where u_1 and u_2 are the velocities of first and second sound. At all temperatures the term in u_2^2 is small compared with the term in u_1^2 and so the attenuation per wavelength is never large. To an accuracy of better than 1%, the velocity of fourth sound is

$$u_4 \sim \left(\frac{\rho_s}{\rho}\right)^{\frac{1}{2}} u_1. \qquad (25)$$

The amplitude of the temperature oscillation is given by

$$\frac{T_0}{T} = -\frac{S}{C}\left(1 - i\frac{2\chi}{\rho\omega dC}\right)^{-1}\frac{\rho_0}{\rho}. \qquad (26)$$

At high frequencies, the term involving χ can be neglected and the temperature oscillation is a first-order effect as well as the density oscillation. At low frequencies, however, there is plenty of time for the heat to escape to the wall and the fractional change in temperature is small compared with the fractional change in density. The amplitude of the oscillating part of the superfluid velocity is given by

$$v_0/u_4 = \rho_0/\rho_s. \qquad (27)$$

Presumably fourth sound is strongly attenuated when v_0 exceeds the critical velocity for superflow through the channel. The critical velocity is much smaller than u_4 (except possibly in the immediate vicinity of the λ point) and so this interesting effect should occur for quite small fractional changes in density.*

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* *Note added in proof.*—Dr. R. H. Walmsley has pointed out that, in Eqs. (23) and (26), S should be replaced by $(S - \alpha u_1^2)$, where α is the isobaric coefficient of expansion. $(1 - \alpha u_1^2/S)$ is 1.6 at 2°K, 0 near 1.1°K, −12.5 at 0.8°K, and −7 near 0°K. Equation (25) therefore remains a good approximation. The temperature amplitude T_0 of Eq. (26) is somewhat modified. It is slightly increased above 1.1°K, becomes zero near 1.1°K, and changes phase with an increased magnitude below 1.1°K.

Some Properties of Green and Red-Green Luminescing CdS

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A series of electro-optical experiments at room temperature have been made with two types of high-purity single crystals of CdS. Those of type A, believed to have near-perfect stoichiometry, luminesce green (5145 A) under 3650 A ultraviolet irradiation, have low dark conductivity (2.5×10^{-11} mho cm^{-1} at 300°K), exhibit no photopeak, and have a relatively short carrier lifetime (about 4 microseconds or less). Those of type B, believed to have a sulfur deficiency, luminesce first strongly red ($\cong 7200$ A), then strongly green (> 5145 A) as the exciting radiation is increased in intensity. Simultaneously both emissions shift toward longer wavelengths. Also, as the red emission intensity begins to saturate, the intensity-rate change of conductivity abruptly changes. It is suggested that red luminescence is the result of a free hole capture by one of the electrons residing in a sulfur vacancy. This trapping sensitizes the crystal but at the expense of increasing carrier lifetime to millisecond magnitudes. Furthermore, some of these vacancies (~ 0.4 ev below the conduction band) act as donors to increase dark conductivity (about 10^{-9} mho cm^{-1} at 300°K).

1. INTRODUCTION

E VER since Lorenz[1] first grew synthetic single crystals of CdS, much has been written in the literature concerning this material's electro-optical properties.[2] One notes, however, that mention has rarely been made concerning green emission of a wavelength corresponding to direct recombination of free holes and electrons. Though green of a type has been analyzed by a few observers,[3,4] such emissions appeared only when the crystals were cooled to low temperatures. Others[5,6] have shown that green electroluminescence can occur with voltage potentials approaching breakdown but the color has been sporadic and not too intense. In view of the notable lack of green emission from the crystals used by various researchers, some doubt arises as to the purity and stoichiometry of their samples and, hence, the accuracy of the data as truly representing intrinsic CdS.

Recently, the authors have been able to grow small quantities of spectrographically "pure" CdS crystals that show photoconductivity and luminescing properties related to what is believed to be a deficiency of sulfur.[7] One class of these crystals, believed to be intrinsic CdS, is identified by its green-only luminescence at room temperature. A second class luminesces both red and

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[2] For review articles with excellent bibliographies, see R. H. Bube, Proc. Inst. Radio Engrs. 43, 1836 (1955); A. Rose, Proc. Inst. Radio Engrs. 43, 1850 (1955).
[3] L. R. Furlong, Phys. Rev. 95, 1086 (1954).
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green in different proportions. This paper describes some properties of these two types of crystals, and interprets their behavior from a sulfur vacancy viewpoint.

2. CRYSTAL GROWTH, SELECTION, AND PREPARATION

The data in this paper have been obtained with crystals grown by a variation[8] of the method first described by Czyzak et al.[9] This method inherently refines the charge each time crystals are grown, so that by successively growing and pulverizing the crystals it becomes possible to eventually obtain specimens having relatively high purity. Furthermore, by controlling the temperature, the temperature gradient at which growth occurs, and the gas composition and pressure in the growing chamber, the crystals can be made to vary in natural appearance and in their luminescing qualities. As these differences between crystals are reproducible and not correlatable with residual impurities (when detected), they are attributed by the authors to deviations from stoichiometry.

The single crystals employed were selected on the basis of their luminescing behavior under excitation with 3650 A ultraviolet light. In general, those crystals which would luminesce emitted light either green, or first red then green as the intensity of the ultraviolet increased to its maximum of about 6 milliwatt/cm². The crystals designated in this paper as of "type A" typify those which luminesce green only, while crystals of "type B" luminesce red and then green.

Care was taken not to contaminate the crystals after it was noted that the luminescing properties could be modified by such things as water, heat, hydrocarbons, and common solvents. A consequence of this was that electrical contacts to the crystals had to be made so that bulk and surface conditions would remain undisturbed. Soldered and plated indium contacts were thus rejected, and silver paint was determined unsuitable since it formed a photovoltaic junction. Carbon ("Dag"
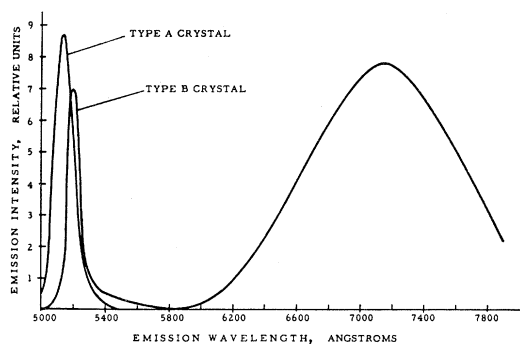

Fig. 1. Emitted luminescence from crystals of types A and B excited with 3650 A ultraviolet at an irradiance level of 2.2 milliwatts/cm².

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[8] D. R. Boyd and Y. T. Sihvonen, J. Appl. Phys. **30**, 176 (1959).
[9] Czyzak, Craig, McCain, and Reynolds, J. Appl. Phys. **23**, 932 (1952).
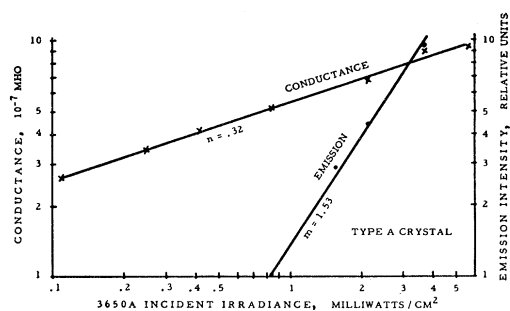

Fig. 2. Type A crystals luminesce green with increasing intensity as the ultraviolet exciting intensity increases and show no break in conductance. The slopes n and m pertain to the exponent of the irradiance associated respectively with conductance and emission.

dispersion No. 194) contacts, however, were found to be adequate and were used for all the conductivity tests.

3. CRYSTAL PROPERTIES

(a) Luminescence

To determine the luminescing qualities of the crystals of types A and B, a Bausch & Lomb 1-meter dual-grating monochromator was utilized as a spectrometer having a resolution of 15.5 A/mm. The crystal was placed directly on the entrance slit and illuminated with a Shannon model 107 ultraviolet lamp. A Corning 7–37 filter interposed between lamp and crystal removed long wavelength components from the radiation, and a Corning 3–73 filter positioned behind the slit removed ultraviolet components that passed through the crystal. Eastman Kodak type I-L spectrographic plates registered the light emitted. Emulsion darkening was read by a recording microphotometer and converted into incident light intensity by routine spectrographic techniques. Ultraviolet irradiance was measured by a CdS crystal embedded in a blue-green fluorescing plastic. The photoconductance of this detector was calibrated against a standard thermopile.

Typical intensity records of the red and green luminescence are shown in Fig. 1. Type A crystals emit a narrow band of green light with a peak at 5145 A. Type B luminesce both a narrow green band having a peak always at a longer wavelength than type A crystals, a broad red band having its peak around 7200 A. The mechanism for red and green emission has been dealt with in a recent paper[7] which ties red emission to the trapping of a free hole by a sulfur vacancy containing two electrons, and the green emission to direct recombination of free carriers. By this model, the wavelength differences between the two green peaks can be attributed to the perturbing influence of the sulfur vacancies in the type B crystal on nearest Cd and S neighbors.

As the ultraviolet intensity is varied, the green emission from type A crystals changes intensity by an amount proportional to a greater-than-unity power of the ultraviolet intensity as seen in Fig. 2, and there is no detecta-
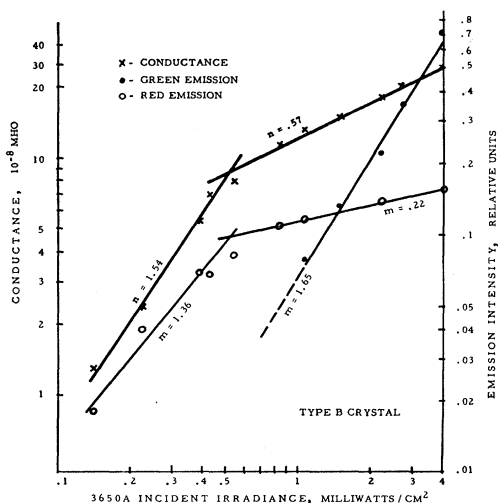
FIG. 3. Type B crystals luminesce strongly red first, and then strongly green as the red-producing centers saturate. Conductance breaks sharply at saturation, with the break-over point occuring at different ultraviolet irradiances depending on the sulfur vacancy density.

ble wavelength shift of the peak. Contrasted with this, the two emissions from type B crystals vary in a more complex manner. First, as seen in Fig. 3, the red emission dominates the green at low ultraviolet irradiance, but eventually the green emission dominates as the ultraviolet intensity is increased. Secondly, both red and green peaks shift toward longer wavelengths with increasing ultraviolet intensity. This shift is shown in Fig. 4.

Extending the aforementioned model to explain the parallel shift of the two luminescing peaks, one can conclude that as holes are trapped by the vacancies, the forbidden gap narrows by the process of the valence band moving toward a fixed S-vacancy level and fixed conduction band. It is believed that this narrowing results from the four nearest cations (Cd^{++}) moving away and the 12 nearest anions (S^{--}) moving toward each singly ionized vacancy. The type A CdS shows no shift since there are no S vacancies.
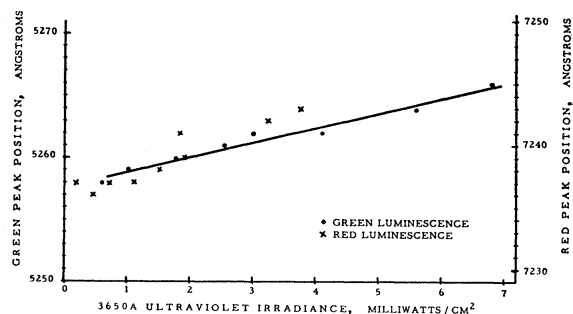

FIG. 4. Type B crystals show a shift toward longer wavelengths for both the red and green peaks that is not present in type A.

(b) Photocurrent

In the absence of light, type B crystals have conductivities that always exceed the dark conductivity of type A, and which are related to the crystals' tendency to luminesce red. If the extent and shape of the red luminescence distribution is taken as a measure of the energy distribution of the electrons residing in the nonionized sulfur vacancies, then these conductivity differences are a natural consequence of some of the vacancy sites acting as donors at room temperature. In Fig. 1, for example, the red luminescence base extends from about 6200 to 8200 A implying that vacancy electrons extend to within 0.4 ev of the conduction band.

The conductance as a function of irradiance has also been plotted in Figs. 2 and 3. Type A crystal conductances vary as some fractional power of the ultraviolet intensity, the exponent usually ranging between 0.3 and
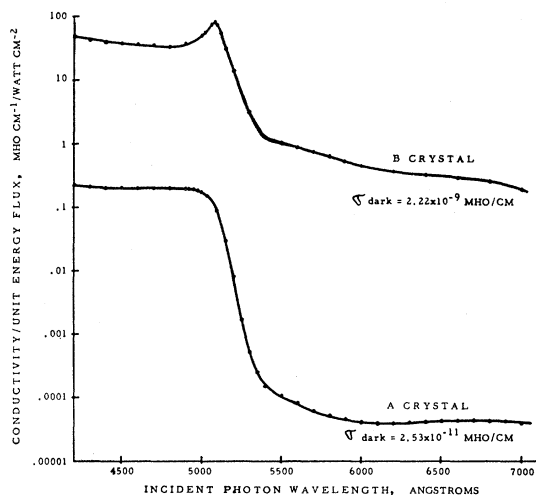

FIG. 5. Photoconductivity as a function of photon wavelength. No photopeak occurs for type A.

0.5. The exponent for type B crystals is generally greater than one until the red-producing centers begin to show saturating effects, after which n becomes less than one. The similarity between the conductance and red luminescence break over points implies that the same centers are responsible for both effects. At higher ultraviolet intensities and after saturation of the vacancies, the green luminescence and the conductance in the type B crystal behave very much like type A as regards the exponents m and n. A simple calculation shows that the break over point in the crystal used for the data of Fig. 3 occurred at a photon arrival rate of 1.1×10^{15} photons/sec cm^2. If each photon is assumed to generate one free hole having a lifetime 10^{-6} second that is subsequently trapped by a sulfur vacancy, it follows that the number of sulfur vacancies is of the order of 10^{11} per cm^3.

Another important conductivity difference exists between the two types of crystals. This difference is shown

in Fig. 5 wherein conductivity has been plotted as a function of incident photon wavelength. Type B crystals possess the well known photopeak that occurs at about 5080 A and also exhibit considerable conductivity out to 7000 A. Type A crystals have less conductivity at 5000 A by two orders of magnitude, and show no photopeak. Whether or not a photopeak really exists is difficult to determine since the crystal begins to luminesce at the absorption edge and thereby self-excites free carriers. From intuitive considerations one would not expect a photopeak to occur in pure and stoichiometrically perfect CdS.

Quantum yields for typical A and B crystals were determined to be 0.2 at 4960 A and 62 at 5080 A, respectively, using an applied potential of 9.1 volts and electrode spacings on the order of 1 mm. The calculations were made from the derived relation

$$Q.Y. = \tau/T_r = KEa\epsilon\Delta\sigma/e l(1 - e^{-ua})\Delta W,$$

where τ = carrier mean life (sec), T_r = carrier transit time (sec), K = a constant = 1.6×10^{-19} (watt sec/electron volt), E = electric field intensity (volt cm^{-1}), a = crystal thickness (cm), ϵ = forbidden band gap width (electron volts), e = carrier charge (coulombs), l = electrode spacing (cm), u = linear absorption coefficient (cm^{-1}), and $\Delta\sigma$ = change in conductivity (mho cm^{-1}), induced by ΔW = change in energy influx (watts/cm^2).

Both determined quantum yields are considerably less than the value commonly associated with CdS. However, a closer spacing of electrodes and/or higher fields on the type B crystals give the high quantum yields usually reported, that is, on the order of (6 to 10)$\times10^3$, but only 40 for the type A.

(c) Frequency Response

As would be expected from phenomenological considerations, the response of type A crystals to variations in light intensity is many orders of magnitude faster than type B. Figure 6 depicts the relative responses to bursts of white light passed by a revolving toothed wheel. The signal was developed across a 0.1-megohm resistor in series with the crystal and a 45-volt battery, and monitored with a Tektronix oscilloscope. The type B crystal response falls off rapidly (in this case 1.5 db per octave), while type A shows a surprising rise to a level at 11 600 pps 12% above the signal level produced when the light is not interrupted. This apparent gain is not understood, but has always been present in type A crystals. Included in this figure, to point out the slowing down effect of additional vacancies, is the frequency response of a crystal selected because it intensely luminesced red only and could not be made to show significant green luminescence with the ultraviolet source employed. This one falls off 6 db per octave. The
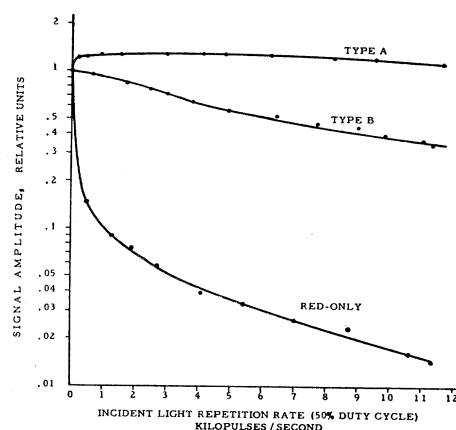

Fig. 6. Frequency response characteristics of crystals of types A and B as determined by a rotating shutter. The inclusion of sulfur vacancies reduces the ability of CdS to follow rapid light changes. The red-only curve pertains to a crystal with even more vacancies than the type B.

responses of other CdS crystals differing in their proportions of red and green luminescence fall uniquely between the green-only and red-only curves.

The ability of the type A crystal to follow the cutting off of the light beam by the shutter made it difficult to accurately determine carrier lifetime by this method. However, making a correction for cutoff time, it is estimated that the mean life is approximately 4 microseconds, as compared with a mean life of 6 milliseconds for the type B crystal of Fig. 6, and 30 milliseconds for the red-only luminescing crystal with its relatively large number of sulfur vacancies.

4. CONCLUDING REMARKS

The properties of green-only luminescing crystals were obtained on small plates 2$\times$5$\times$0.05 mm thick. Successful growth of larger perfect crystals has not been attained, though efforts are being made in this direction by the authors. So far, pure but stoichiometrically imperfect single crystals as large as 28 grams have been synthesized which do not, however, show appreciable green luminescence until excitation energy fluxes reach the very high intensities obtainable with electron beams.[10] At lower excitation energies, these larger specimens exhibit either red luminescence indicating sulfur vacancies, or no luminescence, indicating the presence of nonradiative recombination centers not correlatable with detectable residual impurities. Such centers may arise from complex groupings of sulfur and/or cadmium vacancies.[11,12]

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