stimulated by the production of free holes and corresponds to a level of type *B*.

One may infer then that both levels introduced into CdS by the incorporation of Ag lie close to the conduction band. Furthermore, the work of van Gool shows that both emission bands change wavelength smoothly and continuously as the base lattice is varied in solid solutions going from CdS to ZnS. This could scarcely be the case if the Ag levels were to change from type *B* to type *A* as the solid solution was varied. As a result, it appears that both the 3900A emission band and the usual 4500A emission band in ZnS:Ag also arise from high-lying levels. In summary, then, there is strong evidence that all the emitting levels in CdS:Ag and ZnS:Ag are of the type proposed by Lambe and Klick.

It is tempting to extend these arguments to the case of Cu in sulfides. The similarity of the chemical properties of Ag and Cu and of their emission spectra in the sulfides has led to a general acceptance of the similarity of the energy levels introduced by these materials. Also, the polarization experiments of Birman and Lempicki, as well as those of Halsted and Lambe on electroluminescence, included Cu-activated sulfides. All of this evidence would suggest a general tendency toward levels of the type proposed by Lambe and Klick. However, the complexity of the Cu emission spectra as a function of concentration and the central role occupied by Cu in electroluminescence point to the desirability of having further specific experiments for this case.

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TWO-STAGE OPTICAL EXCITATION IN SULFIDE PHOSPHORS

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The energy absorption and emission processes identified with acceptor impurities such as Cu, Au, and Ag in ZnS-type materials have generally been attributed to electron transitions between the ground state of a luminescent center and excited states near or in the conduction band. Recently, however, optical evidence has indicated that states introduced by the same impurities participate in transitions involving energy levels near or in the valence band.[1,2] The observation of these latter transitions has been advanced as a means of identifying and investigating *p*-type ZnS.[1] The high resistivity of such samples has complicated confirmation of this picture by electrical measurements.[3] This Letter reports optical evidence that clearly demonstrates (1) the existence of both classes of transitions, and (2) the existence of impurity levels common to both classes. Specifically, photons of band gap energy, i.e., "edge emission," can be continuously generated in sulfide phosphors by photons with less than band gap energy. This behavior has been observed in both ZnS and CdS phosphor powders at 80°K. Some results on a CdS sample are described below.

Luminescent grade CdS (General Electric Company) containing no added impurities was fired in a sealed silica tube under approximately 26 atmospheres S_2 pressure at 900°C for one hour. The silica tube was cooled rapidly to room temperature in silicone oil and its contents utilized for the following results. For the data of Fig. 1, approximately 0.10 watt/cm^2 excitation energy was isolated by two Corning No. 2600 filters from a tungsten filament lamp. A 5-cm optical path of $CuSO_4$ solution (100 grams $CuSO_4 \cdot 5H_2O$ per liter of distilled water) was introduced between the sample and monochromator entrance

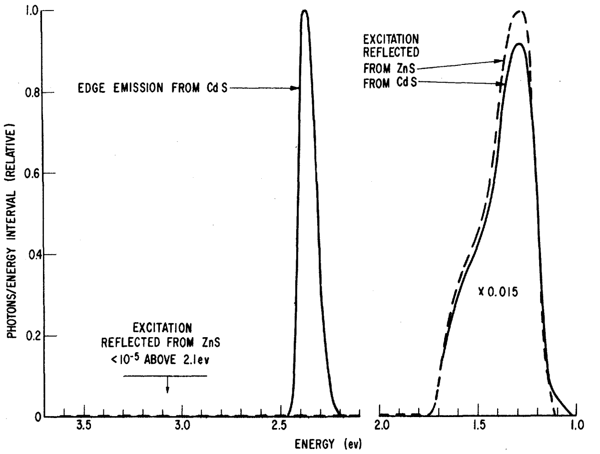

FIG. 1. Radiation emitted and reflected at 80°K by CdS (fired under 26 atmospheres S_2 pressure at 900°C) and by ZnS from an infrared excitation source.

slit to minimize interference from internally scattered long-wavelength radiation. The emission spectrum of the sample for energies greater than 2.1 ev is shown. Also presented is the spectrum of radiation diffusely reflected from the excitation source by a pure ZnS powder in the sample position. The radiation diffusely reflected from a plaque of nonabsorbing powder has the same angular distribution as emission from such a surface. Therefore the absence of stray high-energy source radiation which could excite the CdS edge emission is clearly demonstrated. Infrared emission bands peaking at 1.1, 0.75, and 0.66 ev were also produced by this excitation. The green emission increased as the 1.6 power, the 0.75- and 0.66-ev infrared as the first power of the excitation intensity.

A value of 0.005 was obtained for the efficiency of converting excitation photons, incident from the described source, to observable edge emission photons. This was derived from the relative photon content of the emission and the diffusely reflected excitation radiation. The high reflectance of the CdS sample for radiation in the excitation region as shown in Fig. 1 indicates an internal efficiency in excess of 0.05 for the generation of edge emission photons from absorbed incident photons.

The high sulfur pressure firing treatment has previously been found to yield ZnS:Cu and CdS:Cu phosphors in which a structured infrared emission band is readily generated by long-wavelength excitation.[4] This and related behavior has been interpreted as resulting from transitions between the valence band and Cu impurity levels normally occupied by holes.[1] The existence of optical transitions terminating in the valence band is clearly demonstrated by the present results. The production of 2.4-ev photons at 80°K in CdS by photons not exceeding 1.75 ev in energy requires a two-stage excitation process with transitions terminating in both valence and conduction bands. The previously cited dependence on excitation intensity supports this fact. For a continuous process an impurity configuration common to both transitions is required. The excitation and infrared emission characteristics are consistent with the impurity level position previously attributed to Cu. The observation that this behavior is favored in *p*-type sulfide samples is understandable in terms of a short relaxation time for transitions from the valence band.

The results further provide an excitation mechanism for such phenomena as photoconductivity generated by radiative energy transfer in CdS[5] and the photovoltaic effect in CdS produced by photons of less than band gap energy.[6] They also provide a mechanism whereby the production of many infrared photons can be controlled by a few photons of higher energy.[1,7]

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