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Luminescence of Zinc Oxide Crystals Controlled by  
Electrode Potential and Electrochemical Reactions

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## ABSTRACT

The voltage dependence of the green luminescence of ZnO crystals used as electrodes in an electrochemical cell was investigated and compared with the voltage dependence of the photocurrent. When the exciting light is of shorter wavelength than the band edge of ZnO, this luminescence can be varied from its maximal value to complete extinction by applying small positive voltages. The luminescence resulting from excitation within the long wavelength tail of absorption, however, cannot be influenced.

The potential dependence of the luminescence has been investigated with differently doped crystals under various conditions. The addition of formic acid to the electrolyte causes an increase of luminescence; this is found to be a consequence of photoelectrochemically induced radical reaction by which electrons are injected into the conduction band of the electrode.

The potential dependence of the green luminescence is explained by a mechanism in which the trapping of the holes in recombination centers competes with their extraction, which leads to the generation of the photocurrent. The average concentration of photogenerated holes in the crystal is therefore rate-limiting for the intensity of luminescence, provided that an excess of electrons is available for recombination. At sufficiently large positive potentials, however, when electrons are being depleted in the space charge layer, their concentration also becomes limiting, and electron injection can stimulate luminescence.

The experimentally observed potential dependence of luminescence

and photocurrent, as well as their interrelation, is shown to be consistent with results which were derived from a theoretical treatment of these effects.

It is suggested that this green luminescence may be used as a probe for the study of the space charge layer and of electrochemical reactions.

## INTRODUCTION

There is a series of reports in the literature<sup>1-5</sup> on the influence of electric fields on the luminescence of solid state materials. The observed effects appear to be rather complex: some phosphors show emission of a short light pulse during irradiation when an electric field is applied (Gudden-Pohl effect<sup>1</sup>); in other phosphors luminescence is quenched by an applied electric field (Dechène effect<sup>2</sup>). Stimulation of luminescence by an alternating field has also been observed (Destriau effect<sup>3</sup>). A review of these observations has been given by Ivey.<sup>6</sup>

Various explanations have been suggested for field induced changes in luminescence. Interpretations have been complicated by the use of polycrystalline and sometimes even heterogeneous material with scarcely known impurity concentrations. In single crystals of CdS field induced changes of luminescence have also been observed.<sup>7</sup> Daniel and coworkers<sup>5</sup> found quenching of luminescence at an illuminated zinc sulfide crystal surface, which was placed in contact with a suitable electrode and electrically polarized. The quenching was explained in terms of a decrease in the excess electron density due to the extraction of holes by the field from the illuminated surface.

The aim of our investigations was to ascertain whether field induced luminescence changes could be used as probes for the study of the space charge layer and of electrochemical reactions at single crystal semiconductor electrodes. We chose zinc oxide crystals for our measurements. To our knowledge, electric field induced changes of zinc oxide luminescence have only been observed by I. Filinski and T. Skettrup,<sup>8</sup> who have

used this effect to distinguish between various types of exciton complexes at low temperatures. Those investigations were confined to a narrow spectral range, between 3600 and 3800 Å, near the absorption edge of zinc oxide.

The luminescence spectrum of zinc oxide is characterized by a complex and relatively narrow blue emission near the absorption edge and by a broad green emission band. The relative intensity of both bands is strongly dependent on the doping of the material.<sup>9</sup>

#### EXPERIMENTAL

Three different types of crystals\* were used in these investigations: ZnO without any intentional dopant, ZnO doped with Cu, and ZnO doped with In. While the latter were strongly blue colored, the Cu-doped crystals could barely be distinguished by their faint yellow color from the undoped, noncolored and transparent ZnO.

For the measurements, the crystal needles of about 2 mm diameter were cut into smaller pieces of 5-8 mm length. Indium was diffused into one end of the undoped and the Cu-doped crystals in order to provide an ohmic contact; a metal wire was then attached to this end of the crystal with silver paint and mechanically stabilized with glue. The prepared crystals were mounted in a Teflon holder, which fitted into a 1 cm fluorescence cell. This cell also contained a platinum electrode, and was connected via a salt bridge to a calomel electrode in 1 M KCl. It

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\*We are indebted to Prof. Dr. G. Heiland, Technische Universitaet Aachen, Germany, for his generous gift of these ZnO crystals.



was possible to add solutions to this arrangement with a hypodermic syringe without disturbing the system. Oxygen was displaced in all electrolytes used by flushing them, as well as the sample compartment of the spectrophotometer, with nitrogen.

The associated electrical circuit consisted of a potentiostat applied between the ZnO and Pt electrode, a voltmeter with an input impedance of  $10^{14}$  ohms (to measure the voltage between the ZnO and the calomel electrode), and a nanoammeter. The potential difference between ZnO and Pt electrodes was changed by applying a variable bias voltage and a function generator in series to the appropriate input of the potentiostat. All voltage-dependent investigations were performed dynamically, scanning the range from approximately -0.5 V to about +3.5 V in 500 sec with a triangular function. This scanning rate proved to be slow enough to avoid hysteresis. The experimental arrangement is shown schematically in Figure 1.

The luminescence of the surface parallel to the c-axis of the crystals was measured; this surface was carefully polished and etched with dilute HCl as often as necessary. The temperature in the cell compartment was kept constant at 20°C by means of a thermostat. All measurements were made in an electrolyte of 1 M KCl adjusted to a pH of 1.5 by adding HCl. In order to avoid disturbances by adsorbed buffer molecules, no attempt was made to buffer the solution.

#### Spectra

The luminescence excitation and the luminescence emission spectra were measured with a Perkin-Elmer Fluorescence Spectrophotometer-MPF-2a,

which consists of two grating monochromators identically blazed at 300 nm. The presentation of spectra from both monochromators is linear in wavelength. To eliminate second order and scattered light, use was made of the filters supplied in the emission monochromator. In the excitation monochromator two bandfilters were introduced: UV-D25 with transmission below 400 nm to measure luminescence excitation spectra, and UG-11 (Schott & Gen., Germany) with transmission below 380 nm to measure luminescence emission spectra. Excitation and emission slits were kept constant at 10 nm width for all spectral measurements and for calibration procedures.

The energy distribution of the Xe-lamp/excitation monochromator system was calibrated against a thermopile (Reeder, Type RSL-2c), which was introduced in the place of the sample. In order to calibrate the photomultiplier, the spectrum of the Xe-lamp was first measured with the aforementioned thermopile and again after inserting an MgO covered plate into the sample holder with the emission monochromator open to the photomultiplier.

Since the thermopile reading gives the relative intensities in energy units, each unit must be multiplied by the wavelength to give relative intensities in terms of quanta per unit wavelength interval. In order to obtain quanta per unit frequency or wavenumber interval, they must be multiplied again by  $\lambda^2$ . Further details may be seen in the publication of Parker and Rees.<sup>10</sup>

The calculation of the spectral data to quanta per unit wavenumber interval and the correction for the spectral energy distribution of the

lamp/monochromator system and the spectral sensitivity of the photomultiplier was performed by an XDS Sigma 2 computer. The output of the photomultiplier, after suitable amplification, was digitized and fed into a digital memory unit. The channel advance of this memory unit was synchronized to the scanning speed and different wavelength ranges of the spectrometer. The contents of the 512 channels were then transferred to paper tape and thence to the computer.

The computer program generated a wavenumber from the given starting wavelength for each of these channels and performed the correction of the spectra with the use of the calibration data, also entered by paper tape. The corrected data of relative luminescence intensity in quantal units per unit wavenumber were then plotted versus wavenumber on a Calcomp plotter.

The measurements of the photoconductivity spectra were performed in the same way as the luminescence excitation spectra, except that the output of the nanoammeter was fed into the memory input.

## RESULTS

Upon illumination of a zinc oxide electrode with UV light, photocurrents are generated across the semiconductor-electrolyte interface.<sup>11,12</sup> The photocurrent reaches a limiting value at positive electrode potential which depends on the light intensity; it is caused by holes and leads to photo-corrosion of the semiconductor surface, to oxygen evolution and dissolution of zinc ions.<sup>12</sup> The dependence of the photocurrent,  $I_{PH}$ , on the electrode potential is depicted in Figure 2 (wavelength of excitation is 350 nm). When the green luminescence of zinc oxide (500 nm) is measured

as a function of potential, a complementary behavior is found (Fig. 2). With zero photocurrent luminescence has a maximal value, and when the photocurrent reaches its maximal, limiting value, luminescence is completely extinguished. The steepness of the slopes between the two states depends on the size of the crystals, i.e., on the resistance between site of illumination and contact; the slopes are flatter with higher resistance. The course of luminescence, however, does not exactly follow a mirror symmetric path to that of the photocurrent (depicted as the dashed line in Fig. 2) but drops faster with increasing potential than the photocurrent increases. The potential induced modulation of the green luminescence can be observed visually.

When the green (500 nm) luminescence is monitored and the wavelength of the exciting light is scanned, the luminescence excitation spectrum is obtained. In Figures 3 and 4, luminescence excitation spectra are shown for undoped and Cu-doped single crystals of zinc oxide for different electrode potentials. It can be seen from these curves that the potential dependence of green luminescence is strongly dependent on the wavelength of the exciting light. It is especially interesting that there is a relatively narrow band at approximately 390 nm which absorbs light to yield green luminescence but is insensitive to the applied potential. A comparison with Figure 5, in which the spectral dependence of photocurrents is depicted, shows that the photocurrent is negligibly small in this region, and that the potential independent band is localized at wavelengths slightly longer than the absorption edge of zinc oxide. Figure 6 shows that there is no shift of the fluorescence wavelength, but a gradual diminishing of the green luminescence band with increasing potential.

The penetration depth of monochromatic light depends on the absorption coefficient; this penetration depth also influences the potential dependence of both photocurrent and luminescence, as can be clearly recognized in Figure 7. Here, the photocurrent-voltage as well as the luminescence-voltage characteristics were measured for three wavelengths of exciting light which correspond to three different values of absorption coefficients of the semiconductor electrode. The potential area in which luminescence and photocurrent are varied between their maximal and their minimal values appears to be the narrower the higher the absorption constant. The same behavior of photocurrent and luminescence is evident.

Two reagents added to the electrolyte were found to influence the potential dependence of fluorescence. Formic acid was found to double the photocurrent (usually increased by 60%) by first capturing a hole from the valence band and then, as a formyloxy radical, injecting an electron into the conduction band of the zinc oxide electrode.<sup>13</sup> As shown in Figure 8, this agent (added as 1 M solution) not only increases the photocurrent, but also influences the potential dependence of luminescence in such a way that it better approaches a strictly mirror-symmetric course with respect to that of the photocurrent. Addition of hydrogen peroxide (about 1 M), which is thought to compete as an acceptor for an electron transfer from the formyloxy radical,<sup>13</sup> decreases formate-induced photocurrent and luminescence changes. The influence of a pH change on the emission of green luminescence was investigated, but changes in intensity were not observed. The midpoint potential of the decay of the luminescence shifts completely in parallel to the shift of the photocurrent as the result of a pH dependent double layer on the electrode surface.

Undoped and Cu-doped crystals showed slight differences in the effect of electrode potential on luminescence due probably to different electron concentrations in these crystals. This conclusion is supported by the observation that the luminescence stimulation effect of formate is smaller the smaller the deviation of luminescence from a mirror-symmetric behavior with respect to that of the photocurrent. With indium doped crystals the green luminescence was so small that potential dependencies could not be studied.

#### DISCUSSION

Our experiments have shown a strict correlation between UV photocurrents and green luminescence at zinc oxide electrodes in contact with an aqueous electrolyte. This result suggested the possibility of using luminescence as a probe for the investigation of the space charge layer in this electrode. This would be of considerable advantage, especially for fast kinetic measurements where electrode currents become rate limited by the circuit resistances and capacitances.

In order to use fluorescence as a tool, it is necessary to understand its correlation with the electrode current: The photocurrent across the interface of a positively polarized n-type semiconductor electrode can be calculated along lines similar to the photocurrent through a reverse biased p-n junction of a photodiode.<sup>14</sup> The photocurrent ( $I_{PH}$ ) can be thought of as consisting of two contributions, one due to the minority carriers (holes) generated inside the space charge layer (depletion layer), and another due to carriers generated in the adjacent bulk material and diffusing into the space charge layer. The total current density through the reverse biased electrode surface would then be given by:

$$I_{PH} = I_{SC} + I_{DIFF} \quad (1)$$

where  $I_{SC}$  is the drift current density due to carriers generated inside the space charge layer, and  $I_{DIFF}$  is the diffusion current density of minority carriers generated outside the space charge layer and diffusing into it.

The penetration depth ( $d$ ) of the space charge layer into the semiconductor electrode is potential-dependent and described by the relation

$$d = h_0 (U - U_0)^{1/2} \quad (2)$$

where  $U$  is the electrode potential,  $U_0$  is the flatband potential,<sup>15</sup> and  $h_0$  is a constant which is dependent on the charge carrier concentration in the material.

The generation rate ( $g(x)$ ) for electron-hole pairs at an incident photon flux of  $\phi$  is given by relation

$$g(x) = \phi a(\lambda) \exp \{-a(\lambda)x\} \quad (3)$$

$a(\lambda)$  is the monochromatic absorption constant.

The drift current density can therefore be written

$$I_{SC} = e \int_0^d g(x) dx = e\phi [1 - \exp \{-a(\lambda)h_0 (U - U_0)^{1/2}\}] \quad (4)$$

where  $e$  = elementary charge.

In order to determine the diffusion current for holes from outside the space charge layer, a differential equation has to be solved:

$$D_p \frac{\partial^2 p}{\partial x^2} - (p - p_0)/\tau_p + g(x) = 0 \quad (5)$$

$D_p$  is the diffusion constant for holes,  $p$  is the hole density,  $p_0$  is the equilibrium hole density,  $\tau_p$  is their lifetime;  $D_p$  and  $\tau_p$  are related to the diffusion length  $L_p$  by  $L_p = (D_p \tau_p)^{1/2}$ .

Appropriate boundary conditions,  $p = p_0 = 0$  for  $x = \infty$ , and  $p = 0$  for  $x = d$ , yield the following relation for  $I_{DIFF}$ :

$$I'_{DIFF} (x = d) = e D_p \frac{\partial p}{\partial x} = [(e\phi a(\lambda)L_p)/(1+a(\lambda)L_p)] \exp(-a(\lambda)d) \quad (6)$$

The total photocurrent is therefore

$$I_{PH} = I_{SC} + I_{DIFF} = e\phi [1 - \exp \{-a(\lambda)h\nu_0(U-U_0)^{1/2}\} / (1+a(\lambda)L_p)] \quad (7)$$

To derive the relation for the potential dependence of the green luminescence, it is reasonable to assume that utilization and extraction of the minority carriers (holes) as photocurrent competes with their participation in the generation of green luminescence.

Evidence has been presented that the green luminescence of zinc oxide is generated by the recombination of electrons from the conduction band with trapped holes.<sup>9</sup> The rate at which holes are trapped should therefore determine the intensity of luminescence emission, provided that there are sufficient recombination centers and an excess of electrons in the conduction band. This condition should be fulfilled for our crystals which show a high n-type conduction due to an excess of zinc atoms at interstitial sites in the crystal lattice.

The rate constant for trapping holes at suitable recombination centers will be proportional to the average concentration of holes in the valence band of the crystal. This concentration is determined by production, extraction (photocurrent), and recombination of holes according to the relation:

$$e\phi - I_{PH} - p/\tau_p = 0 \quad (8)$$

The intensity of green luminescence ( $I_L$ ) will correspond to the holes trapped in suitable centers ( $\tau_T$  = trapping time):



$$I_L = p/e \tau_T = \tau_p (e\phi - j_{pH})/\tau_T \quad (9)$$

With (7), the following relation can be derived for the potential dependence of the green luminescence:

$$I_{Lmax} = \phi \tau_p \exp \{-a(\lambda) h_0 (U-U_0)^{1/2}\} / \tau_T (1+a(\lambda)L_p) \quad (10)$$

This relation for the potential dependence of green luminescence describes an idealized situation in which every hole trapped at a suitable recombination center will find an electron for recombination and light emission. This situation should be the case in our crystals at low values of overpotential  $U-U_0$ , since there is an excess of electrons present in their conduction bands. At higher values of overpotential  $U-U_0$ , however, a deviation from relation (10) is to be expected, resulting from the depletion of electrons in the electrode surface. Because of the bending of the energy bands as a result of the electrode potential, there will be a decrease of electrons according to the Boltzmann relation

$$n_s = n_0 \exp \{-e(U-U_0)/kT\} \quad (11)$$

where  $n_s$  = electron concentration on the surface and  $n_0$  = electron concentration in the bulk. Especially on the surface there should be a loss of holes which are trapped at potentially fluorescing reaction centers, but, due to the low concentration of electrons, are again detrapped and lost in an electrochemical reaction.

The true curve of the potential dependence of luminescence should therefore fall somewhat below that described by relation (10), and the relative deviation should increase with increasing overpotential  $U-U_0$ . This was actually confirmed experimentally (Fig. 2).

The correct course of the potential dependence of luminescence can therefore be described by

$$I_L = I_{L \max} - I_{L \text{ loss}} (U - U_0) \quad (12)$$

in which  $I_{L \max}$  is described by relation (10) and  $I_{L \text{ loss}}$  is a correction factor which describes the loss of luminescence due to a potential dependent decrease of the electron concentration in the surface. A calculation of this correction function has not been attempted, since it would presuppose a knowledge of the distribution of trapped holes in the space charge layer and at the surface. However, a qualitative experimental confirmation of these considerations was sought.

One way to provide additional electrons for recombination in the conduction band at the electrode surface would be to inject them from the electrolyte. The formyloxy radical reaction, investigated by Morrison and Freund,<sup>13</sup> provides an efficient means to such injection. According to these investigators, formate is oxidized at the illuminated zinc oxide electrode by capturing a hole from the valence band of the crystal. The resulting formyloxy radical is a strong reductant and injects an additional electron into the conduction band of the electrode. The addition of formate therefore doubles the photocurrent (doubling is usually not reached). Figure 8 shows that on addition of formate to the electrolyte the photocurrent increases and, at the same time, the potential decay of luminescence increases considerably with the electrode potential. The luminescence course in the presence of formate closely approaches the mirror symmetric relation to the photocurrent (in the absence of formate), as described by (7) and (10). Since the capture of holes from the valence band of zinc oxide by formate could not stimulate

luminescence, it must result from the transfer of the electron from the formyloxy radical into the conduction band of the electrode. This conclusion has been verified by the addition of hydrogen peroxide to the electrolyte. This agent is believed to prevent electron injection from the formyloxy radical by providing faster electron capture.<sup>13</sup>

It can be seen from Figure 8 that addition of  $H_2O_2$  also abolishes the formate-induced increase in luminescence. In some cases it also decreased somewhat the limiting value of fluorescence at lower potentials, indicating that it additionally extracts electrons from the electrode surface. The  $H_2O_2$ -induced blocking of electron injection from the formyloxy radical is also reflected in a clear decrease of formate-induced current amplification. The formyloxy radical therefore decreases the luminescence loss ( $I_L$  loss in relation (12)) by providing additional electrons in the electrode surface for recombination with trapped holes. The magnitude of the deviation of fluorescence from relation (10) and the formate-induced fluorescence effect was dependent on the crystals used.

Relations (7), (10) and (12) describe very well the potential dependence of photocurrent and fluorescence, and their symmetric behavior as well as deviations therefrom. Relations (7) and (10) predict a parallel dependence on a change in the absorption coefficient on the course of both photocurrent and luminescence. The lower the absorption constant, the smoother should be the potential dependence. This was verified by illuminating the crystal electrode at three different wavelengths corresponding to three different absorption coefficients of the crystal (Fig. 6); since the intensity of luminescence and the magnitude

of the photocurrent are also wavelength dependent (Figs. 3-5), a normalization of these dependencies for identical limiting values has been made. These results make it easy to understand the potential dependence of the luminescence excitation spectra (Figs. 3,4): only in the spectral region where photocurrents are excited there is a potential dependence of luminescence excitation. The variation of the potential dependence with the wavelength of the exciting light can also be understood easily with help of relations (7) and (10). Of special interest is the narrow luminescence excitation band at 390 nm, slightly to longer wavelengths from the absorption edge of the semiconductor, which evidently does not contribute to the photocurrent (Fig. 5). In this spectral region a broad-band phonon assisted edge emission and a series of bound exciton complexes have been determined by several investigators.<sup>9,16-20</sup> The potential independence of green luminescence, excited in this 390 nm band, may be related to the properties of these special transitions. Alternatively, however, would be an explanation of the potential independence of this band in terms of a high penetration depth of the exciting light according to relation (10). This penetration should be approximately 200 times deeper than for light inside of the absorption edge of zinc oxide,<sup>9</sup> and there would not be enough holes in the space charge layer existing at the small electrode potentials applied to generate a significant photocurrent which could influence the emission.

#### SUMMARY AND OUTLOOK

Our experimental and theoretical investigations have demonstrated a strict correlation between electrode photocurrents and green luminescence

at zinc oxide single crystal electrodes. This result suggests the use of luminescence as a probe for the study of the space charge layer and of electrochemical reactions. Luminescence measurements would be of considerable interest, especially for the investigation of the kinetics of fast reactions which are not accessible for electrochemical studies because of the long time constants in the electrochemical circuitry. The convenient control of charge carriers, which is possible when a crystal is used as an electrode in contact with an electrolyte, further suggests this arrangement for studies of the mechanism of luminescence itself.. The possibility of controlling luminescence from its maximal value to total extinction by applying only a few volts might also be of practical interest for image display devices.

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## FIGURE LEGENDS

Fig. 1. Scheme of experimental arrangement.

Fig. 2. Voltage dependence of luminescence intensity and photocurrent density. Exciting wavelength, 350 nm. The dashed curve shows the mirror image of the photocurrent density. Undoped crystal.

Fig. 3. Luminescence excitation spectra of undoped ZnO at different voltages. Luminescence wavelength, 500 nm.

Fig. 4. Luminescence excitation spectra of Cu-doped ZnO at different voltages. Luminescence wavelength, 500 nm.

Fig. 5. Spectral dependence of the photocurrent of undoped and Cu-doped ZnO.

Fig. 6. Luminescence emission spectra of undoped ZnO at different voltages. Excitation wavelength, 350 nm.

Fig. 7. Voltage dependence of luminescence intensity and photocurrent density at different exciting wavelengths (adjusted for equal limiting values). Undoped ZnO.

Fig. 8. Voltage dependence of luminescence intensity and photocurrent density. (1) Initial curves; (2) after addition of formate; (3) after addition of formate and  $H_2O_2$ ; (4) mirror image of the initial photocurrent curve. Cu-doped crystal.

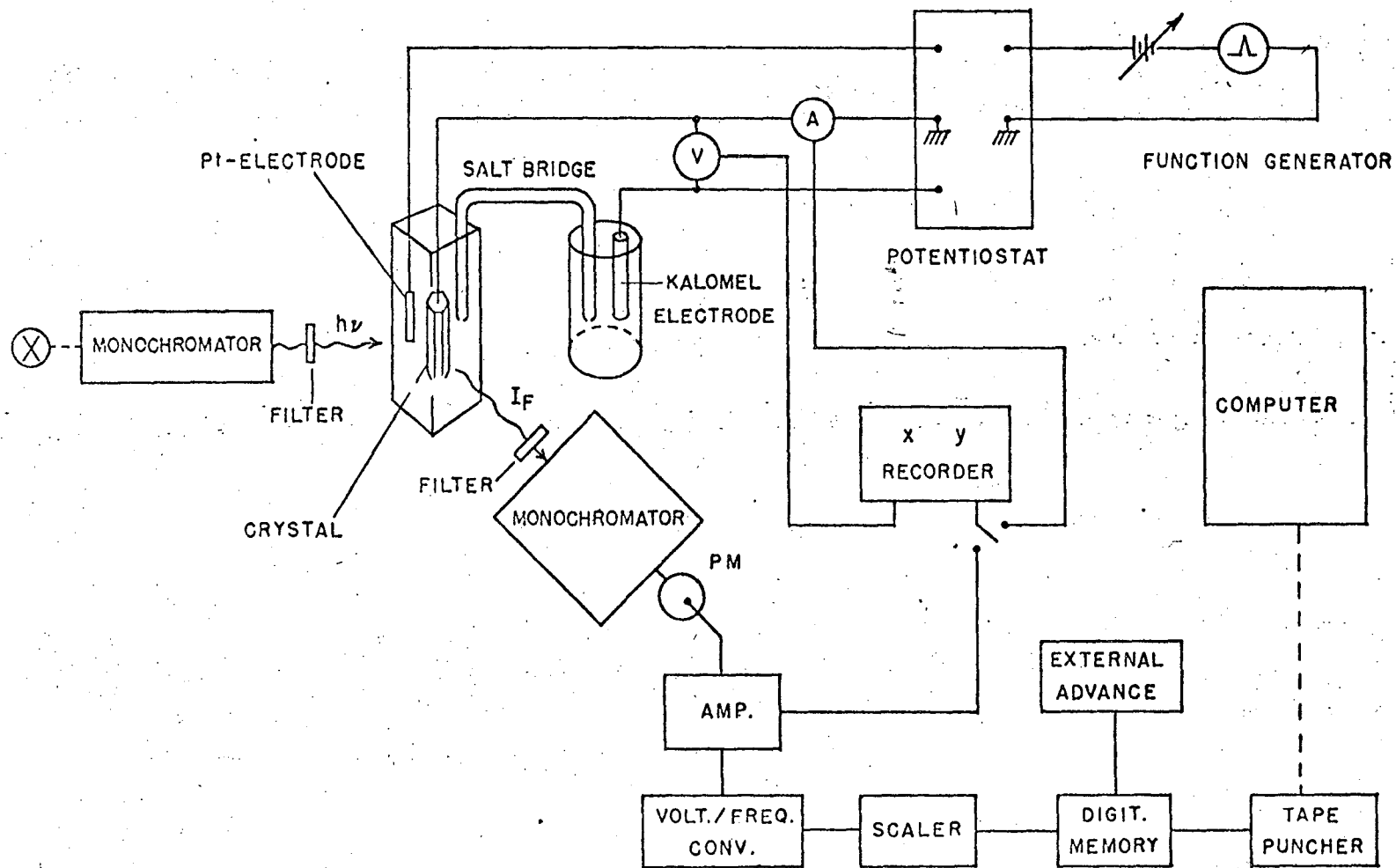
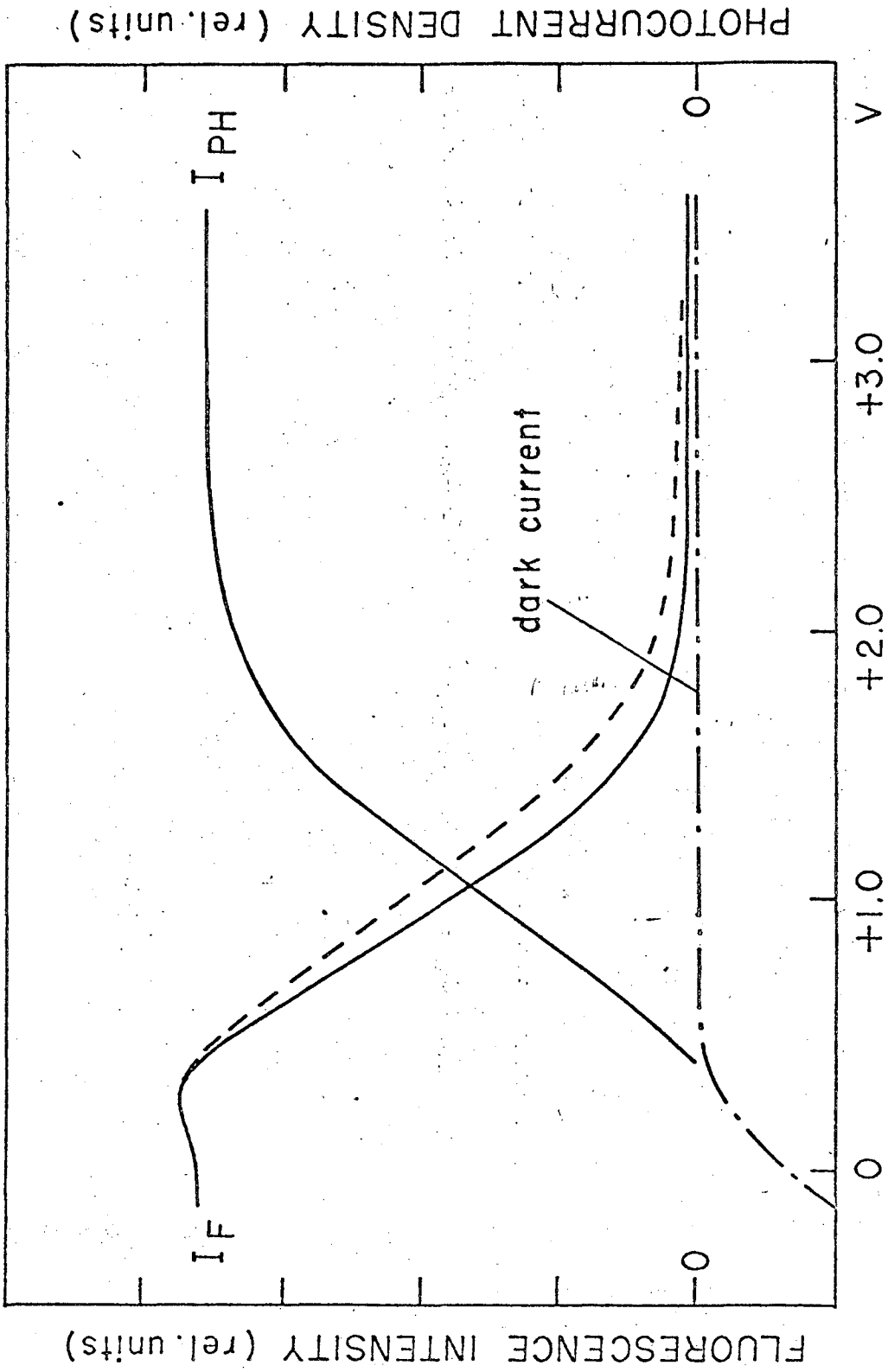


Fig. 1

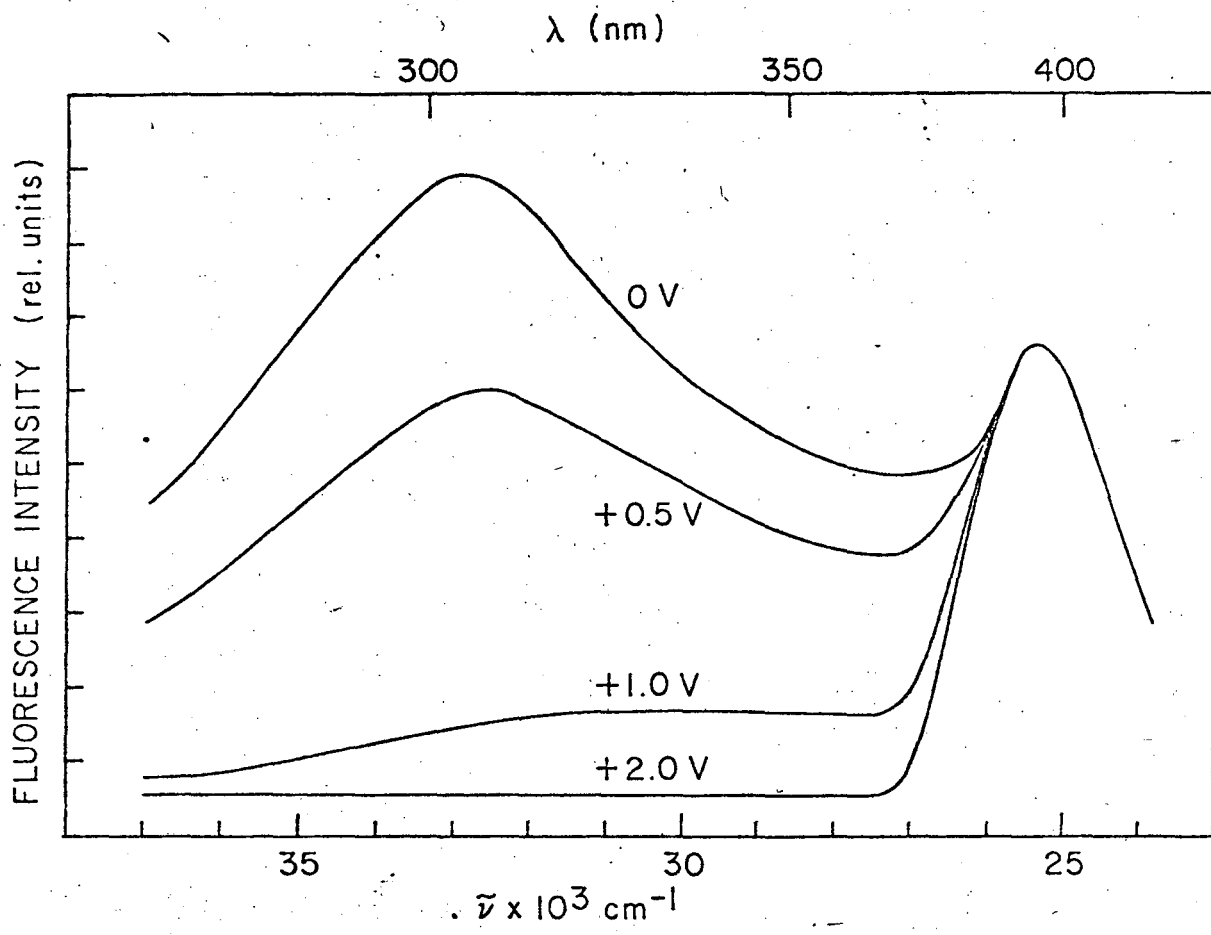


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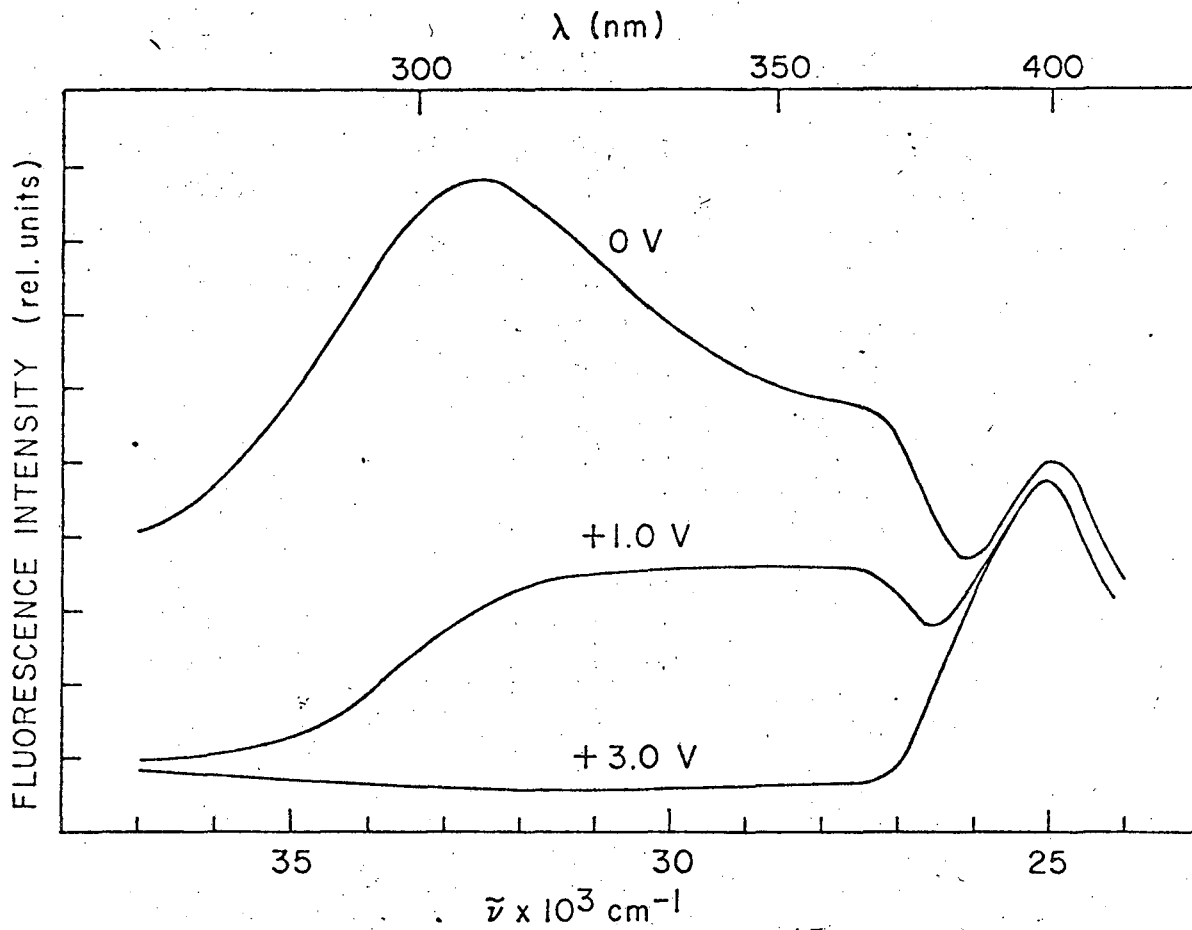
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Fig. 2



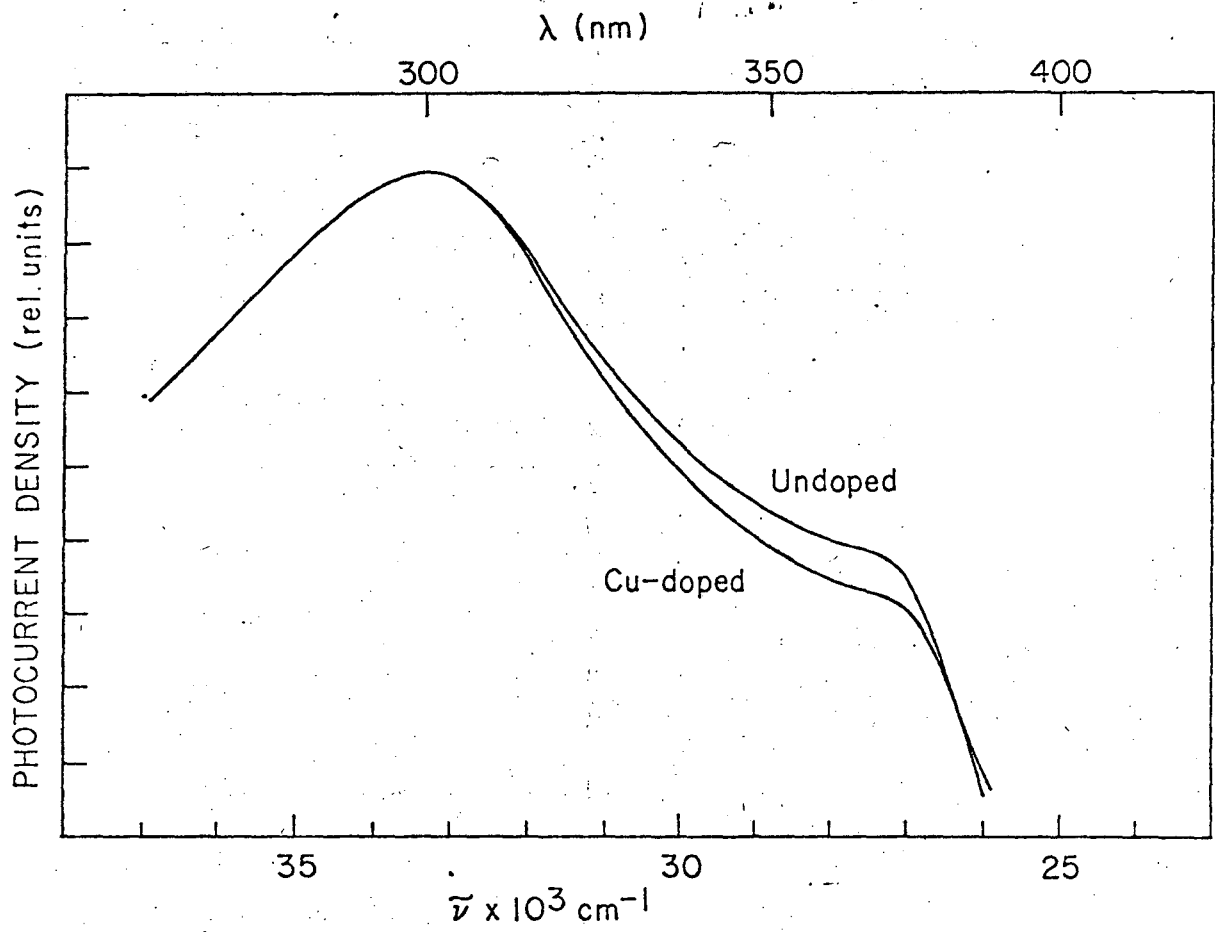
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Fig. 3



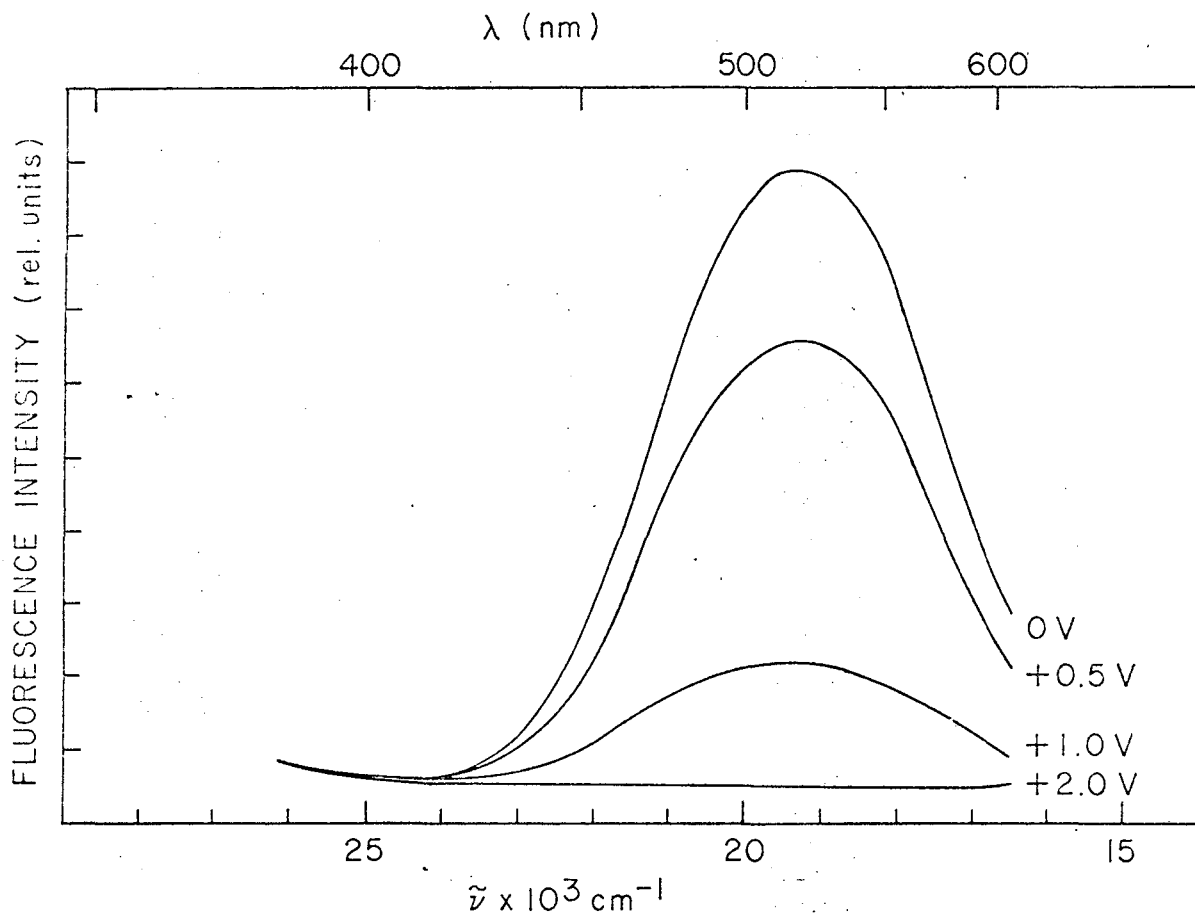
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Fig. 4



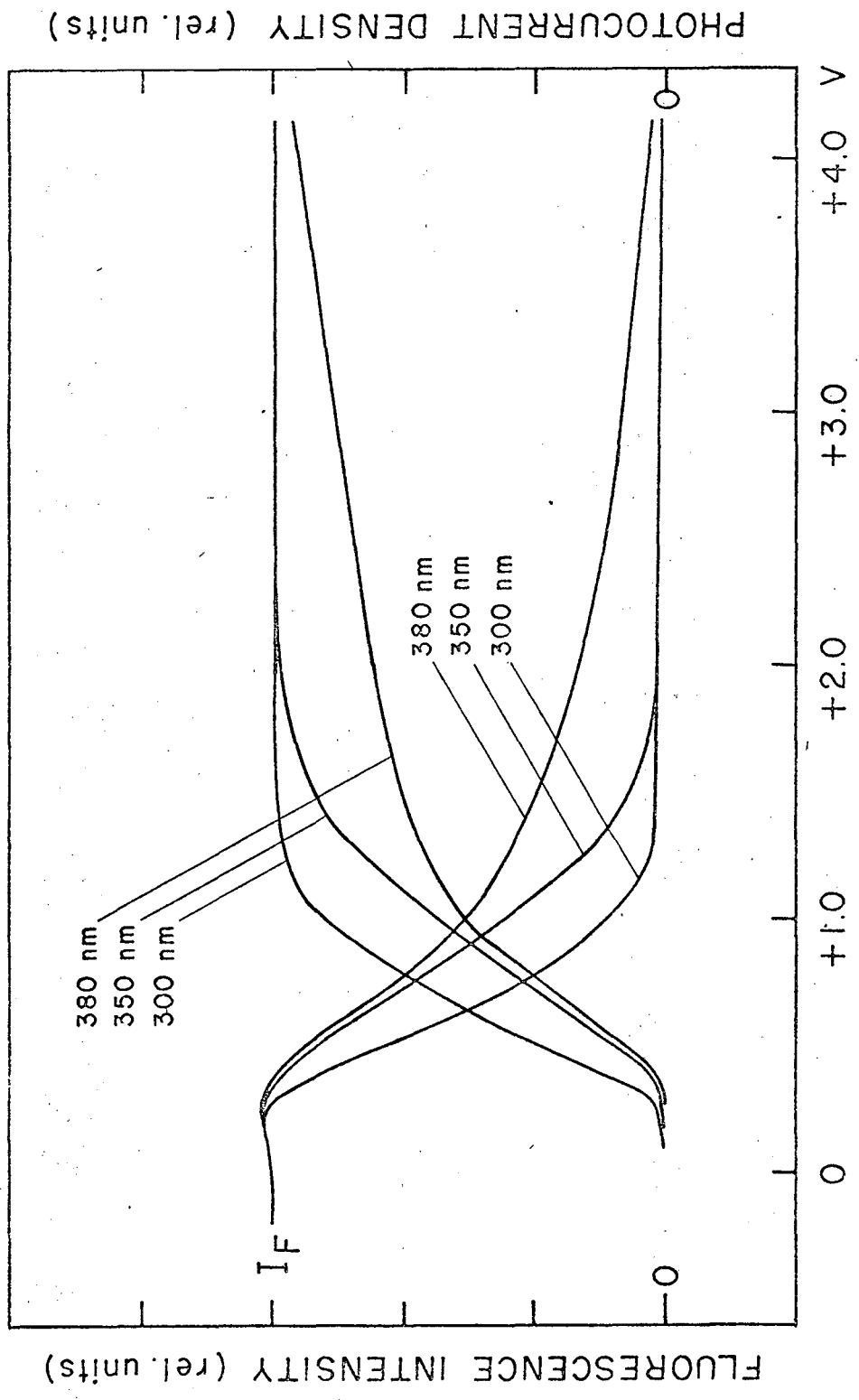
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Fig. 5



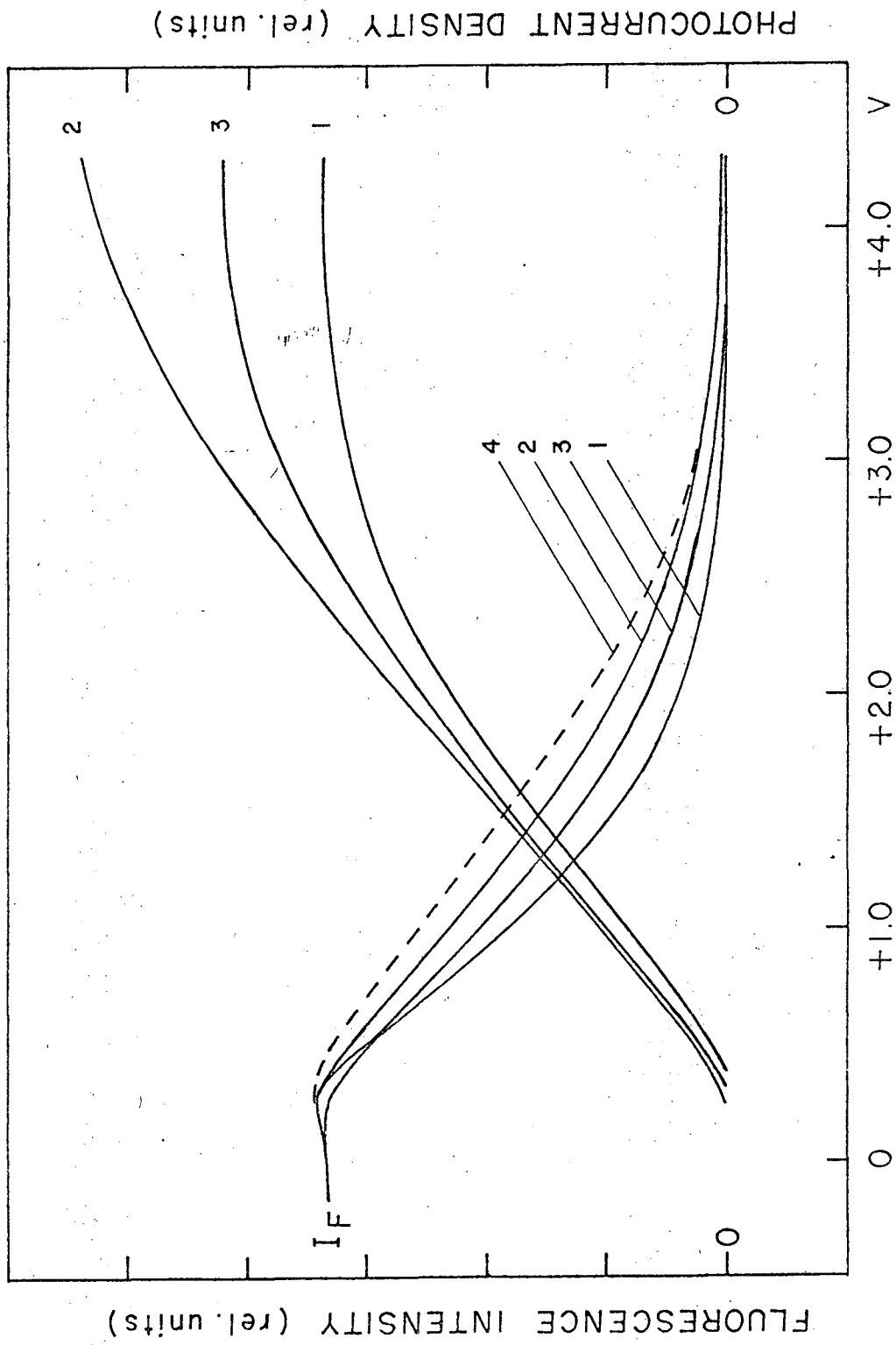
XBL7111-5461

Fig. 6



XBL7III-5457

Fig. 7



XBL 7111-5463

Fig. 8

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