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CORRELATION OF ULTRAVIOLET EXCITED LUMINESCENCE AND INTERBAND TRANSITIONS IN HEXAGONAL ZINC SULFIDE

William C. Walker*
National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

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Measurements of the ultraviolet luminescent excitation spectrum, reflection spectrum, and photoemission of single crystal hexagonal zinc sulfide for the spectral region 3 to 11 eV are presented. A tentative assignment of reflection peaks to specific interband transitions is made and used to discuss the structure observed in the luminescent excitation spectrum on the basis of assumptions concerning the luminescent mechanism. Evidence is presented to support the contention that the structure in the excitation spectrum is mainly controlled by the dependance of the electron transport and trapping efficiency on the final states of the various interband transitions.

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I. INTRODUCTION

Tremendous progress has been made recently in our understanding of ultraviolet absorption in solids and its interpretation through the identification of structure in the optical[1-3] and photoemissive[4] spectra with specific interband transitions and excitons at or near critical points in the joint density of states function[5,6]. It is now possible to specify the initial and final states of the majority of the strong interband transitions in a broad range of solids. This advance has opened the way for detailed studies of a variety of secondary processes associated with the trapping, recombination, scattering and ejection of the excited electrons. The recent verification of the conservation of tangential electron momentum in photoemission from silicon[7] is a fine example of the results to be reaped from such studies.

Luminescence is another example of a secondary process which should greatly profit by taking advantage of the new knowledge. Various aspects of luminescence have been studied for many years[8]. Only recently, however, has interest revived in the use of luminescent phenomena to study intrinsic solid state properties[9,10]. This is partly due to the fact that emphasis on the defect nature of the luminescent mechanism has overshadowed the fact that in many cases the initial electron excitation and subsequent transport and trapping at the luminescent center are intimately connected with the host lattice. It should thus be possible to use the luminescent process as a tool to study the transport of highly excited electrons and the relative trapping efficiency for electrons in specific states as well as an aid in the identification of various interband transitions[11].

Previous measurements of ultraviolet induced luminescence, with the exception of some very recent papers[9], have been devoted mainly to the search for efficient phosphors for specific purposes[12]. As a result many of the measurements were carried

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out on samples which were unsuitable for detailed analysis of intrinsic effects. These studies are, however, invaluable in providing a guide for the selection of materials for detailed study.

In the present paper initial data of ultraviolet induced luminescence excitation spectra, reflection spectra and the spectral dependance of the photoemission are reported for a single crystal of hexagonal zinc sulfide in the region 3 to 11 eV. The aim of the study was to establish a correlation between the luminescent excitation process and the states of the excited electrons. Zinc sulfide was chosen for initial study because (a) the luminescent excitation process is known to involve the host lattice, (b) the major defects responsible for the common luminescence are reasonably well established[13], (c) the crystal is transparent to its luminescent radiation and (d) sufficient theoretical guides are available to allow a reasonable identification of the interband transitions[6].

II. EXPERIMENTAL

All the measurements to be reported were carried out on a single crystal of hexagonal zinc sulfide obtained from Semi Elements, Inc. The crystal, whose size was 2 cm x 1 cm x 2 mm, was clear and colorless with no traces of the discoloration sometimes found in such crystals. Observation of the typical green phosphorescence centered at 5200A under 2537A irradiation showed that trace amounts of Cu^+ were present to act as the luminescent center[13]. The long lifetime of the phosphorescence, measured to be of the order of one-half hour, indicated that another impurity, probably Al^{+++}, was present to provide a source of thermally released electrons.

A McPherson, model 225, monochromator equipped with a current regulated, low pressure hydrogen discharge source was used to provide monochromatic ultraviolet radiation for the measurements. The monochromator was operated with a spectral resolution ranging from 0.02 eV (100 micron slits) for the reflection spectra to 0.2 eV (1 mm slits) for the relative photo-yield measurements. An Electro-Mechanical Research #541A photomultiplier having a dark current of 10^{-11}A at a gain of 5×10^5 at room temperature was used to monitor both the ZnS luminescence and that from a sodium salicylate reference. Since the quantum efficiency of soidum salicylate is known to be reasonably constant over a broad spectral range[14], the ratio of the two luminescent spectra gave a direct measure of the spectral dependance of the ZnS luminescence.

Reflection spectra of the ZnS crystal were recorded with a vacuum reflectometer employing a rotatable, sodium salicylate coated light pipe and an EMI 6256N photomultiplier. The measurements were made at an angle of incidence of 20° on a cleaved surface. Because the cleaving was done in air, the reflection spectrum can not be considered that from a pure surface. Experience with ZnS and related materials, however, has shown that while moderate surface contamination reduces the magnitude of the reflectivity it does not obscure the structure due to interband transitions.

To aid in the interpretation of the luminescent data, the spectral dependence of the photoemission was measured by collecting the electron emission from the cleaved surface of the crystal and comparing it to the luminescence response of a sodium salicylate screen. Since the detailed behavior of the photoemission is sensitive to the nature of the surface, all that could be hoped for in this measurement was an estimate of the photo-threshold and perhaps an indication of structure due to the onset of interband transitions. As will be seen, even under these relatively poor conditions, the photoelectric data can aid significantly in the interpretation of the realts.

III. RESULTS AND DISCUSSION

A. Reflection and photoemissive spectra

The reflection spectrum of hexagonal ZnS taken with unpolarized light is shown in Fig. 1. Data were taken at about one-hundred points with an instrumental resolution of

0.02 eV. Reflection peaks were observed at 3.65, 5.75, 7.00, 7.35, 7.63 and 9.55 eV. An addition shoulder which is probably real appeared at 10.3 eV. For comparison the transmission spectrum near the fundamental energy gap is also shown. As will be discussed in more detail later, these peaks can be identified with interband transitions mainly at the center of the Brillouin zone and give a good picture of the order and relative magnitudes of the electronic states at this point.

The spectral dependance of the photoemission is shown in Fig. 2. Only gross features of this curve warrant attention because of the nature of the surface. As shown in the insert of Fig. 2, there is a weak threshold at 7.5 ± 0.2 eV together with a stronger increase near 9.0 eV. Beyond 9.0 eV the yield is linear with photon energy as predicted by Kane[15] for direct transitions. An interpretation of these data will be given in the following section.

B. Band Structure

The assignment of structure in optical or photoemissive spectral with specific features of the band structure is a difficult procedure and in general, requires either data on a broad range of related structures or a highly reliable set of band calculations. Since neither exist at present for wurtzite structures only a tentative assignment of the structure of Fig. 1 can be made. Fortunately, there do exist preliminary band calculations for hexagonal ZnS by Herman and Skillman[16] and an analysis of experimental data by Phillips[6] for the related material CdSe which can be used as guides in interpreting the ZnS spectrum. According to Phillips, the lowest energy direct transitions (3.65 eV) would be expected to correspond to transitions at the center of the Brillouin zone between the valence band maximum at Γ_5^v and the conduction band minimum Γ_1^c.[17] Thus, the fundamental band gap is associated with a direct transition rather than an indirect one as suggested by Herman and Skillman. Indeed, it does not seem possible to get a consistent interpretation of the measurements presented here on the basis of an indirect gap. The remaining reflection peaks, with the exception of the one at 5.75 eV, are consistent with transitions at the Γ point. The 5.75 peak in ZnS probably corresponds to the 5.0 eV peak in CdSe which Phillips tentatively assigns to transitions near the M or K points. Using the condition of steepest slope for the transmission data of Fig 1, a direct band edge of 3.6 ± 0.1 eV is obtained. This together with the 7.5 ± 0.2 eV photo-threshold yields an electron affinity E_A of about 3.7 eV and serves to fix the vacuum level. Assuming that Herman's numerical results at the center of the Brillouin zone are approximately correct, allowed transitions in the range 7 to 9 eV should occur between valence band states Γ_5^c, Γ_1^c, Γ_6^c. There are thus sufficient transitions at this point to account for the observed complex structure of the 7 and 9 eV peaks. Because $\Gamma_5^v \rightarrow \Gamma_5^c$ is expected to be strong[6] it is assigned to the main 7.00 eV peak. The remaining peaks can then be assigned to conform to the photoemission results. Since the true photo-threshold certainly exceeds 7.00 eV, the state Γ_5^c must fall below the vacuum level and hence the 9.55 eV peak is assigned to $\Gamma_5^v \rightarrow \Gamma_6^c$ rather than $\Gamma_6^v \rightarrow \Gamma_5^c$ as suggested by Phillips[6] for the corresponding peak at 9 eV in CdSe. The 7.35 eV peak could be either $\Gamma_1^v \rightarrow \Gamma_5^c$ or $\Gamma_5^v \rightarrow \Gamma_1^c$ from energy considerations; it is assigned to the later transition in order to enable it to contribute to the photoemission near the threshold. The order of the electronic states at the center of the Brillouin zone deduced from this analysis is shown in Fig. 3. The rapid rise in the photoyield near 9 eV is attributed in part to the onset of the $\Gamma_5^v \rightarrow \Gamma_6^c$ transition. On the basis of the photoyield data the vacuum level can be located near Γ_1^c to within ± 0.2 eV but the data are not good enough to determine if Γ_1^c is above or below the vacuum level. The author favors placing Γ_1^c just above the vacuum level and adopting the lower value of 7.3 eV for the photo-threshold thus allowing $\Gamma_5^v \rightarrow \Gamma_1^c$ to contribute to the photoemission.

C. Luminescent Excitation Spectrum

The luminescent excitation spectrum measured at room temperature is shown in Fig. 4. Luminescent radiation emerging from the back surface of the crystal was monitored. The emission spectrum excited at 2537A consisted of the broad band centered on 5200A which is typical of the Cu^+ activator. The significant features of the spectrum are a rapid rise beginning at 3.9 eV, a broad peak near 5 eV with an enhancement at 5.9 eV and a decrease beginning near 6.5 eV, and a plateau starting at 7.6 eV having a magnitude about three tenths of the peak value. These features will be interpreted on the basis of the following assumptions:

1. The luminescent mechanism is the recombination of an electron trapped at a Cu^+ site with a hole in the valence band.
2. The efficiency of the luminescence depends on the direct interband transition probability and the transport and trapping efficiency of electrons and holes.
3. The contribution of a specific interband transition to the electron-hole pair density is proportional to the product of the oscillator strength of the transition and the magnitude of the joint density of states at the singularities. It can then be shown[18] that the relative contributions of two transitions are in the approximate ratio $E_i R(E_i)/E_j R(E_j)$, where $R(E_i)$ is the reflectivity at E_i.

On this basis, the luminescent onset near 4 eV can be attributed to the transition $\Gamma_5^v \rightarrow \Gamma_1^c$. That the excitation curve does not rise abruptly at 3.6 eV is due probably to the fact that for the final state of this transition the average electron velocity $\hbar^{-1} \nabla_k E(k) = 0$ so that the transport of the electron to the trapping sites is retarded. Thus, it is not until transitions slightly removed from $k = 0$ occur that significant luminescence begins. Since the 5.75 eV transition occurs for k other than zero, it is reasonable that the luminescence output should continue to rise toward this transition. As soon as transitions to higher states set in, e.g., near 7.0 eV to the Γ_5^c state, the trapping efficiency appears to be reduced and the luminescence decreases. The fact that the break in the excitation spectrum at 7.6 eV nearly coincides with the photo-threshold and that from this point to higher energy the spectrum is nearly structureless indicates that once transitions to final states far removed from the conduction band minimum occur, the transport and trapping efficiencies are roughly averaged out to a constant value.

The energy dependence of the photon absorption depth with the associated variations in direct electron-hole surface recombination might be raised as an alternative interpretation to that given. Considerations of the optical constants for a variety of materials have shown that ϵ_2, R, and k display approximately the same spectral dependence so that the reflectivity can be taken as a rough index of absorption. In this case, Fig. 1 shows that the transitions near 6, 7 and 9 eV correspond to roughly the same absorption coefficient so that the absorption depths for these transitions are comparable and major variations in surface recombination rates would be unlikely.

A comparison of the ratios of the luminescent response to the interband transition contribution to the electron-hole pair density for two energies gives a rough measure of the efficiency of the transport and trapping of electrons at luminescent sites and of the subsequent emission. For the transitions near 5.8, 7.0 and 9.6 eV the relation given above[18] yields the following ratios in order of increasing energy from 5.8 eV - 1:0.5:0.1. Thus, electrons excited to the Γ_6^c state by 9.6 eV photons are one-tenth as efficient in producing luminescence as are those excited by 5.8 eV photons.

These measurements may also bear on the model for the luminescent mechanism. Two models, the Lambe-Klick and the Schön-Klasen models, have been proposed.[19] The models differ principally by the order in which the Cu^+ sites are filled by electron trapping. In the Schön-Klasen model the Cu^+ sites are initially empty and are filled by the photo-excited electrons and subsequently radiate. In the Lambe-Klick model the Cu^+ sites are initially filled and the radiation occurs through recombination with the free hole released by the incident light. The Cu^+ sites are subsequently reset by trapping photo-released electrons. The pertinent point of the present data is that the luminescent efficiency appears to depend on the final state of the electron through the transport and trapping process. For example, the transitions $\Gamma_5^v \rightarrow \Gamma_5^c$ and $\Gamma_5^v \rightarrow \Gamma_6^c$ having the same initial state but different final states yield widely different luminescent yields. Such dependence is more easily accounted for by the Schön-Klasen than the Lambe-Klick model.

Since the explanation proposed above for the correlation of the spectral distribution of the luminescent excitation spectrum and ultraviolet interband transitions should apply more generally, it will be of interest to extend the measurements to materials involving other luminescent mechanisms such as the alkali halides, magnesium oxide and diamond.

FIGURE CAPTIONS

Fig. 1. Reflection spectrum of hexagonal ZnS. Data were taken at room temperature with unpolarized light.

Fig. 2. Spectral dependance of the photoelectric yield of hexagonal ZnS. The insert shows the foot of the curve expanded by a factor of ten.

Fig. 3. Electronic states of hexagonal ZnS at the center of the Brillouin zone. The zero of energy is taken at the valence band maximum Γ_5.

Fig. 4. Luminescent excitation spectrum of single crystal hexagonal ZnS. The reflection spectrum, in arbitrary units, is included for comparison.

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18. This ratio follows if the momentum matrix element is taken to be nearly constant in the expression for the interband transition probability. The ratio of transition probabilities at E_i and E_j is then

$$P(E_i)/P(E_j) = E_j\rho(E_i)/E_i\rho(E_j)$$

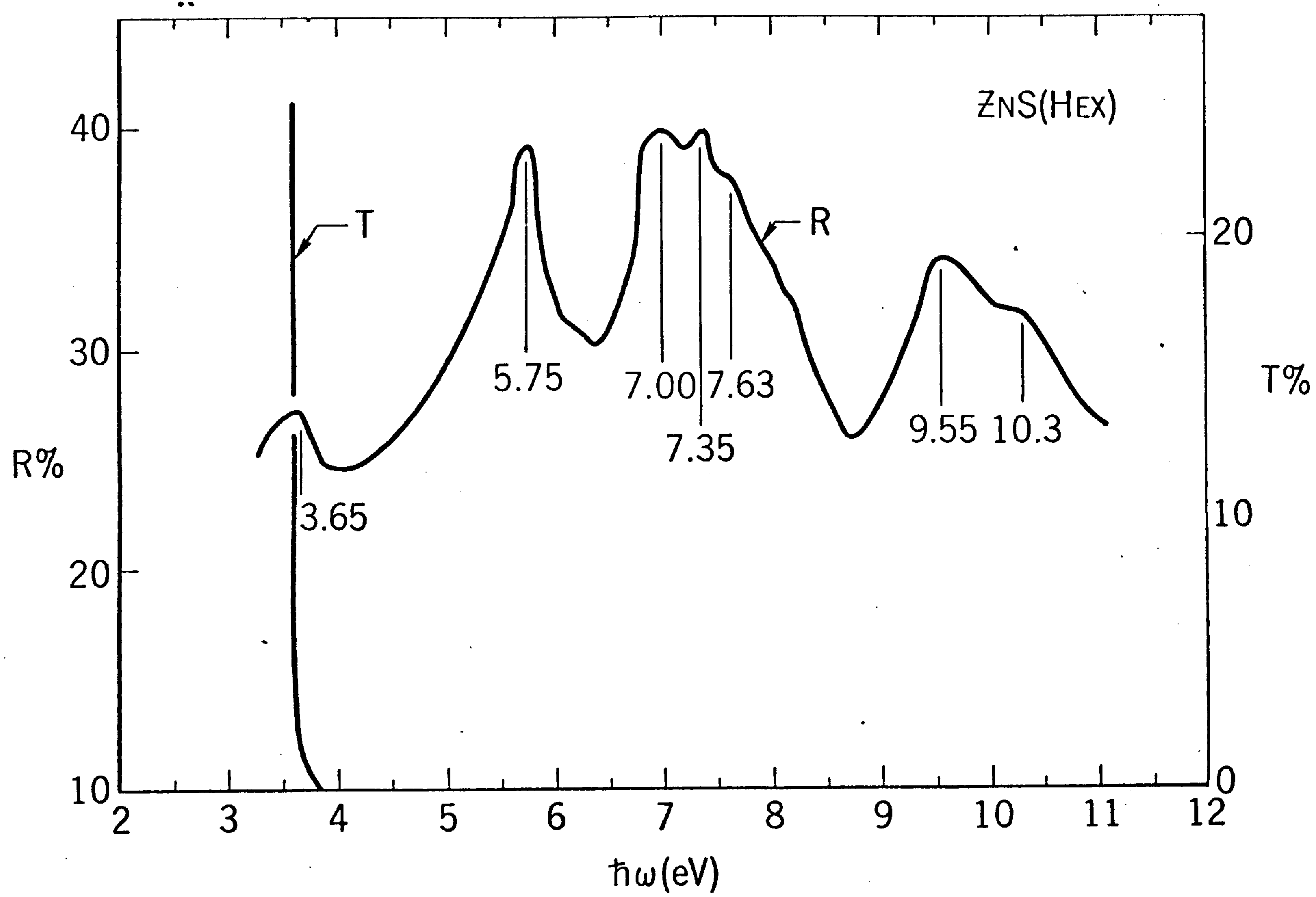
where $\rho(E)$ is the joint density of states. The ratio $\rho(E_i)/\rho(E_j)$ is given by

$E_i{}^2\,\epsilon_2(E_i)/E_j{}^2\epsilon_2(E_j)$ or approximately

$E_i{}^2R(E_i)/E_jR(E_j)$. Combining these expressions we get

$$P(E_i)/P(E_j) = E_iR(E_i)/E_jR(E_j)$$

19. See reference 13, pp. 157-158.


ZnS(HEX)
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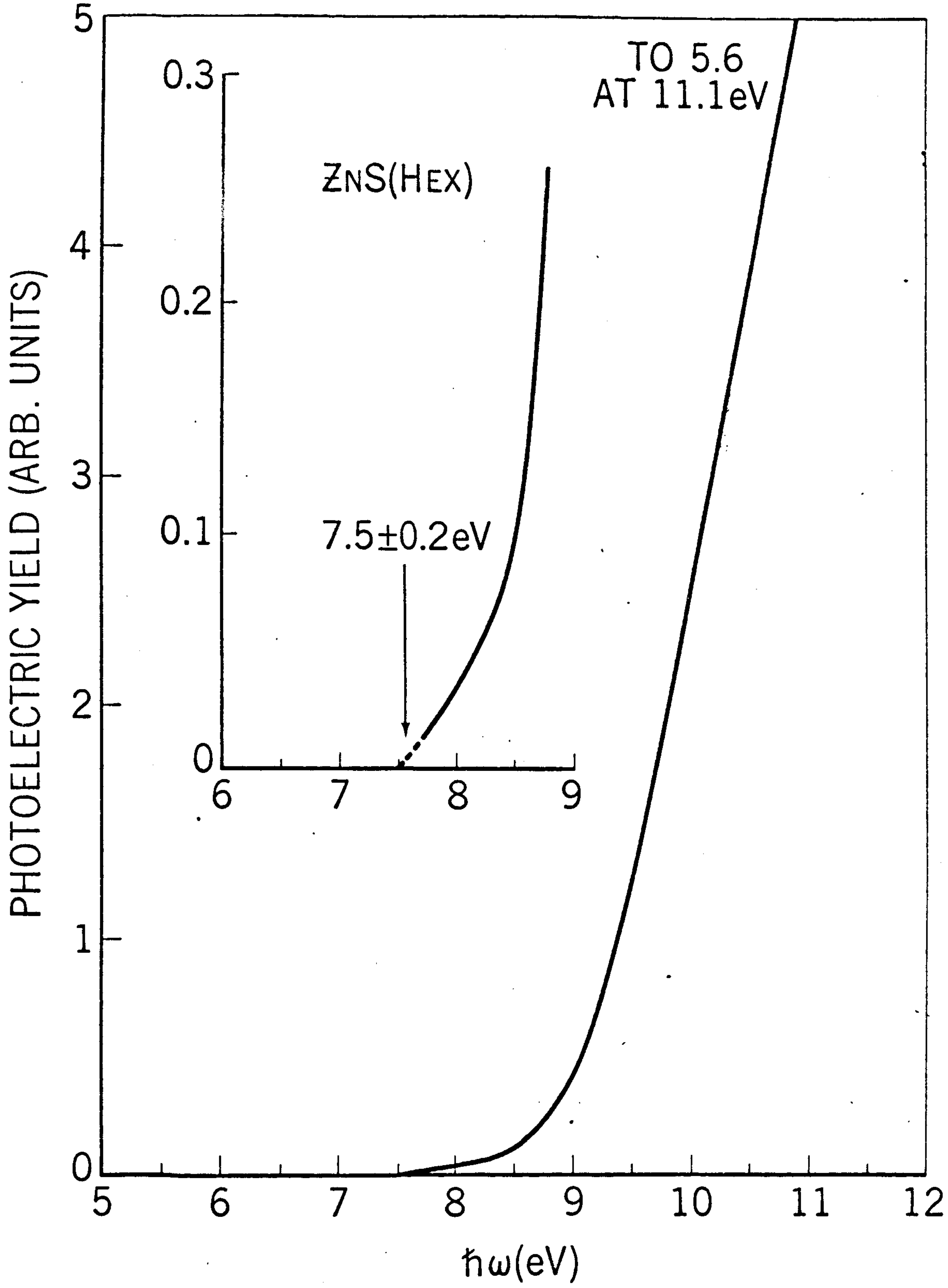
PHOTOELECTRIC YIELD (ARB. UNITS)
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ZnS(Hex)
7.5±0.2eV
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0.2
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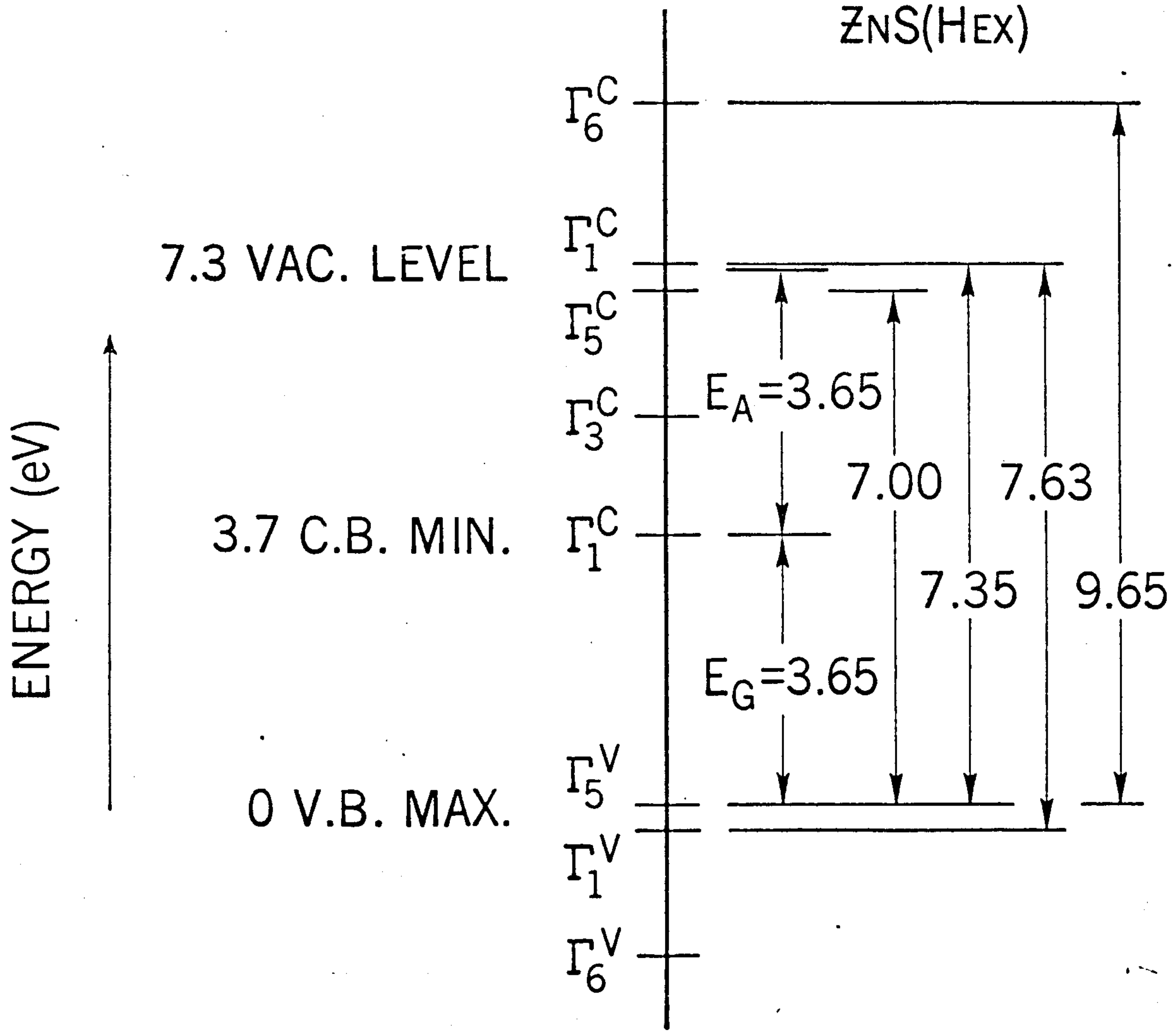
ZnS(Hex)
ENERGY (eV)
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3.7 C.B. MIN.
0 V.B. MAX.
Γ_6^C
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Γ_3^C
Γ_1^C
Γ_5^V
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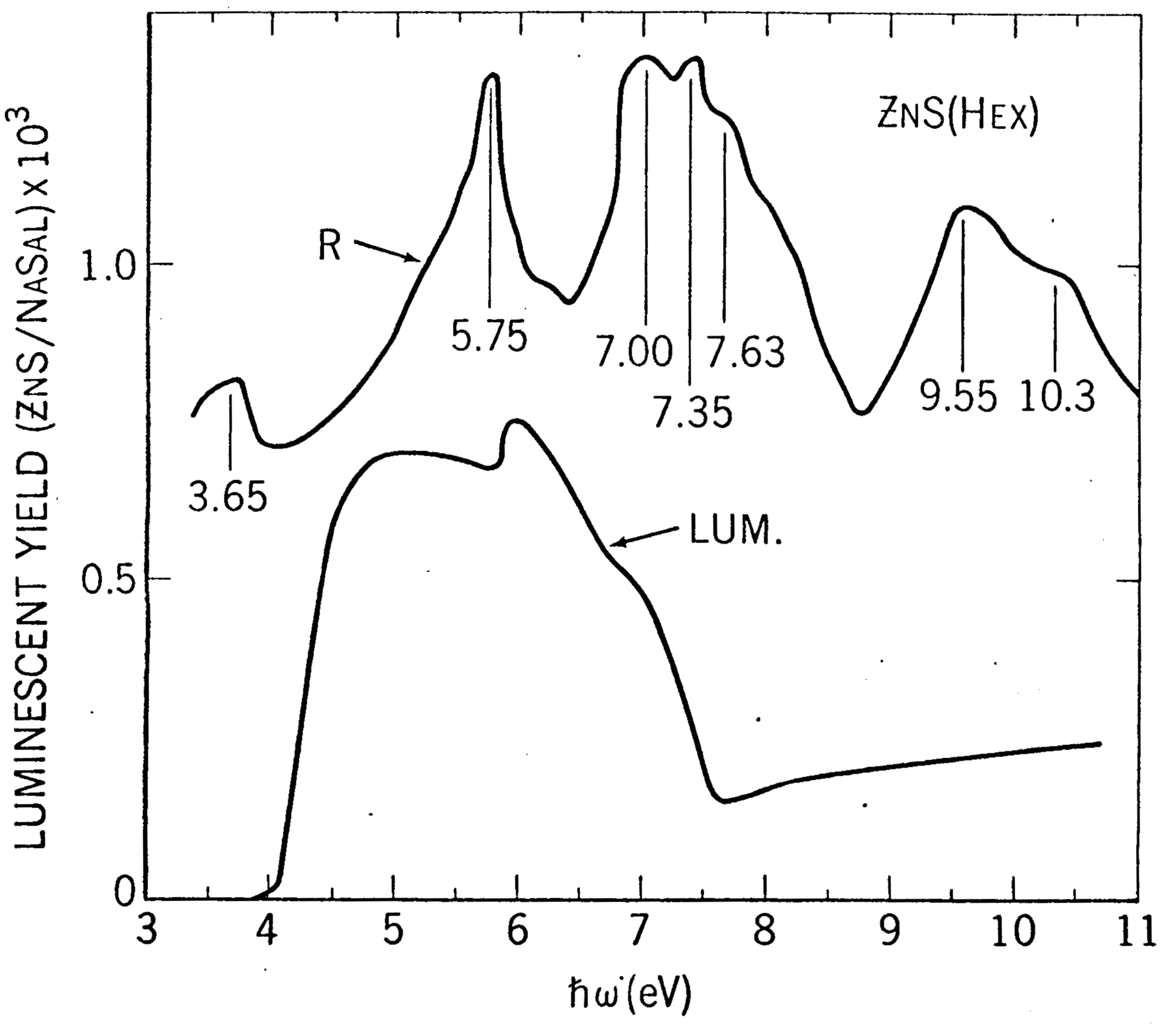
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