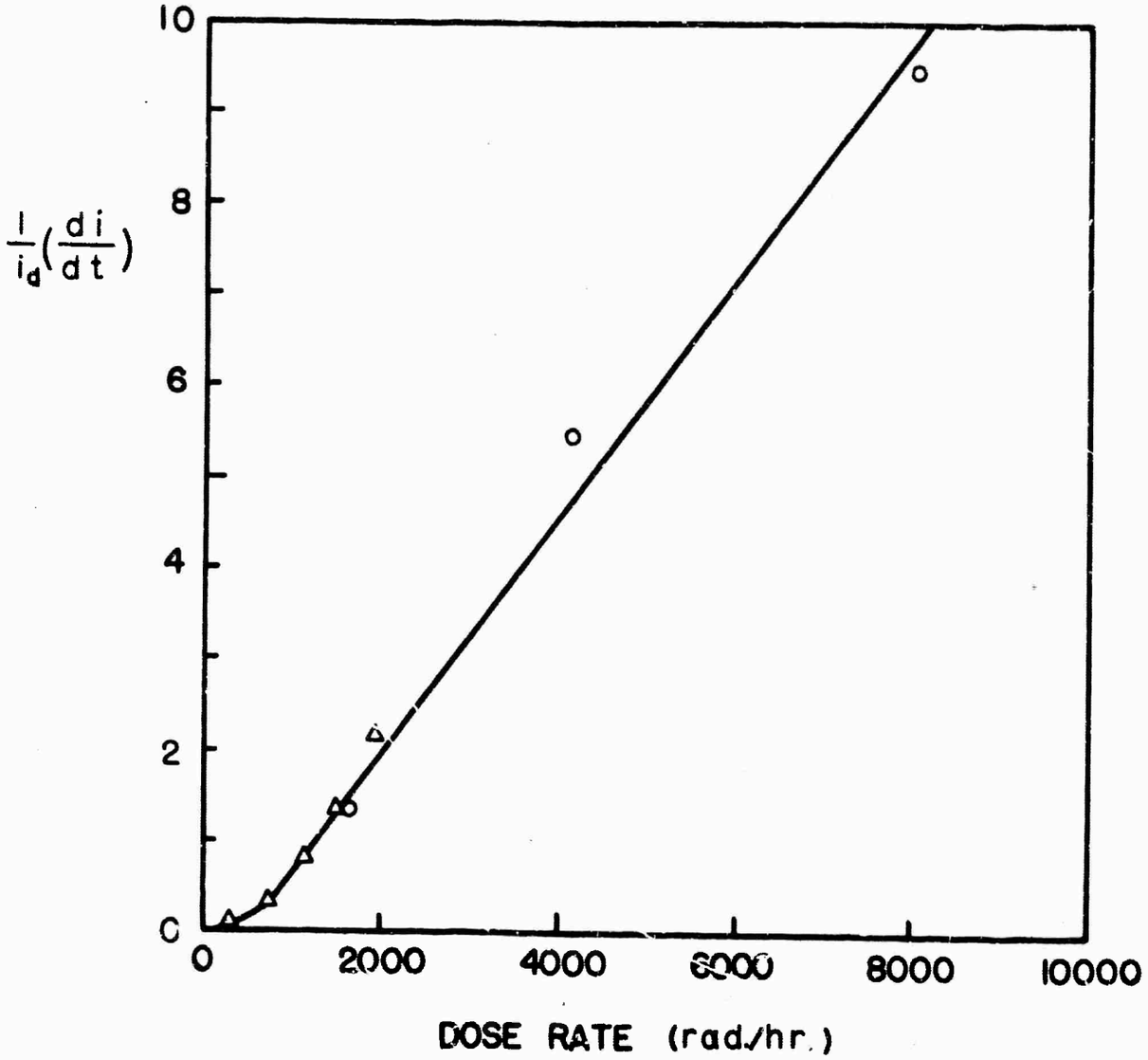
10
8
6
4
2
0
$\frac{1}{i_d}(\frac{di}{dt})$
0
2000
4000
6000
8000
10000
DOSE RATE (rad./hr.)

Fig. 5

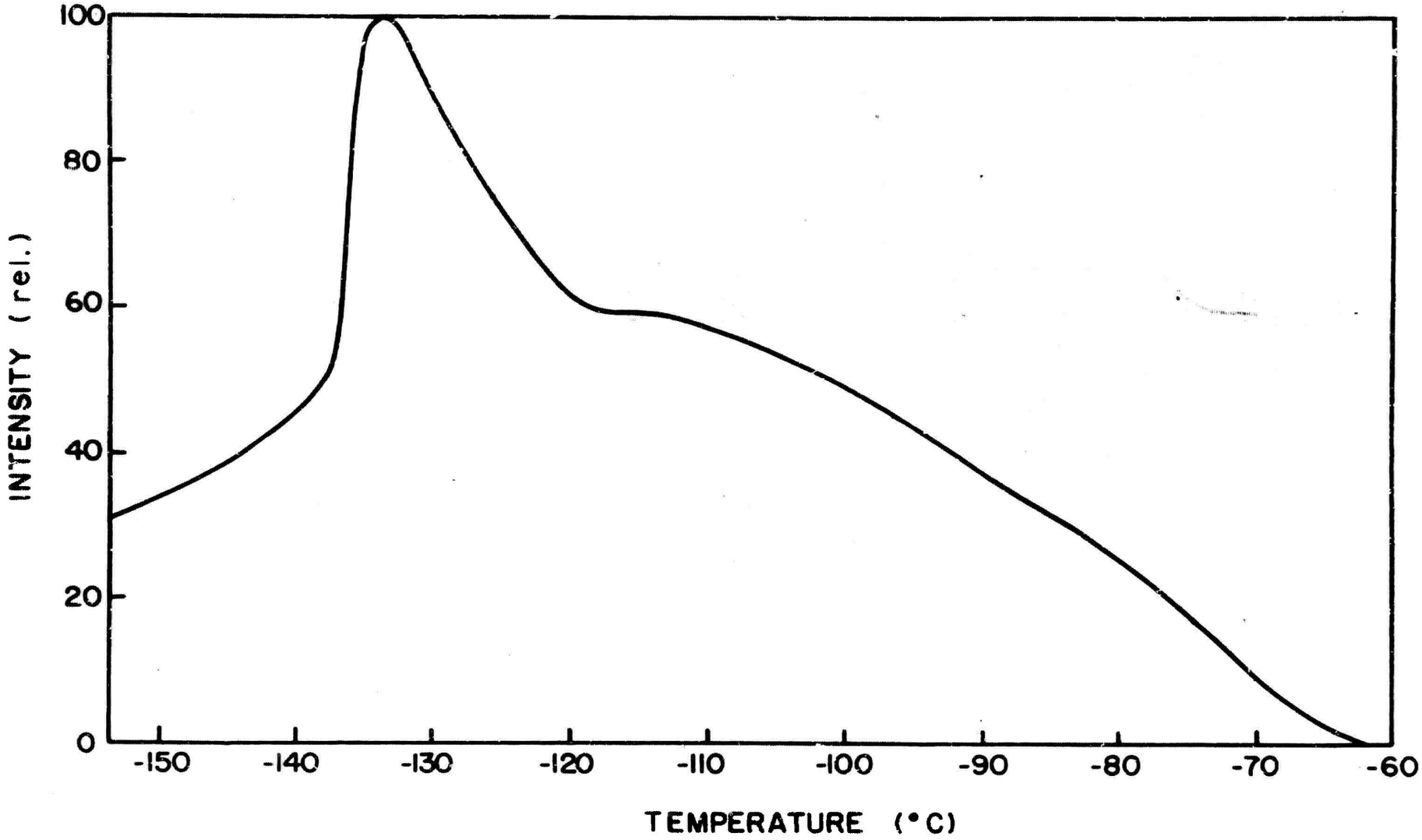
100
80
60
40
20
0
INTENSITY (rel.)
-150
-140
-130
-120
-110
-100
-90
-80
-70
-60
TEMPERATURE (°C)

Fig. 6

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Spectral Modulation of White Light as Observed with an Interferometer*

ANDRZEJ BACZYNSKI† AND GERALD OSTER
Polytechnic Institute of Brooklyn, Brooklyn, New York 11201
(Received 20 April 1965)

A HIGH-FREQUENCY modulation in the photocurrent was observed by Alford and Gold[1] by superposing on a photoelectric detector two slowly and coherently modulated light beams from a common light source, although the path difference was much greater (about 100 m) than the coherence length. Givens[2] has suggested that the same effect should be observable with two stationary coherent but unmodulated light beams. Mandel[3] has shown theoretically that the superposition of two coherent light beams with a path difference greater than the coherence length leads to a spectral modulation which depends on the path difference. The present note is a description of experiments with polychromatic light which gives such spectral modulation. In addition to giving a measure of the temporal degree of coherence, our method also has some practical implications. Essentially we examine spectrally the real interference diagram (i.e., lens-free[4]) obtained with a Michelson interferometer, the observations being made of the central spot of the diagram.

The diagrammatic representation of the Michelson interferometer is given in Fig. 1, where S is the source whose images S_1 and S_2 obtained from the reflections of the mirrors M_1 and M_2 (separated by a distance s) produce, with monochromatic light, interference rings on the screen at O–Y lying perpendicular to the X axis. For this lens-free system the radius of the mth-order ring for light of wavelength λ is given by the expression for the superposition of two Huygens wave fields[5]

$$Y_m=\left\{x^2\left[\frac{(n+\frac{1}{2})^2\lambda^2}{(n+\frac{1}{2}-m)^2\lambda^2}-1\right]+\frac{(n+\frac{1}{2})^2\lambda^2-(n+\frac{1}{2}-m)^2\lambda^2}{4}\right\}^{\frac{1}{2}}, \quad (1)$$

where the distance between mirrors $s=(n+\frac{1}{2})\lambda/2$ (taking into account the phase difference in the half-silvered beam splitter), n being on integer. Our observations are concerned with the central spot, namely, the zero-order condition; i.e., $Y_0=0$. Since our condition is equivalent to the observation of two coherent sources in the direction of the line joining them, all correlation functions will depend on the delay time only (cf., Ref. 6, p. 500).

The light source used was a strip tungsten lamp operated at a temperature of 2300°K. The light from the Michelson interferometer (Atomic Laboratories type M-4) was examined with a grating monochromator (Perkin-Elmer model 112, slit opening 0.7 mm and hence resolution about 20 Å) along the axis S_1S_2O of the interferometer at a distance of 2 meters. In Figs. 2 and 3 are shown the photoelectrically recorded intensity distribution as a function of wavelength for two different distances between the mirrors. The dotted curve of Fig. 2 is the result when the mirror separation is large (0.1 mm). The spectral modulation such as shown in Figs. 2 and 3 depends on the mirror separation; the smaller the separation the greater is the amplitude and the greater is the wavelength difference between the maxima. When the mirror separation is a few wavelengths, the spectral-modulation curve is very sensitive to air currents, owing to changes in optical path length resulting in a continual shifting of the peaks. Hence the system was shielded against such influences.

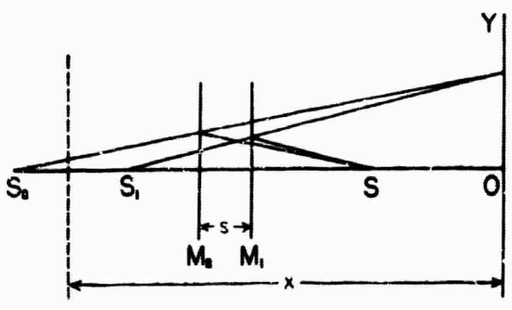

FIG. 1. Diagrammatic representation of the Michelson interferometer.

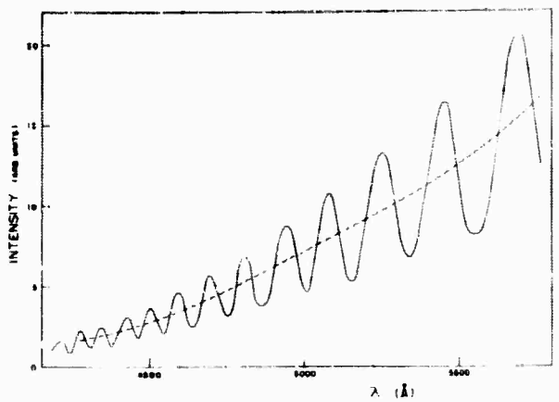

FIG. 2. Spectral modulation for blackbody radiation (2300°K) at path difference 194×10^{-4} cm. Dotted curve is for large path differences ($>10^{-2}$ cm).

The spectral curves of Figs. 2 and 3 can be described by the formula

$$\Phi(\nu)=\Phi_0(\nu)[1+f(T)\cos2\pi\nu T], \quad (2)$$

where $\Phi_0(\nu)$ is the spectral distribution of the blackbody radiation and T is the delay time of the two beams ($T=2s/c$). Our results show (Table I) that the factor $f(T)$ is a monotonically decreasing function of T_0. The function $f(T)$ may be readily calculated from the modulation curves since it equals $[\Phi(\nu)^{\max}-\Phi^{\min}]/[\Phi(\nu)^{\max}+\Phi(\nu)^{\min}]$, where $\Phi(\nu)^{\max}$ and $\Phi(\nu)^{\min}$ are the envelopes of the modulation which themselves are of the form $\Phi_0(\nu)$; i.e., in our case, the blackbody radiation distribution. The separation of the two mirrors is determined by the expression $2s=(n+\frac{1}{2})\lambda_n=(n+3/2)\lambda_{n+1}$ etc. and $\lambda_n>\lambda_{n+1}$. For example, from the modula-

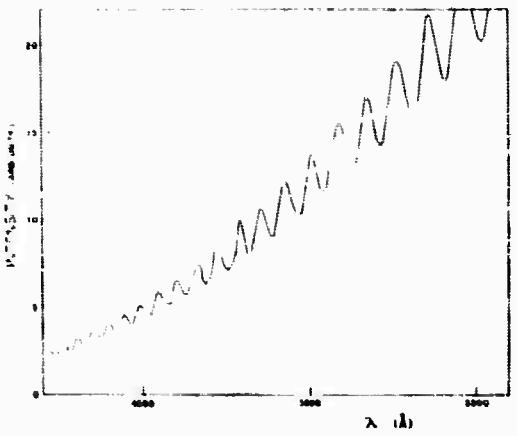

FIG. 3. Same as Fig. 2 but for path difference of 342×10^{-8} cm.

tion curve of Fig. 2 we calculate $2s$ to be 0.0194 mm, accurate to about one hundred angstroms. With a higher resolution monochromator, than the one we employed proportionally greater accuracy could be obtained. The wavelength position of the peaks shifts with changes in s, which clearly indicates changes in the mirror separation amounting to a fraction of a wavelength. Similarly, by this technique changes in optical path length can be measured without any mechanical displacement of the mirrors of the interferometer.

The path differences in our system for which spectral modulation appears (Table I) are some two orders of magnitude greater than the coherence length. Thus Mehta[7] calculates for blackbody radiation a coherence length $0.67\ hc/kT$, using Wolf's definition of coherence time.[8] (Mandel's definition[9] gives about twice this value.) Hence at 2360°K the coherence length is 4.14×10^{-5} cm. For such large path differences as in our case, no interference should be expected but nevertheless spectral modulation can occur.[7] For two cross-spectrally pure[10] light beams of equal intensities Mandel's theory[3] yields an equation of the form of Eq. (2) but now his $\gamma_{12}(0)$, the temporal degree of coherence at zero path difference, is replaced by $f(T)$. As seen in Table II the factor $f(T)$ is independent of wavelength. The same is true for the temporal degree of coherence for blackbody radiation as shown in the theory of Bourret[11] and of Kano and Wolf.[12] This suggests that the factor $f(T)$ is proportional to the temporal degree of coherence.

TABLE I. Modulation factor $f(T)$ as a function of path difference.

$2s\times10^{8}$ (cm)	$T\times10^{18}$ (sec)	$f(T)$
194	6.47	0.3525
219	7.30	0.262
342	11.4	0.106

TABLE II. Modulation factor $f(T)$ as a function of wavelength ($2s=342\times10^{-8}$ cm).

λ (Å)	Φ^{max} (rel.)	Φ^{min} (rel.)	$f(T)$
4300	160	130	0.103
4400	205	165	0.108
4500	260	213	0.097
4600	327	265	0.101
4700	402	327	0.103
4800	490	392	0.111
4900	580	465	0.110
5000	672	547	0.103
5100	767	628	0.100
5200	875	708	0.105
5300	995	792	0.114
5400	1134	888	0.121
		av.	0.106

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† Permanent address: Department of Physics, Nicolas Copernicus University, Torun, Poland.

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