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Polarization Effects in the Luminescence of Cadmium Selenide Electrodes

by

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Polarization properties of the emission from single-crystal, n-type CdSe samples have been examined. When excited with several ultraband gap wavelengths, a-plates of n-CdSe (wurtzite structure) exhibit polarized photoluminescence (PL) spectra consistent with the reported electronic structure of the solid. The spectra consist of two bands near the band gap energy ($\sim$1.7 eV), assignable to transitions between the conduction band and a split valence band having its two highest-energy band edges separated by $\sim$0.022 eV;

the lower-energy band is preferentially polarized with $E \parallel c$, while the other band displays no polarization preference. Time-resolved PL data, obtained with 620-nm excitation from a N_2-pulsed dye laser, were independent of polarization. Intensity-time curves yielded a decay time ($\tau_{1/e}$) of ~20 ns for both bands, providing evidence that the two emissive excited states are in thermal equilibrium. Emissive properties of n-CdSe, a-plate electrodes were also consistent with thermal equilibration. Polarized electroluminescence (EL) spectra, obtained using the solid as a dark cathode in aqueous peroxydisulfate electrolyte, closely resemble their PL counterparts, demonstrating attainment of similar excited-state populations in the two experiments. And when the semiconductor is used as the photoanode of a photoelectrochemical cell employing diselenide electrolyte, the two PL bands resulting from 514.5- or 632.8-nm excitation are quenched in parallel by the electric field present in the semiconductor.

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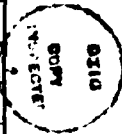
We recently reported on the photoluminescence (PL) and electroluminescence (EL) of single-crystal, n-type CdSe electrodes.[1,2] Emission is an easily-measured probe of electron-hole ($e^- - h^+$) pair recombination which serves to provide insight into the electronic structure and excited-state deactivation routes of the solid. These features are crucial to the semiconductor's ability to mediate optical energy conversion through its incorporation in photoelectrochemical cells (PECs).[3] For n-CdSe electrodes, we found that luminescence could be influenced by electrochemical processes; specifically, PL was perturbed and EL was initiated by interfacial charge-transfer events.

An aspect of luminescence which, to our knowledge, has not previously been examined with semiconductor electrodes is its polarization. A powerful tool in optical studies of solids, polarization effects can be anticipated for the uniaxial semiconductors with which we have worked and should provide additional information regarding their electronic structure and excited-state processes.[4] Cadmium selenide is an appealing candidate for such an investigation in that it is known to exhibit substantial polarization effects in its 77 K PL spectrum[5], as well as in its absorption,[6,7] reflection[7] and photoaction (photoconductivity as a function of wavelength)[8] spectra.

We report in this paper that both the PL and EL spectra of single-crystal, n-CdSe electrodes possess polarization characteristics consistent with the reported electronic structure of CdSe.[5-8] In particular, two emission bands with different polarization properties are observed at 295 K near the band gap energy ($\sim$1.7 eV [9]), corresponding to transitions between the conduction band and a split valence band. Moreover, under these conditions corresponding to multiple emission, polarized PL spectra of an n-CdSe-based PEC and EL spectra can be used in conjunction with energetic and kinetic features of the emission to infer that the excited states are in thermal equilibrium.

Results and Discussion

Our previous studies of emission from n-CdSe electrodes were conducted
exclusively with single-crystal samples cut perpendicular to the c-axis, i.e.,
with the 0001 or 000$\bar{1}$ face exposed to the electrolyte.[1,2] The polarized PL and EL
properties of the c-plates are compared in this paper with those of a single-crystal
a-plate having the 10$\bar{1}$0 face exposed to the electrolyte. In sections below we
describe the PL properties of n-CdSe and its electronic structure, EL from the
solids, and PL properties in a PEC.

A. PL Properties and Electronic Structure. As reported previously, samples of
single-crystal, n-CdSe exhibit cherry-red PL when excited by lines from an Ar^{+}
or He-Ne laser corresponding to ultraband gap energies.[1,2] Front-surface, polarized
PL spectra of n-CdSe were obtained using the experimental arrangement shown in
Figure 1. Both c- and a-plates were employed. In the latter case, the c- or optic
axis lies in the sample and is perpendicular to the incident light beam which
irradiates the solid "head-on". PL spectra were obtained with and without a polarizer
present. For the a-plate, the polarizer could be rotated to analyze for light
emitted with its electric vector oscillating parallel and perpendicular to the
c-axis, $E_{em}||c$ and $E_{em}\perp c$, respectively.

Figure 2 displays the polarization properties of PL from n-CdSe a- and c-plates
excited with 514.5-nm light.   In the absence of a polarizer, the a-plate exhibits
a sharp band at roughly the band-gap energy ("edge emission"[10]) with λ_{max} ∿713 nm.
Figure 2 reveals that insertion of the polarizer so as to examine $E_{em}\perp c$ and $E_{em}||c$
produces bands with λ_{max} values of ∿715 and 708 nm, respectively. PL from a CdSe
c-plate taken under similar experimental conditions is shown for comparison in the
bottom panel of Figure 2. As expected, this spectrum closely resembles in shape
and energy the PL spectrum of the a-plate having $E_{em}\perp c$.

From previous studies, the two PL bands observed for the CdSe a-plate likely
have their origin in a split valence band, as shown in Figure 3. A tight-binding

treatment in which the conduction and valence bands are derived from Cd 5s and Se 4p orbitals, respectively, leads, at k = (0,0,0), to the electronic structure of Figure 3 upon incorporation of crystal-field and spin-orbit effects.[6-9,11] The irreducible representations to which the indicated bands belong can be used in conjunction with the electric-dipole selection rules to predict the allowedness and polarization properties of transitions between the conduction band and valence bands.[11] All of the band-to-band transitions of Figure 3 are allowed; those involving two Γ_7 states are predicted to be unpolarized, whereas a transition involving a Γ_7 and Γ_9 state should be polarized with $E \perp c$.

Prior to our studies, low-temperature, polarized spectra based on photo-conductivity,[8] and on optical reflection[7] and absorption[6,7] had revealed excitonic structure consistent with the electronic structure of Figure 3. These spectra also permitted the determination of the magnitudes of the valence-band splittings, values indicated in the figure. The polarized PL spectra of Figure 2 and 77 K PL data[5] are in accord with the electronic structure shown in Figure 3. In particular, the peak at 708 nm exhibiting little polarization dependence may reasonably be assigned to the transition connecting the conduction band and the middle valence band (Γ_7,Γ_7), and the 715-nm band polarized with $E_{em} \perp c$ is logically a composite of the 708-nm band and the transition involving the conduction band and uppermost valence band (Γ_7,Γ_9). Subtraction of the 708-nm band from the 715-nm peak should thus yield a spectral distribution corresponding to the lowest-energy, band-to-band transition. Figure 4 demonstrates that such a deconvolution yields a single band with $\lambda_{max} \sim 717$ nm. The energetic separation of the two bands in Figure 4, based on the positions of their maxima, is ~ 0.022 eV, in good agreement with a value of ~ 0.019 eV estimated from 295 K photoconductivity data.[8]

A point which should be made in connection with the polarized PL spectra is that they are not corrected for the dichroism of the solid. PL with $E \perp c$ is preferen-tially absorbed in much of this spectral region, and self-absorption effects could

thus influence the PL spectrum. From literature data, however, we estimate that dichroic corrections should be relatively small.[6]

We should also mention that although our data are consistent with describing these transitions as band-to-band, the emission may involve states near the band edges resulting from lattice defects, impurities, etc.... If such states have the same symmetry as the band edge with which they are associated, they will follow the same selection rules with respect to polarization.[8]

The energetic proximity of the two emissive excited states prompted us to investigate excited-state communication through time-resolved and variable-temperature studies. The former were conducted with the CdSe a-plate using the unpolarized 620-nm output of a N_2-pumped dye laser for excitation. We found that the measured decay time, $\tau_{1/e}$, was ~20 ns and independent of polarizer orientation and the portion of the PL spectrum monitored. A similar decay time was reported for the c-plate.[1,2,12] For the a-plate, the comparable PL intensity-time plots for the two emission bands is evidence that the two excited states are thermally equilibrated, a reasonable expectation in view of their energetic separation of ~kT. In terms of Figure 3, the time-resolved data suggest that holes at or near the two uppermost valence band edges are thermally equilibrated prior to recombining with electrons at or near the conduction band edge.

We also attempted to acquire evidence for thermal equilibration from variable-temperature studies of steady-state polarized PL spectra: For such experiments, a semilog plot of the intensity ratio for the two bands of Figure 4 ($E_{em}||c$ and the deconvoluted band) vs. reciprocal temperature is expected to be linear with a slope corresponding to the state separation energy. For the temperature range employed (298-323 K), the anticipated change in the intensity ratio is ~7%. We did observe only modest changes in this ratio with temperature, but our experimental error was sufficiently large that it precluded a quantitative analysis.

B. **EL Properties.** An alternative means for populating the excited-state manifold of an n-type semiconductor electrode is based on the use of the solid as a dark cathode in a strongly oxidizing electrolyte. A number of n-type semiconductor electrodes have exhibited EL while carrying out the reduction of peroxydisulfate $(S_2O_8^{2-})$ ions in aqueous alkaline solutions;[2,13] the proposed key mechanistic step is the injection of a hole into the semiconductor's valence band by an intermediate, SO_4^{-}.[13a-c]

We examined polarized EL spectra from the n-CdSe a-plate in peroxydisulfate electrolyte using a slight modification of the experimental setup used for polarized PL spectra. Because the EL intensity was quite weak, the electrode was placed directly in front of the emission detection optics, allowing just enough room for insertion of the polarizer. As in previous studies, the electrode is repetitively pulsed between a potential where no current flows and a potential sufficiently cathodic to initiate $S_2O_8^{2-}$ reduction. Sweeping the emission monochromator during this pulse sequence yields a series of lines constituting the EL spectrum.

Figure 5 presents polarized EL spectra of the a-plate along with data previously reported for the c-plate;[1,2] Steady-state EL spectra, though far weaker in intensity, are essentially superimposable on those of Figure 5. As was the case for PL, the EL of the a-plate appears to be a composite of two bands. Band maxima and relative intensities approximately match those observed in the polarized PL spectra, providing additional support for the n-CdSe electronic structure of Figure 3. Moreover, the spectral accord demonstrates that the population of the emissive excited states is similar in the two experiments, consistent with the rapid attainment of thermal equilibrium. As observed in the PL spectra, the spectral distribution of the c-plate matches that of the a-plate for the $E_{em} \perp c$ orientation.

C. PL Properties in a PEC. In earlier studies, we demonstrated that PL from
n-CdSe photoanodes could be quenched by the electric field present in the
semiconductor during PEC operation; no change in spectral distribution with
potential was observed.[1,2] These studies, conducted with ultraband gap
excitation of n-CdSe c-plates and aqueous diselenide electrolyte, highlighted
the competitive nature of photocurrent and PL: increasingly positive potentials
enhance band bending within the solid, promoting the separation of
$e^- - h^+$ pairs and inhibiting their radiative and nonradiative recombination.[3a]
The fractional quenching of PL between open- and in-circuit potentials
$(\frac{\phi_{r_o} - \phi_r}{\phi_{r_o}}$, where ϕ_{r_o} and ϕ_r are the open- and in-circuit radiative quantum
efficiencies, respectively) can be rationalized in terms of a dead-layer model,
developed for solid-state, Schottky-barrier systems, which assumes that $e^- - h^+$
pairs formed within some fraction of the depletion width do not contribute to
PL.[14,15]

The quenching observed with n-CdSe c-plates is mimicked in the polarized PL
spectra of a-plates. Figure 6 presents current-PL intensity-voltage (iLV) curves
obtained with 514.5-nm excitation for a PEC employing an a-plate of n-CdSe and
diselenide electrolyte. The PL spectral distribution for each polarizer orientation
was independent of potential between open circuit and -0.3 V vs. SCE, providing the
expedient of monitoring PL intensity at a single wavelength. Shown in Figure 6
are PL intensities monitored at 712 nm (unpolarized), 707 nm ($E_{em}||c$), and 719 nm
($E_{em}\perp c$), the latter two wavelengths having been chosen as representative of the
individual PL bands. The key observation is that the two PL bands are quenched
in parallel by the electric field present in the semiconductor; monitoring several
other wavelengths throughout the PL spectrum also yielded parallel quenching curves.
A similar insensitivity of fractional PL quenching to the PL band which is
monitored was observed with 632.8-nm excitation.

The aforementioned observations made with the PEC provide additional insight into the electronic structure and excited-state processes of the n-CdSe electrode. With regard to electronic structure, the insensitivity of each polarized PL spectral distribution to potential indicates that all of the band edges involved in the emissive transitions bend in parallel in the presence of an electric field. A similar conclusion was drawn for the intraband gap states and band edges of another multiply-emissive electrode, Te-doped CdS (CdS:Te).[16]

The most striking feature of the polarized PL spectra in a PEC, parallel quenching of the two PL bands between open- and in-circuit potentials, is consistent with the thermal equilibration of the two excited states inferred from the time-resolved and EL experiments. Parallel quenching is expected so long as the quenching rate is sufficiently slow that it does not disrupt the interconversion involving the two excited states.[17] Although other schemes not requiring thermalization can also lead to parallel quenching,[18] the energetic proximity of the two emissive excited states is conducive to very rapid thermal equilbration and makes this process, we believe, the most likely explanation for the emissive properties we observe.

Experimental Section.

Materials. Single-crystal a- and c-plates ($\sim$10x10x1 mm) of n-CdSe were obtained from Cleveland Crystals, Cleveland, Ohio. The crystals were vapor-grown with resistivities of $\sim$2 ohm-cm. After being cut to dimensions of $\sim$0.25 cm^2 x 1 mm, the samples were etched in Br$_2$/MeOH (1:10 v/v) and mounted as electrodes as described previously.[16] The direction of the c-axis in the a-plate was determined by comparing a- and c-plate spectra (see text) and by chipping the crystal at its edge; striations observed in the sample after chipping are parallel to the c-axis.[6] The preparation of peroxydisulfate[19] and diselenide[20] electrolytes has been described; the latter was modified to increase solubility of the chalcogenide species using a method analogous to that reported for ditelluride electrolyte.[21]

PL Measurements. Uncorrected PL spectra were obtained on the Aminco-Bowman
($\sim$1-8-nm bandwidth) and McPherson-based spectrophotofluorometers ($\sim$0.3-nm bandwidth)
described previously.[1,2] Polarized PL spectra were taken with the experimental
geometry illustrated in Figure 1: a 5x5-cm polarizer (source unknown) or a
Melles Griot Model 03-FPG-001 polarizer was employed. Correction factors for
the polarization introduced by each spectrometer's monochromator were obtained
between 600 and 800 nm by passing the horizontally- and vertically-polarized
output of a tungsten lamp through each instrument's detection optics. The intensity
ratios observed indicated that the two spectrometers favored opposite polarizations
and raw polarized PL spectra obtained on the two instruments were, in fact, quite
disparate. However, after correcting the PL spectra with the aforementioned factors,
good agreement was obtained. All spectra shown in the figures were taken with
the Aminco-Bowman spectrometer ($\sim$1-nm bandwidth) and are corrected for detector
sensitivity.[1]

For steady-state PL spectra, excitation from either the 514.5-nm line of
a Coherent Radiation Model CR-12 Ar^+ laser or the 632.8-nm line of a Coherent
Radiation Model 80 He-Ne laser was employed. The Ar^+ laser output was linearly
polarized; that of the He-Ne laser was unpolarized but, when polarized in
some experiments by using a Melles-Griot Model 04-LPB-003 laser-polarizing
beamsplitter, no difference in polarized PL spectra was observed. The
laser beams were 10X-expanded and masked to $\sim$2x3-mm dimensions for sample
excitation. Corning 2-64 and Melles Griot 03-FCG-098 filters were placed before
the PMT to reject incident 632.8- and 514.5-nm excitation, respectively; the
filters did not affect the polarized spectral distributions. Variable-temperature
polarized PL spectra were acquired by suspending the sample in water in a cell
previously used for such studies; the vessel was heated resistively using nichrome
wire, and temperature, controlled to $\pm$ 0.5°C, was measured with a calibrated
thermometer.[22]

Time-resolved PL spectra of the samples in air employed the 620-nm output of an

NRG-DL-0.03 dye laser ($\sim$7 ns fwhm) which was pumped by an NRG 0.7-5-200 pulsed-N_2

laser (0.7-MW peak power); the dye laser output was passed through a 620-nm

interference filter. The detection system consisted of the Aminco-Bowman spectrometer

equipped with a Hamamatsu R928 PMT whose output across a 50-ohm-to-ground resistor

was measured by a Tektronix Model 466 storage oscilloscope. Decay curves were

obtained by operating the oscilloscope in variable-persistence mode which

averaged several hundred pulses. A pulse rate of $\sim$20 s^{-1} was used. Peak

laser intensities, estimated as described previously,[18] of $\sim$25 and 3 kW/cm^2

were used with no observable difference in results. PL was detected from

$\sim$680-740 nm ($\sim$5-nm bandwidth) in both polarizer orientations and in the absence

of a polarizer. A combination of Corning 2-64 and Melles Griot 03-FCG-055

filters was placed before the PMT in these experiments.

PEC and EL Experiments. Potentiostatic iLV curves were obtained as a function

of polarizer orientation using cells[16] and electrochemical equipment[1] previously

described. Both 514.5- and 632.8-nm excitation was used for these experiments

with the laser beams expanded and masked to fill the electrode surface. Incident

light intensities were measured with a Tektronix J16 radiometer equipped with

a J6502 probe head by reassembling the cell outside the Aminco-Bowman

spectrometer used in determining iLV data.[16] EL spectra as a function of

polarizer orientation were obtained in N_2-purged peroxydisulfate electrolyte

using a pulse technique previously described.[1,2] The experimental geometry differed

from that shown in Figure 1 in that the weak EL signal required placement

of the emitting electrode directly in front of the emission detection optics.

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Figure Captions

Figure 1. Top view of the experimental arrangement used for studying

polarization effects in PL from a CdSe $\underline{a}$-plate. A, laser beam; B,

n-CdSe $\underline{a}$-plate positioned with its $\underline{c}$-axis perpendicular to the laser

beam, as drawn; C, mirror used to deflect front-surface PL into detection

optics; D, slit; E, rotatable polarizer; F, monochromator; G, PMT.

Figure 2. Corrected, polarized PL spectra of n-CdSe $\underline{a}$- and $\underline{c}$-plates, top

and bottom panels, respectively. Samples were excited in the experimental

arrangement of Figure 1 with $\sim$13 mW/cm^2 of linearly-polarized 514.5-nm light;

for the $\underline{a}$-plate, this light was polarized with $E \perp a,c$. The position of the

polarizer for each spectrum is indicated in the figure.

Figure 3. Band structure and corresponding symmetries for n-CdSe at $k = (0,0,0)$.

Band-to-band transitions involving Γ_9 and Γ_7 are allowed only for $E \perp c$, whereas

those involving two Γ_7 bands are allowed for both $E \perp c$ and $E || c$. Energetic

separations between bands are indicated at the left-hand side of the diagram.

Adapted from ref. 8.

Figure 4. Corrected, polarized PL spectrum of the n-CdSe $\underline{a}$-plate of Figure 2,

deconvoluted by subtracting the $E_{em} || c$ curve (dashed line) from the $E_{em} \perp c$ band

(solid line). The deconvoluted spectrum, presumably corresponding to the low-energy

$E_{em} \perp c$ transition of figure 3, is pictured as the dot-dash curve.

Figure 5. Corrected, polarized EL spectra for the n-CdSe $\underline{a}$-plate of Figure 2.

The electrode was continuously pulsed between 0.00 V (6 s) and -1.50 V vs. SCE

(1 s) in 5M OH$^-$/0.1 M $S_2O_8^{2-}$ electrolyte while the emission spectrum was scanned

at 12 nm/min. The position of the polarizer is as indicated in the figure panels,

and the bottom panel shows the EL spectrum of a n-CdSe $\underline{c}$-plate for comparison.

Figure 6. Photocurrent (bottom panel) and polarized PL intensity (top panel) vs. potential for a single-crystal, n-type CdSe $\underline{a}$-plate electrode in 5M KOH/ 0.12 M Se^{2-}/0.002 M Se_2^{2-} electrolyte. The solid PL intensity curve corresponds to detection at 712 nm without a polarizer; the dashed curve to detection of 719-nm light with $E_{em} \perp c$; and the dot-dashed curve to 707-nm PL intensity with $E_{em} || c$. The ~ 0.25-cm^2 exposed area of the electrode was uniformly irradiated with ~ 1.1 mW of 514.5-nm light with a beam-expanded Ar^+ laser. These iLV curves were swept at 10 mV/s and the electrolyte redox potential was -0.97 V vs. SCE. An identical photocurrent curve was obtained in each sweep.
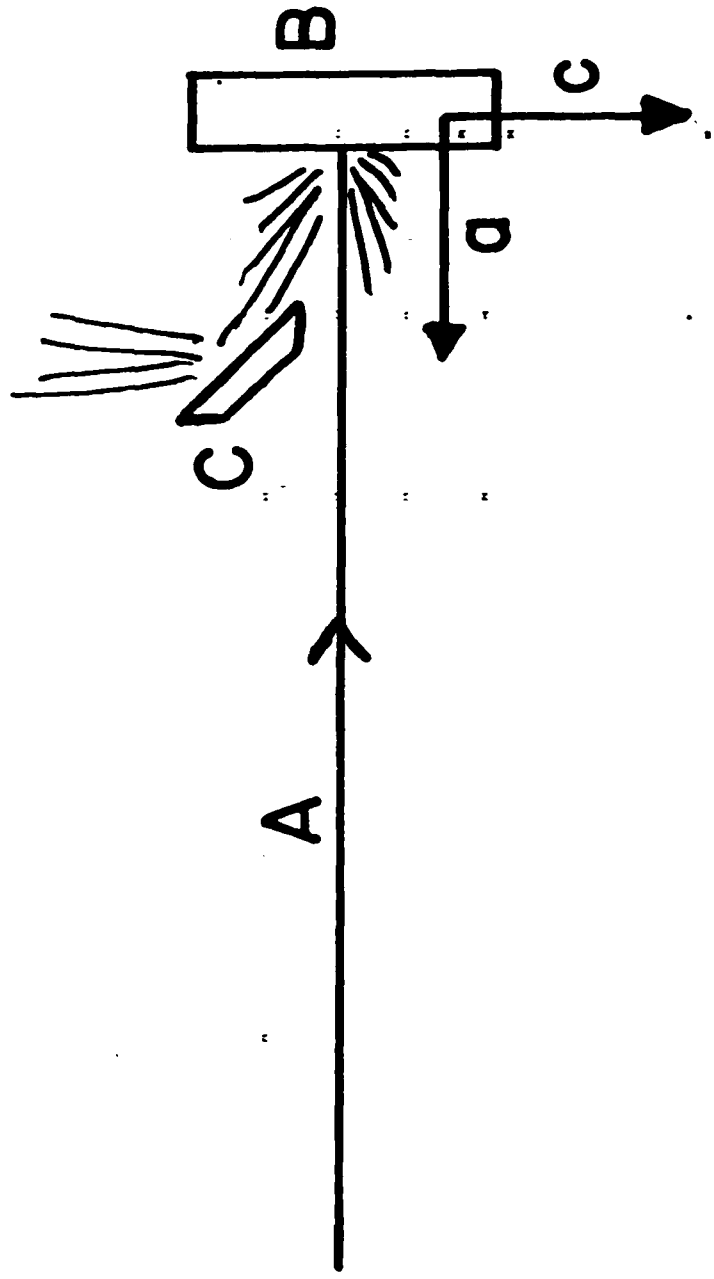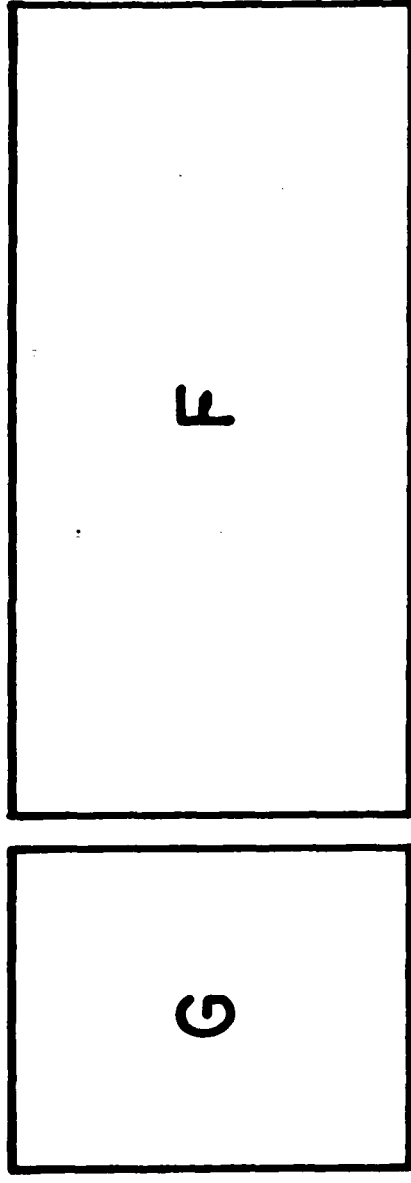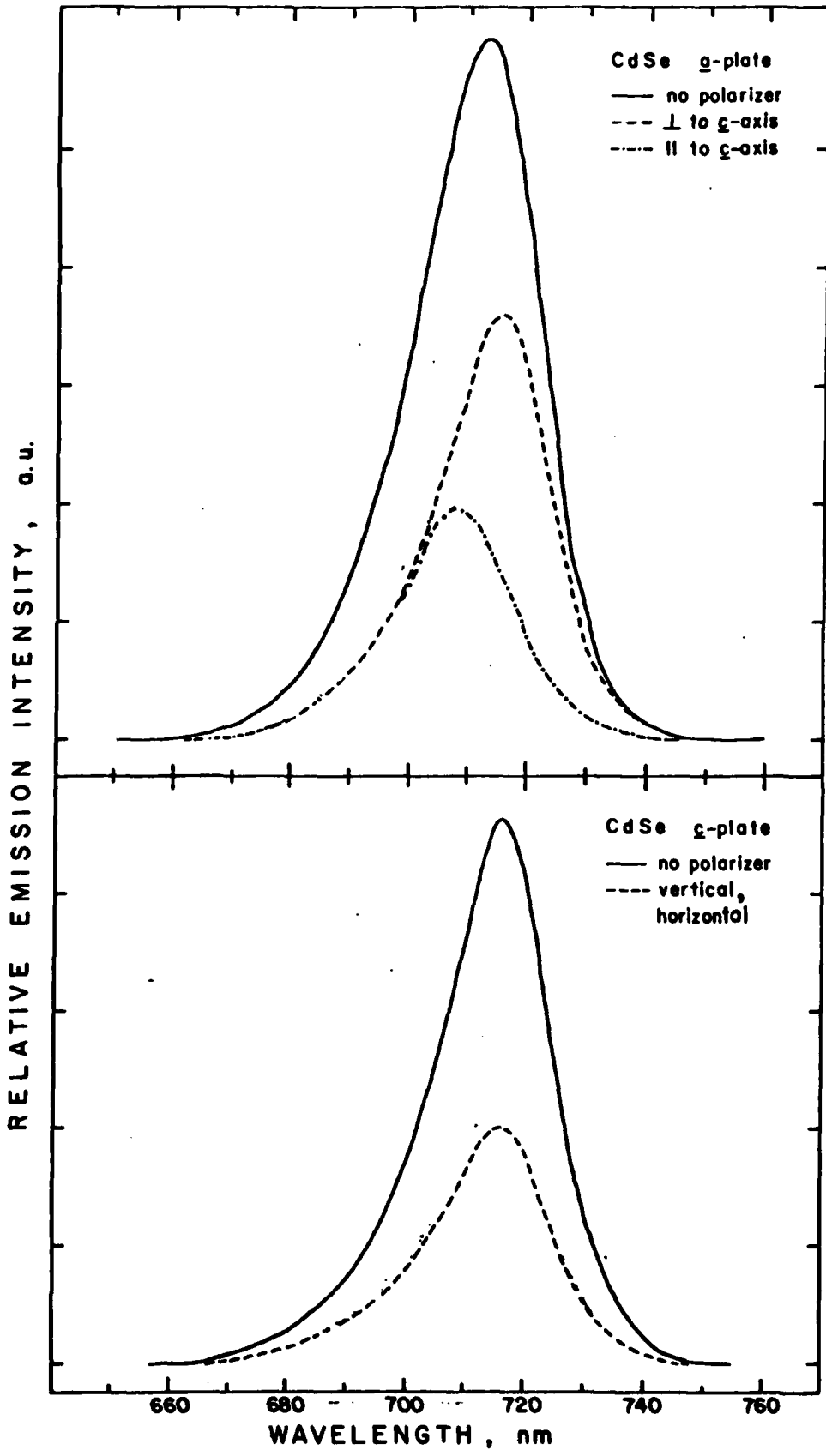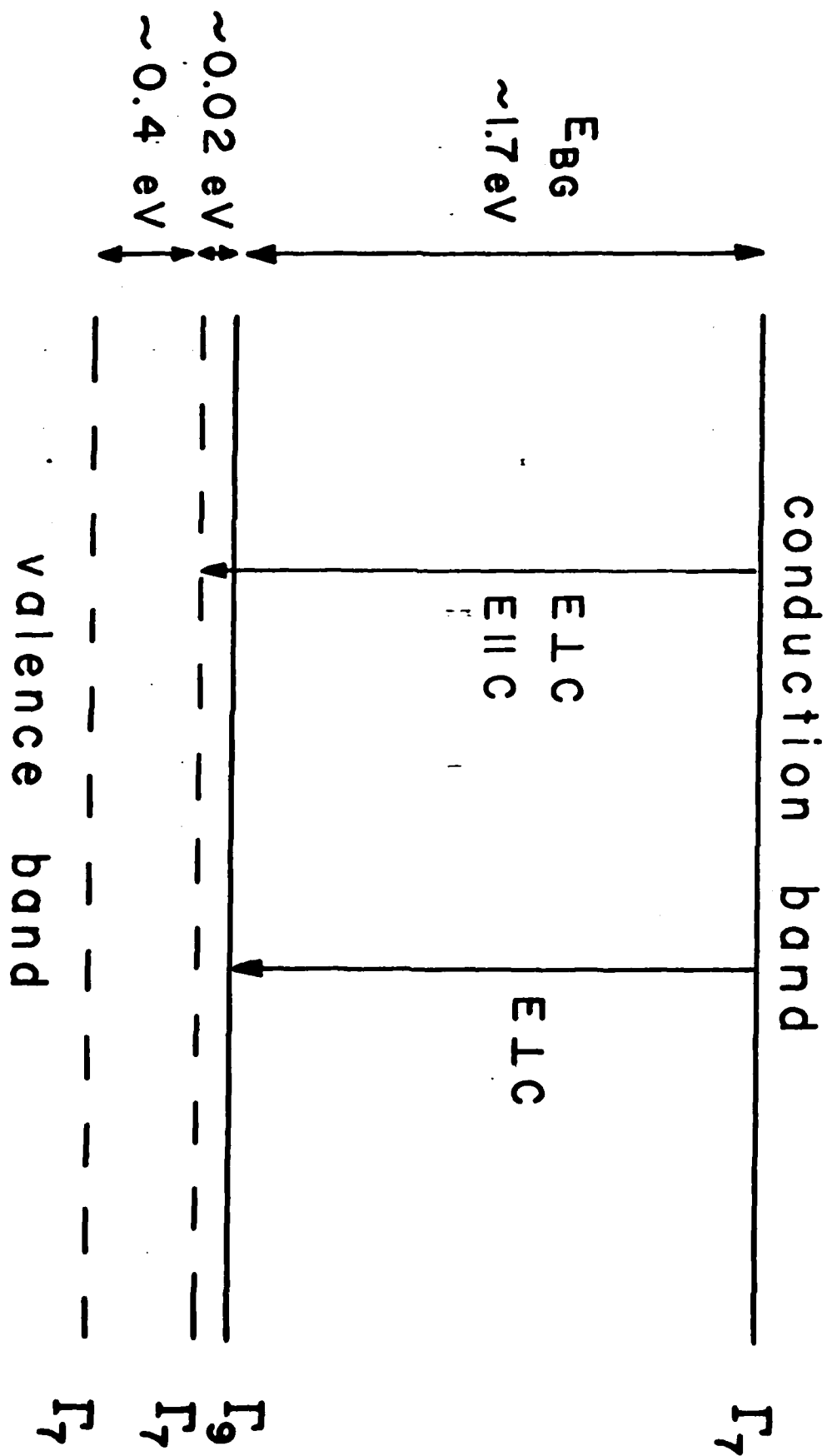
FIG 1

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FIG 2
16

CdSe a-plate
—— no polarizer
- - - ⊥ to c-axis
-··-··- ‖ to c-axis

CdSe c-plate
—— no polarizer
- - - vertical,
horizontal

RELATIVE EMISSION INTENSITY, a.u.

WAVELENGTH, nm

Fig 3
17

E_{BG}
$\sim 1.7 eV$

$\sim 0.02 eV$
$\sim 0.4 eV$

conduction band

$E \perp C$
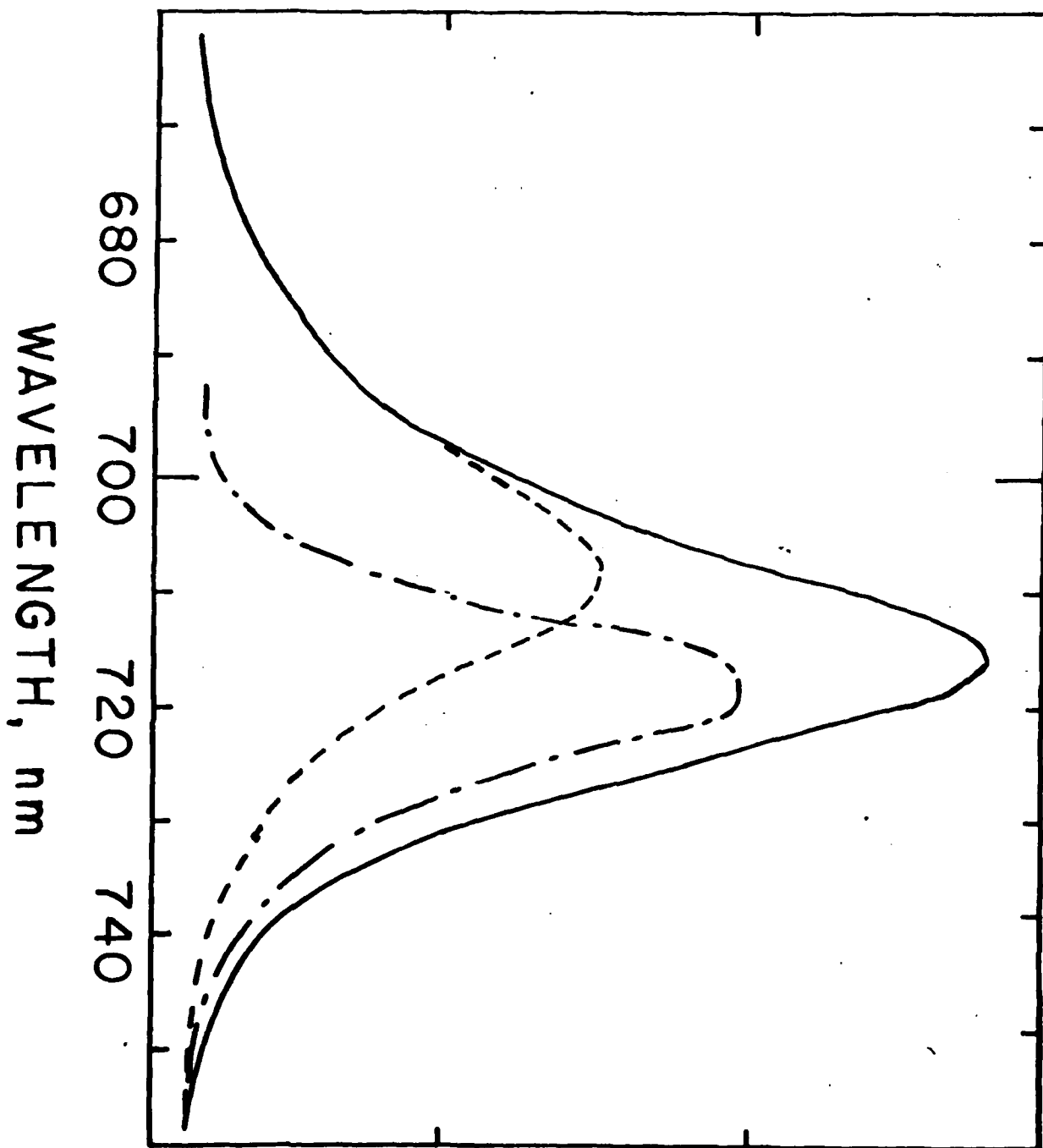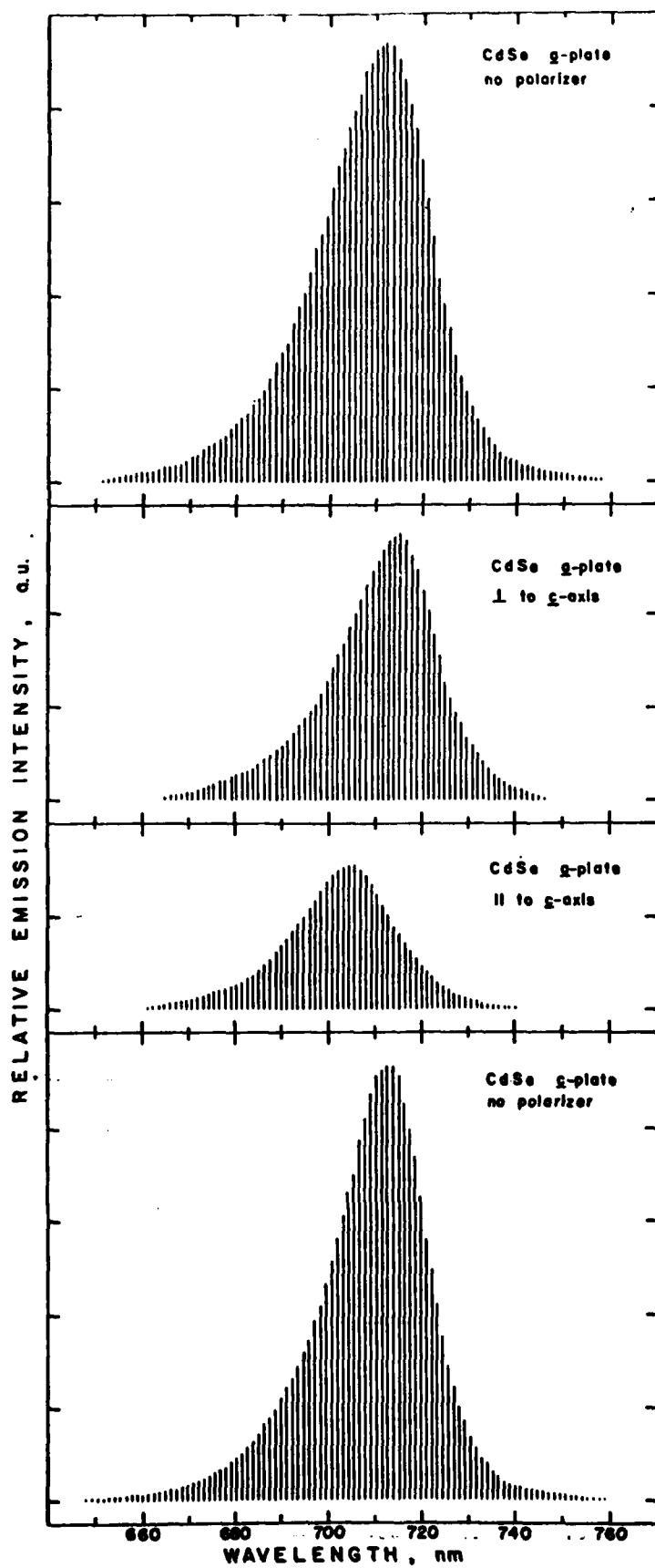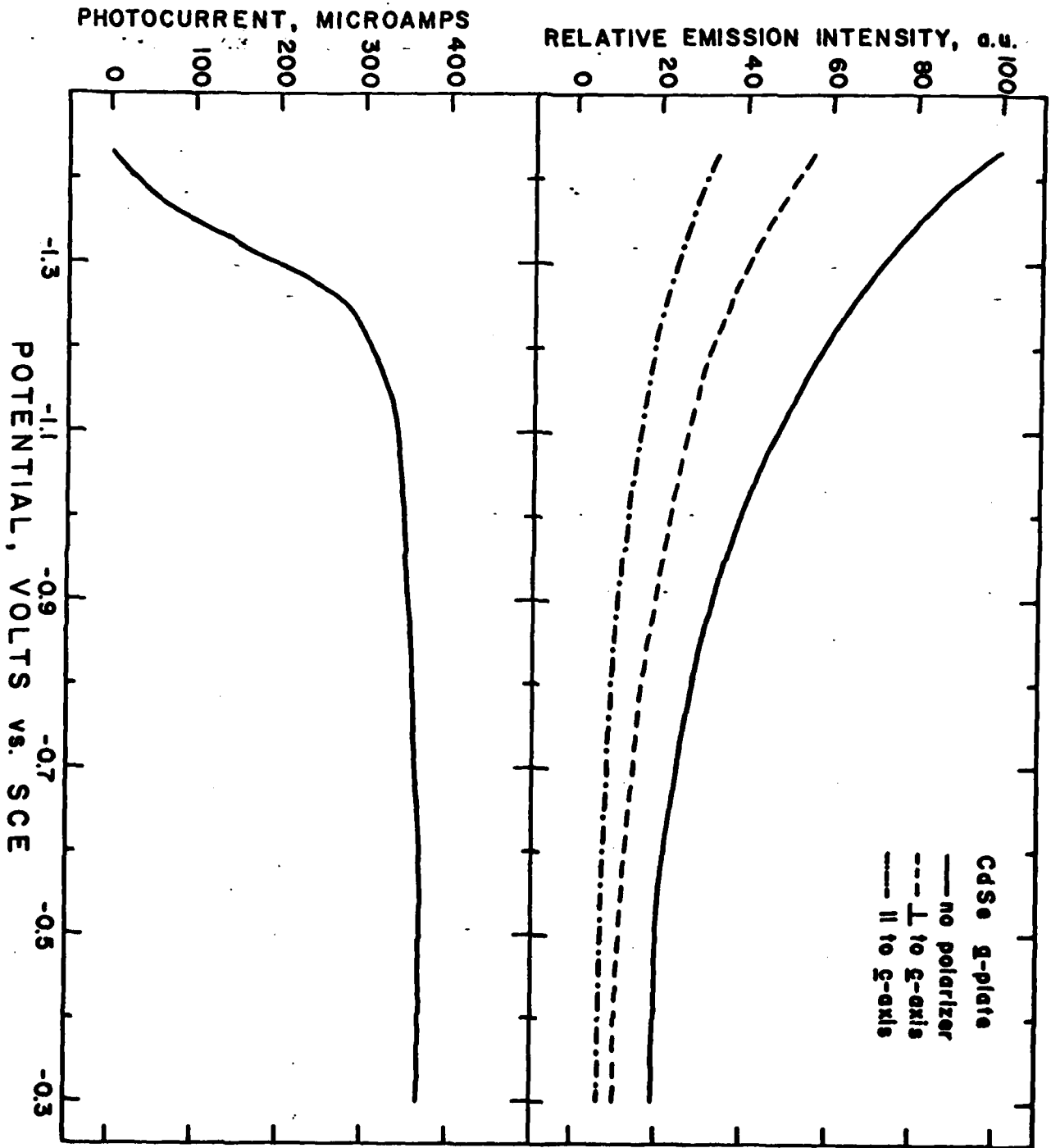$E \parallel C$

$E \perp C$

valence band

Γ_7
Γ_7
Γ_9
Γ_7

FIG 4

18

RELATIVE EMISSION
INTENSITY, a.u.

WAVELENGTH, nm

680   700   720   740

FIG 5

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CdSe g-plate
no polarizer

CdSe g-plate
⊥ to c-axis

CdSe g-plate
ll to c-axis

CdSe g-plate
no polarizer

RELATIVE EMISSION INTENSITY, a.u.

WAVELENGTH, nm

FIG 6

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