

represents an interesting class of ferroelectrics because of the following features:

(a) Chemical composition: they are the first ferroelectrics containing mercury and halogens.

(b) Temperature independence of the dielectric constant.

(c) The polarization does not decrease with temperature.

(d) Unusual switching behavior.

The difficulties in growing large, perfect crystals and the slow switching time, however, are serious limitations for technical applications.

Edge Emission in CdS Crystals that Show Mechanically Excited Emission

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The characteristic green fluorescence of CdS single crystals that exhibit mechanically excited emission has been examined spectroscopically at 4.2° and 77°K. The fluorescence of the crystals was stimulated by either ultraviolet irradiation, or the application of an electric field. The uv-stimulated and field-induced emission spectra are compared and discussed. The low-temperature behavior of the conductivity (storage properties) in these crystals is also discussed. The uv-stimulated edge emission peaks in these crystals differ from those in normal CdS; these differences are discussed and quantitative comparisons are made. A simple trapping model is applied to the uv-stimulated emission data at 77°K. On the basis of this model, the mean number of optical phonons cooperating in the optical transitions is shown to be higher than in normal CdS. The field emission, believed to be due to carrier injection, is explained on the basis of a previously proposed energy model of Warschauer and Reynolds for mechanically excited emission.

I. INTRODUCTION

THE phenomenon of mechanically excited emission is one in which radiative emission is obtained by mechanical excitation of optically or thermally stimulated CdS crystals. It has been previously shown by Warschauer and Reynolds¹ that selected cadmium sulfide crystals, cooled to 77°K and then stimulated with light, will respond to mechanical excitation; moreover, it has been determined that the threshold

for the stimulating radiation is 6900 Å. After stimulation, the crystal is completely shielded from light. If the crystal is now tapped in the dark in the direction of the *c* axis, one finds that a green flash of light is emitted from the body of the crystal. From a reasonably well stimulated crystal, several hundred flashes at the rate of one flash per tap can be obtained. It has also been determined that ultraviolet or visible light is not necessary for stimulation of the crystal. In fact, thermal background radiation is of sufficient intensity in the proper wavelength range to stimulate the crystal. It has further been shown that a crystal of this type, cooled to 77°K, then warmed in total darkness to approximately 200°K, with subsequent immersion in liquid nitrogen, will show flashes of the green edge emission when mechanically tapped. However, the emission is completely exhausted after only a few taps.

These CdS crystals, hereafter referred to as "tap-effect" crystals, as distinguished from "normal" or "ordinary" CdS crystals, also show storage properties. A given crystal at 77°K may increase in conductivity by as much as eleven orders of magnitude when exposed to the stimulating radiation. If the stimulating radiation is removed, the conductivity remains high and will remain so indefinitely. During stimulation, the conductivity increases slowly to a relatively high level after which it is observed to hold constant (in the dark at 77°K) for periods as long as 66 hr. Figure 1 shows how the storage varies as a function of temperature. Here current through the crystal is plotted as a func-

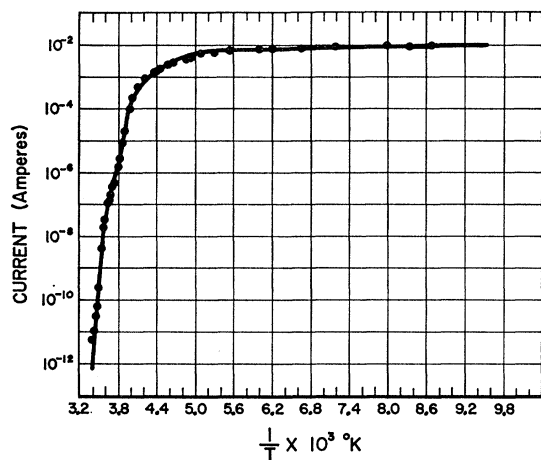


FIG. 1. Current through a "tap-effect" CdS crystal vs $10^3/T$. The temperature ranged from 115°K to 300°K.

¹ D. M. Warschauer and D. C. Reynolds, J. Phys. Chem. Solids 13, 251 (1960).

tion of reciprocal temperature as the sample is warmed from 77°K. With the crystal at 77°K in the unstimulated state, the current is quite low; after exposure to the stimulating radiation, it increases from 10^{-12} to 10^{-2} amp. The current decays slowly until the crystal reaches approximately 200°K, after which it begins to decrease rapidly.

The experiments reported were here undertaken primarily to investigate spectroscopically the electric-field-induced and uv-stimulated edge emission in "tap-effect" CdS crystals. It was felt that field-induced emission might show line structure, and, if so, that the emission peaks might be significantly different, say, in relative intensity, wavelength, width, etc., from those in normal CdS. The nature of both the uv-stimulated and field-induced emission spectra at 77° and 4.2°K might lead to a better understanding of the stimulation and emission mechanisms in "tap-effect" CdS, including, perhaps, a possible explanation of how the mechanical excitation is energetically coupled to the optical transitions. It is the purpose of this paper to report the new emission data, make some quantitative comparisons between "tap-

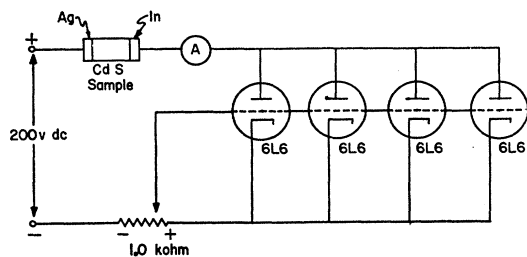


Fig. 2. Current limiter circuit diagram. The 6L6 screen grids, not shown, are commonly connected to B^+ .

effect" and "normal" CdS emission data, and propose an interpretation of these data in terms of a previously proposed energy model.¹

II. EXPERIMENTAL ARRANGEMENT

The single crystals used in these investigations were grown from the vapor phase by a method due to Greene *et al.*² Parallel opposing faces (for application of electrodes) were ground on some of the crystals, while other samples were selected with nearly parallel and fairly regular as-grown or cleaved faces. Each of the crystal samples was etched in boiling HCl (concentrated), washed, and thoroughly dried. Finally, an indium electrode and a silver electrode were applied to the freshly etched surfaces of the crystal. Indium solder (Indalloy No. 1) was used for the indium electrodes and was applied to the pre-heated samples with a 25-w Sonobond ultrasonic soldering gun. The silver electrodes were formed from Silver Print circuit paint which was brushed onto the crystal surface and allowed to air-dry for at least 30 minutes.

² L. C. Greene, D. C. Reynolds, S. J. Czyzak, and W. M. Baker, J. Chem. Phys. 29, 1375 (1958).

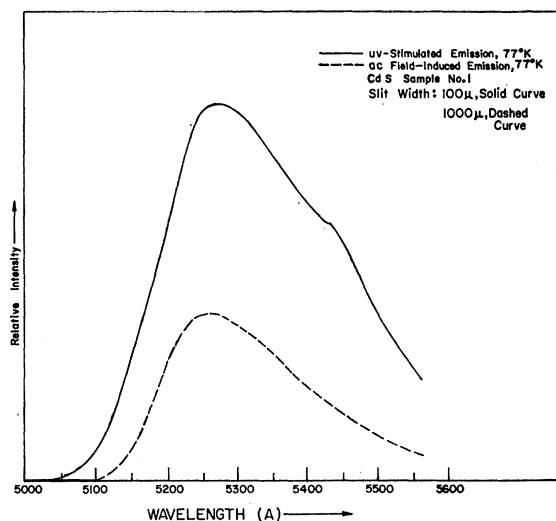


Fig. 3. Emission spectra of a "tap-effect" CdS crystal at 77°K (sample No. 1). The higher intensity spectrum is the ultraviolet-stimulated emission and the lower curve is the emission induced by an ac electric field.

The crystals were cooled by immersion in either liquid nitrogen (77°K) or liquid helium (4.2°K). The smaller crystals were glued with rubber cement to the end of a glass rod and placed in the Dewar, while the larger samples were simply placed on a piece of Styrofoam wedged in the Dewar tip.

Both dry-cell batteries and a dc power supply were used to supply dc potential for the field-induced emission, while ac voltage was supplied by either a Variac or a variable-frequency power supply. Control of the current through the sample at 4.2°K was accomplished with the vacuum tube current limiter shown in Fig. 2. For uv-stimulated emission spectra, the crystals were

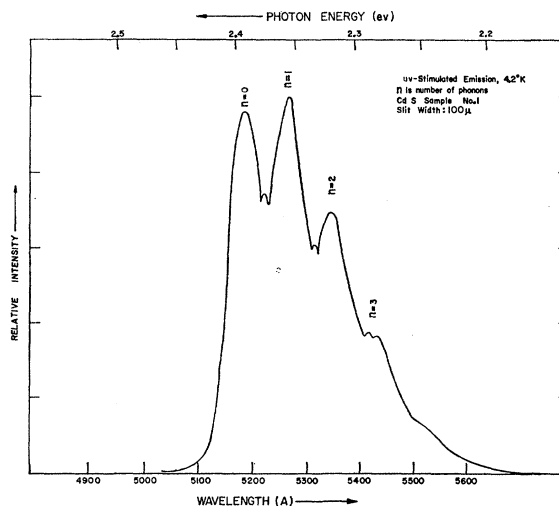


Fig. 4. "Tap-effect" CdS emission spectrum. Sample No. 1 at 4.2°K. n is the number of longitudinal optical phonons participating in a transition.

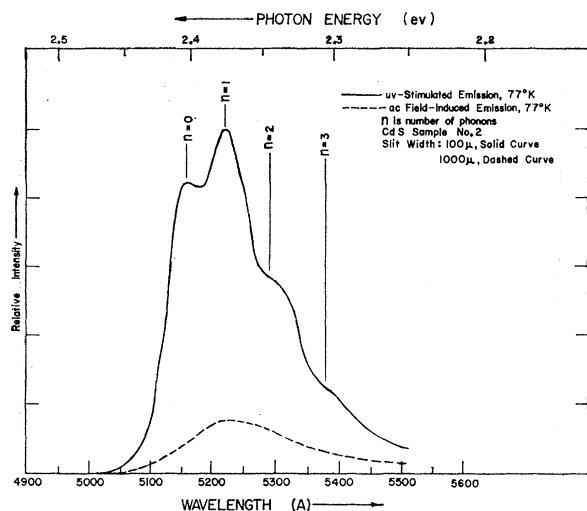


FIG. 5. Emission spectra of "tap-effect" CdS. Sample No. 2 at 77°K. The solid and dashed curves are, respectively, the uv-stimulated and field-induced emission.

irradiated with an H100-SP4 G.E. mercury lamp equipped with a No. 41 Kopp filter.

The fluorescence from the crystals was focused on the entrance slit of a $\frac{1}{2}$ -meter, $f/4.4$, Bausch & Lomb grating monochromator, equipped with a 1200 lines/mm (10 cm \times 10 cm) grating blazed to 3000 Å, giving a linear dispersion of 16 Å/mm in first order. The monochromator was equipped with a 1P28 photomultiplier detector.

III. EXPERIMENTAL RESULTS

We have recently found that a cooled "tap-effect" CdS crystal, to which one silver and one indium electrode has been applied, shows green emission in the stimulated state when an ac or dc electric field is applied to the electrodes. As nearly as could be ascertained, the emission intensity was largely frequency independent.³ When the crystal was cooled to 77°K in the dark, fields of the order of several thousand volts/cm could be applied without producing an observable emission. When the sample was stimulated with radiation of the proper wavelength, however, fields of the order of 10 volts/cm produced a relatively intense green emission.

The field-induced emission covers the same spectral range as the uv-stimulated fluorescence in a given crystal. Figure 3 shows both the uv-stimulated and the field-induced emission spectra for a crystal (sample No. 1) at 77°K. This particular crystal did not show line structure in its uv-stimulated spectrum, but rather a broad continuum. The intensity of the uv-stimulated fluorescence is at least two orders of magnitude greater than that induced by the electric field, although this is not obvious from the data. The monochromator slits were set at approximately 1000 μ while recording the

field emission spectrum and were reduced to about 100 μ for the uv-stimulated emission. The spectrum of the uv-stimulated fluorescence from sample No. 1, cooled to 4.2°K, is shown in Fig. 4. At this temperature, line structure is observed in the crystal emission; moreover, the emission spectrum is quite similar to that observed in the edge emission of normal CdS, except that the first peak is not the most intense of the series. Also, not unlike the normal edge emission spectrum of CdS, a second series of less intense lines are observed between the principal peaks. This second series of lines make up the primary transitions at liquid nitrogen temperature, as has been shown by Reynolds and Pedrotti.⁴

The uv-stimulated emission spectra for a crystal that does show line-structure in its emission at 77°K is shown in Fig. 5. The field-induced emission, also shown in Fig. 5, apparently does not possess line structure. However, structure may have been present even though it was not resolved, since the lower intensity of the emission made it necessary to use wide monochromator slits with consequent loss of spectral resolution. As is usually observed in normal CdS, a comparison of Figs. 4 and 5 reveals that the emission peaks of a "tap-effect" crystal are sharper and better resolved at 4.2° than at 77°K.

With a simple arrangement, where the potential was applied directly to the sample electrodes, several attempts to record the field-induced emission spectra from two "tap-effect" crystals at 4.2°K proved unsuccessful. The principal difficulty was an apparent "avalanche effect" in the conductivity which occurred when the electric field was increased to a value high enough to induce an emission of measurable intensity. The conductivity increased so rapidly that excessive current was drawn through the crystal with subsequent destruction of the electrodes and rapid decay of the emission. When the measurements were repeated with the arrangement shown in Fig. 2, the current could be stabilized to a pre-set value; it was then possible to

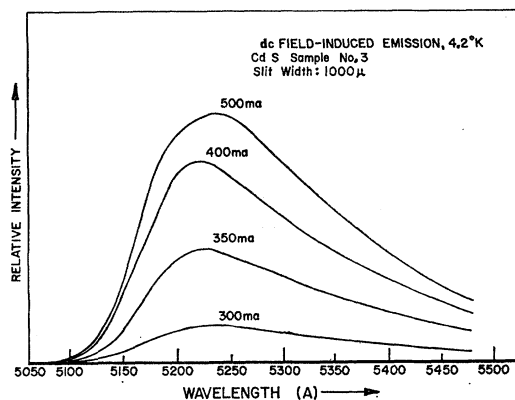


FIG. 6. Field-induced emission from sample No. 3 at 4.2°K. Currents through the crystal range from 300 to 500 ma.

³ In some samples, it was found that increasing the frequency of the applied ac potential resulted in a very slight increase in the emission intensity.

⁴ L. S. Pedrotti and D. C. Reynolds, Phys. Rev. **119**, 1897 (1960).

obtain field-induced emission at 4.2°K of sufficient intensity and duration to permit spectral recording. Several spectra of sample No. 3, for currents ranging from 300 to 500 ma, are shown in Fig. 6. The intensity of the emission increased with increasing current, but line structure was not observed. The field-induced emission from sample No. 3 at 77°K showed no evidence of line structure either. The spectra, for several crystal currents, are shown in Fig. 7. The emitted intensity increased until a current of approximately 500 ma was reached; further increase in current produced very little increase in intensity.

For comparative purposes, the uv-stimulated fluorescence of sample No. 3 was observed. The spectra at 77°K and 4.2°K are given in Figs. 8 and 9, respectively. An inspection of the emission from this crystal reveals that it is quite similar to that of crystal No. 1 (shown in

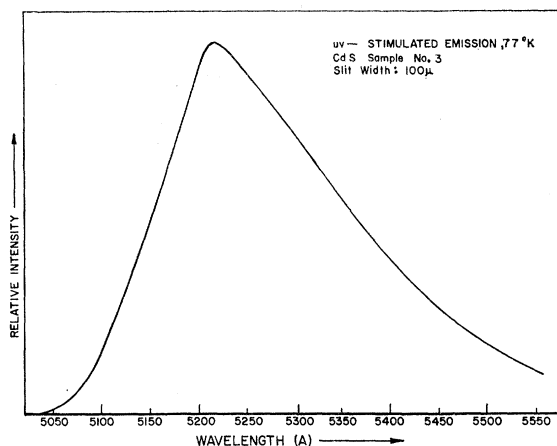


FIG. 8. Ultraviolet stimulated emission from sample No. 3 at 77°K.

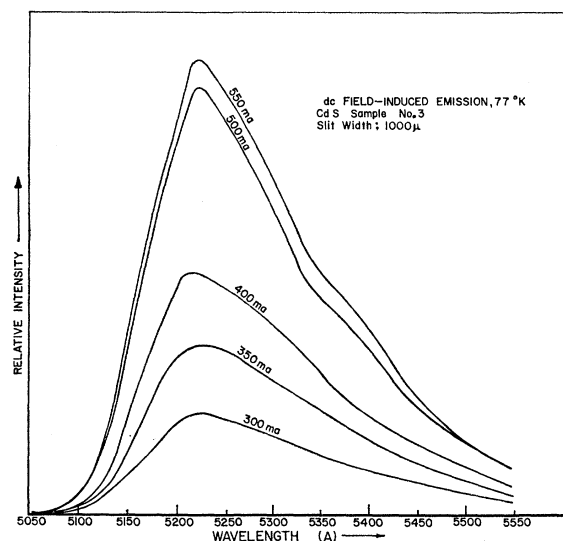


FIG. 7. Field-induced emission from sample No. 3 at 77°K. Currents through the crystal range from 300 to 550 ma.

Figs. 3 and 4). In particular, the spectral distribution of the emission at 77°K is very broad, peaking at about 5215 Å, while the fluorescence at 4.2°K shows the characteristic spectrum of "tap-effect" CdS.

IV. DISCUSSION AND CONCLUSIONS

A. Ultraviolet-Stimulated Fluorescence

Green edge emission in normal CdS is composed of a series of emission lines or peaks which are located on the long-wavelength side of the fundamental absorption edge.⁵ The first of these peaks (the primary or no-phonon transition) appears at approximately 0.14 eV from the absorption edge (at 77°K) and one usually attributes it to either of two possible recombination-

radiation mechanisms.⁶⁻¹⁰ It has previously been shown that the center responsible for green edge emission in CdS at 77°K is due to the sulfur interstitial atom.¹¹ The first peak is followed, at successively longer wavelengths, by a series of equally spaced peaks, each of which is less intense than its predecessor; successive peaks are separated by approximately 0.04 eV, the longitudinal optical phonon energy.^{12,13} On the basis of this evidence, the primary transition is said to be accompanied by phonon cooperation. It is important to note that the first or zero-phonon peak is always the most intense in spectra of crystals that do not show mechanically excited emission. It should also be empha-

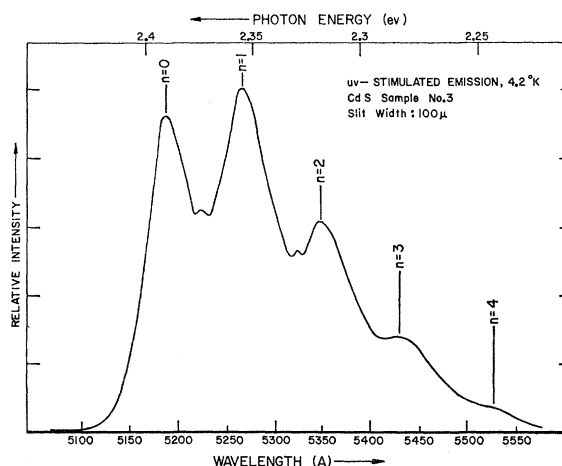


FIG. 9. Ultraviolet-stimulated emission from sample No. 3 at 4.2°K.

⁶ C. C. Klick, Phys. Rev. **89**, 274 (1953).

⁷ J. Lambe and C. C. Klick, Phys. Rev. **98**, 909 (1955).

⁸ J. Lambe, Phys. Rev. **98**, 985 (1955).

⁹ D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

¹⁰ L. S. Pedrotti and D. C. Reynolds, Phys. Rev. **120**, 1664 (1960).

¹¹ B. A. Kulp and R. H. Kelley, J. Appl. Phys. **31**, 1057 (1960).

¹² J. J. Hopfield, J. Phys. Chem. Solids **10**, 110 (1959).

¹³ R. J. Collins, J. Appl. Phys. **30**, 1135 (1959).

⁵ C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

sized that not all crystals show mechanically excited emission; the differences between crystals that do show the "tap-effect" and those that do not are not obvious from casual observation.

Two differences that are experimentally observed in the "tap-effect" crystal are:

(1) The first peak in the uv-stimulated edge emission is always less intense than the second peak.

(2) The linewidths are appreciably wider in the edge emission structure.

The first peak is the zero-phonon peak, with the longer wavelength lines arising from phonon interaction, just as in normal CdS. This can easily be seen from Klick's data.⁵

Hopfield¹² has recently adopted a shallow-trap model and developed a theory of edge emission in CdS, ZnS, and ZnO. On the basis of this model, the transition probability for a multi-phonon process is found to be

$$P(n) = C |H|^2 \exp(-\sum_{\mathbf{k}} |f_{\mathbf{k}}|^2) (\sum_{\mathbf{k}} |f_{\mathbf{k}}|^2)^n / n!, \quad (1)$$

where C is an arbitrary constant, $|H|^2$ is the square of the optical matrix element for a transition between free and trapped carriers, n is the number of phonons, and

$$f_{\mathbf{k}} = -i \left(\frac{2\pi e^2}{V \hbar \omega_0} \right)^{1/2} \left(\frac{1}{n^2} - \frac{1}{\epsilon_0} \right)^{1/2} \frac{\rho_{\mathbf{k}}^*}{|\mathbf{k}|}, \quad (2)$$

where V is the crystal volume; e is the electronic charge; $\hbar \omega_0$ is the energy of a longitudinal optical phonon; \mathbf{k} is the wave vector; and $\rho_{\mathbf{k}}^*$ is the \mathbf{k} th Fourier coefficient of the electronic charge density. The n and ϵ_0 are, respectively, the optical index of refraction and the static dielectric constant.

Normalizing (1) and letting

$$\bar{N} = \sum_{\mathbf{k}} |f_{\mathbf{k}}|^2, \quad (3)$$

one obtains the Poisson distribution in familiar form (for fixed \bar{N})

$$P(n) = \exp(-\bar{N}) \bar{N}^n / n!, \quad (4)$$

\bar{N} is the mean number phonons for the distribution.

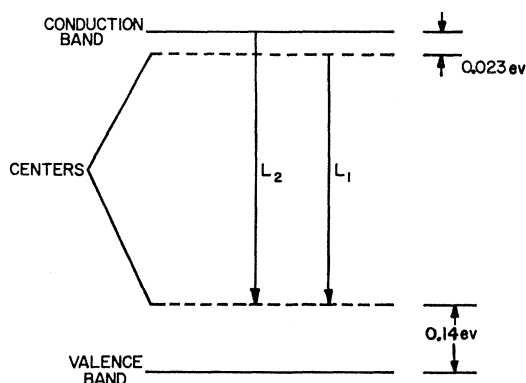


FIG. 10. Energy model for green fluorescence in CdS.

Hopfield¹² fitted a Poisson distribution (with fixed \bar{N}) to the photoelectric measurement of the peak heights of the edge emission of normal CdS crystals as measured by Klick.⁵ From this he found that $\bar{N} = 0.87$ for CdS at 4.2°K. In order to check the model and the theory, he calculated the radius of the bound state corresponding to $\bar{N} = 0.87$, assuming that the charge distribution of the trapped carrier could be approximated by a Gaussian,

$$\rho(r) = (\pi^{1/2} a)^{-3} \exp(-r^2/a^2). \quad (5)$$

Using (3) and (2) with this charge distribution, one finds that

$$\bar{N} = \frac{e^2}{a} \left(\frac{1}{\hbar \omega_0} \right) \frac{1}{(2\pi)^{1/2}} \left(\frac{1}{n^2} - \frac{1}{\epsilon_0} \right), \quad (6)$$

where a is the radius of the trapped carrier. This gives a value for a in CdS of approximately 11 Å, or approximately 2 lattice constants. In \mathbf{k} space, this is approximately one-sixth of the distance from the center to the edge of the Brillouin zone. Hopfield points out that the limited \mathbf{k} -space extension of the trapped carrier seems to be consistent with an original assumption of near-cubic symmetry for the trapping potential well, requiring that the component wave functions for the trapped particle be contained in a small part of the Brillouin zone; likewise, he feels that a mean radius of 22 Å (mean radius = $2a$) is not inconsistent with the binding energy of the trapped carrier.

At the time the shallow-trap model was proposed and applied to CdS edge emission, Hopfield was not aware of some recent work on the temperature dependence of edge emission.^{4,10} On the basis of this work, it turns out that the shallow trap model could have been more meaningfully applied (physically, at least) to edge emission at temperatures appreciably higher than 4.2°K. Pedrotti and Reynolds¹⁰ have recently shown that the anomalous wavelength shift in CdS green fluorescence, observed as the crystal is warmed from 4.2° to 77°K, is due to a change in the centers responsible for emission, rather than a change in the intrinsic band gap. These investigators found that the optical transition at 4.2°K is predominantly center-to-center with phonon interaction, while at 77°K it is band-to-center accompanied

TABLE I. Measured and calculated edge emission line intensities for normal CdS at 77°K, $\bar{N} = 0.91$. The measured peak heights are from Klick's data.⁵ The calculated peak heights $P(n)$ are multiplied by $\exp(\bar{N})$ (\bar{N} is fixed) in order to normalize the $n=0$ peak to unity.

No. of phonons	Measured peak height	Theory [$P(n) \exp(\bar{N})$]
0	1.00	1.00
1	0.89	0.91
2	0.44	0.42
3	0.15	0.13
4	0.04	0.03

* See reference 5.

TABLE II. Measured and calculated edge emission line intensities for tap-effect CdS at 77°K, $\bar{N}=1.18$.

No. of phonons	Measured peak height		Calculated peak heights	
	Normalized to first peak	Normalized to 2nd peak	Multiplied by $\exp(\bar{N})$	Multiplied by $\exp(\bar{N})\bar{N}^{-1}$
0	1.00	0.85	1.00	0.85
1	1.18	1.00	1.18	1.00
2	0.66	0.56	0.70	0.59
3	0.29	0.25	0.27	0.23

by the usual phonon series. It should be pointed out, however, that Hopfield originally proposed a substantially equivalent explanation of the emission anomaly.⁹ From Klick's data, it is not obvious that the shallow-trap model (with a single trapping center) should not apply at 4.2°K, since a comparison of calculated and measured peak heights at¹² 4.2°K indicates that the model does fit the data. Moreover, it may well be that the excellent agreement between model and experiment for normal CdS at 4.2°K, at least for the first four peaks, is not fortuitous. In principle, it seems quite possible that the substitution of a trapped-carrier wave function for the free-carrier wave function in Hopfield's model, with corresponding changes in the effective Hamiltonian, could lead to an essentially equivalent multiphonon transition probability, particularly if the substituted trapped-carrier were very shallow, say, approximately 0.02 eV from a band. Of course, the simple trapping model does not perfectly fit the 77°K emission spectra either. This can be seen from a peak-height comparison of the data in Tables I and II. Some of this discrepancy between model and experiment is undoubtedly due to errors in the measured peak heights, particularly for the $n=2$ and $n=3$ peaks in the tap-effect crystal spectrum (Fig. 5). These peaks were not well resolved, but the photon energy at which the peak heights were measured was determined on the basis of a one-phonon spacing between peaks. An energy model is shown in Fig. 10. The essential feature of this model is a shallow, electron-trapping level (0.023 eV below the conduction band) and a hole-trap level located 0.14 eV above the valence band. L_1 and L_2 are the transitions at 4.2° and 77°K, respectively: L_1 is a transition resulting from recombination of trapped electrons with trapped holes and L_2 is emission resulting from the recombination of free electrons with trapped holes. Here it is assumed that the electrons, trapped at the 0.023-eV level at 4.2°K, are thermally ionized to the conduction band as the temperature increases to 77°K. As it turns out, L_1 , though dominant at 4.2°K, is accompanied by some transitions of energy L_2 . The same phenomenon occurs for "tap-effect" CdS, as can be seen from the data in Figs. 4 and 9 where a second set of peaks of lesser intensity exists between the principal peaks. It should be pointed out that a model in which the given centers are mirror-reflected about the center of the forbidden energy gap would serve equally well.

A Poisson distribution was fitted to the peak heights of Klick's edge emission data for normal CdS at 77°K. Both measured and calculated peak heights are given in Table I. The mean number of phonons for the distribution was determined to be 0.91. With $\bar{N}=0.91$, the trapped carrier radius is found to be approximately 10 Å, which is not appreciably different from its radius at 4.2°K. If one now makes a similar analysis of the line structure for a tap-effect crystal, one finds, using the data of Fig. 5, that $\bar{N}\approx 1.2$. The results are given in Table II. This gives a trapped carrier radius of approximately one-fourth of the distance from the center to the edge of the Brillouin zone.

As was previously pointed out, the uv-stimulated emission spectra (Figs. 4, 5, and 9) show that the first-phonon ($n=1$) peak in tap-effect CdS is always the most intense. A peak-height comparison at 4.2°K reveals that the zero-phonon peak is approximately 94% of the first-phonon peak, while at 77°K the $n=0$ peak is 85% of the $n=1$ peak. Here it seems that there is a greater probability for one-phonon transitions than for no-phonon transitions. This is opposite to what one might expect and is contrary to what is usually observed in CdS: in ordinary crystals, the zero-phonon transition (first peak) is always the most probable. At a given temperature, the $n=0$ peaks appear at the same wavelength for both tap-effect and normal CdS. We believe that the observed intensity reversal of the first two emission peaks is significant and we speculate that there are differences in the "tap-effect" CdS lattice that are somehow responsible for both the peak reversal and the mechanical stimulation of emission. It should be emphasized, however, that such thinking is speculative, since little justification can be advanced in its defense, save the fact that the emission spectrum is different and there appears to be a difference in the longitudinal optical phonon distribution. Two interpretations are possible for the observed difference in the spectra of the two types of crystals:

(1) It may be that the $n=0$ peak in tap-effect crystals is suppressed by some mechanism (e.g., changes in selection rules) while the phonon peaks remain essentially unchanged.

(2) On the other hand, it may very well be that the $n=0$ peak in a tap-effect crystal is essentially the same (in intensity) as that of a normal crystal but is accompanied by a considerably more intense series of peaks due to phonon interaction.

The data do not distinguish between the two possibilities, since the two types of emission were observed under entirely different experimental conditions.

In a simple trapping model, suppose that the trapped carrier is a hole and that the emission is due to recombination of free electrons with trapped holes. It is interesting to contemplate, but difficult to prove, that such a trapped carrier, despite the fact it is more extended in \mathbf{k} space, could play a unique role in both the uv- and

mechanically stimulated emission of a "tap-effect" crystal. The carrier is not only trapped in a potential well, but also weakly coupled to the lattice; it is possible that such coupling might be of sufficient strength in tap-effect CdS to make the center more susceptible to lattice disturbances of all types, including those of optical, mechanical, and acoustical origin. In this way a lattice disturbance (including lattice waves) combined with an external excitation of some type might alter the center's dipole moment, relax selection rules, and cause an otherwise forbidden radiative transition to proceed. In particular, the lattice disturbance might be a moving dislocation, started by an impulse.¹⁴ It is also possible, as previously suggested,¹ that a moving dislocation might release the trapped carrier (in the present argument, a hole) allowing it to recombine with either trapped or free electrons. If the proposed moving dislocation were an edge dislocation, it would be likely that an instantaneous piezoelectric field would exist at the dislocation line, moving along with it at an appreciable fraction of the acoustic velocity¹⁵; consequently, it is quite possible that such a field, though rapidly traversing the distance of one lattice constant, could transfer energy to the trapped carrier and excite its release, provided the carrier were close enough to the path of motion.

It is highly unlikely that mechanically excited emission could arise from coupling due to a steady-state piezoelectric field. In the stimulated state, "tap-effect" crystal resistivities are much too low (<100 ohm-cm) to permit the build-up of a piezoelectric field of any magnitude. Equally unlikely is the possibility that such a piezoelectric field might play a significant role in the edge emission anomaly (peak intensity reversal) observed in some CdS emission spectra. Recently, an optical pumping spin resonance experiment with "tap-effect" CdS showed that, when storage occurred, the crystal conductivity was as great at the microwave frequency (2.4×10^{10} cps) as is observed at low frequency.¹⁶ Hence, it is improbable that an impulsive force of reasonable intensity might contain Fourier components, of frequencies $> 2.4 \times 10^{10}$ cps, with sufficient amplitude to influence the optical transitions.

A search for observable differences between "tap-effect" and "normal" CdS lead to a consideration of the restrahl parameters. (The restrahl parameters have not been measured for a crystal known to show the "tap-effect"). Suppose, e.g., that the static dielectric constant or the restrahlen frequency were somewhat different in "tap-effect" CdS, say, a higher ϵ or a lower

ω (either, but not necessarily both). The polaron coupling constant, α , on the order of 2 for CdS, could be significantly higher in the "tap-effect" crystals as a consequence of either a higher ϵ , or a lower ω . This coupling constant¹⁷ is a measure of the electron-phonon coupling and is given by

$$\alpha = \frac{e^2}{2\hbar c} \left(\frac{2mc^2}{\hbar\omega} \right)^{\frac{1}{2}} \left(\frac{1}{n^2} - \frac{1}{\epsilon} \right). \quad (7)$$

Here only the long wavelength longitudinal optical mode is considered, the frequency of which is given by $\omega = \omega_t(\epsilon/n^2)^{\frac{1}{2}}$, where ω_t is the frequency of the transverse optical mode. A higher polaron coupling constant could account for the increased phonon participation observed in the optical transitions of these crystals.

Emission line broadening is one of the observable differences between "tap-effect" and "normal" CdS; consequently, it is worthwhile to consider processes that might contribute to the broadening of these lines. Line broadening mechanisms, known to be present in ordinary CdS, are probably operative in "tap-effect" crystals, but to a greater degree. Hopfield¹² has estimated the optical phonon dispersion in CdS. On the basis of an approximate phonon dispersion relation (reasonably valid near the center of the zone), he estimates a linewidth of about 2 Å which is an order of magnitude smaller than the line widths observed by Klick⁵ (10 Å at half-maximum). A second source of line broadening within Hopfield's theory is the kinetic energy of the free carriers. On the basis of a simple model (spectral shape of $E^{\frac{1}{2}}e^{-E/kT}$), estimates of this broadening would give linewidths which are a factor of 2 too small to fit the data at 77°K and an order of magnitude too small to fit the data at 4.2°K. Other suggestions which might account for the increased broadening, not included in the theory, include acoustical lattice vibrations, influence of imperfections on the binding energy of the trapped carrier and lifetime broadening. Since the wave function of the trapped carrier in "tap-effect" crystals is more extended over \mathbf{k} space in the first Brillouin zone, one would expect the optical transitions to be more strongly influenced by acoustical lattice vibrations, resulting in the increased line broadening which is observed in these crystals.

The thermal stimulation of tap-effect CdS raises the very interesting question of how (i.e., by what mechanism) the stimulating energy is absorbed. One would expect the absorption to be quantized; hence, one plausible argument is the existence of many impurity and defect levels throughout the forbidden gap, giving rise to a multi-step absorption process. There is at least qualitative support for such an argument. According to Greene,¹⁸ the best tap-effect crystals seem to come from

¹⁴ J. D. Eshelby, Phys. Rev. **90**, 248 (1953). See also J. D. Eshelby, Phil Mag. **40**, 507 (1949); F. R. N. Nabarro, *ibid.* **42**, 313 (1951).

¹⁵ H. G. Van Bueren, *Imperfections in Crystals* (North-Holland Publishing Company, Amsterdam, 1960), p. 70. Some representative dislocation velocities in a polar crystal, measured from impulse-induced dislocation motion, are given by W. G. Johnson and J. J. Gilman, J. Appl. Phys. **30**, 129 (1959).

¹⁶ D. R. Locker and P. B. Dorain (private communications).

¹⁷ T. D. Lee, F. E. Low, and D. Pines, Phys. Rev. **90**, 297 (1953).

¹⁸ L. C. Greene (private communication).

furnace-runs where the least attention is paid to the purity of the starting materials.

B. Electric-Field-Induced Emission

The field emission in these crystals can be explained on the basis of the model proposed to explain mechanically excited emission.¹ It should be pointed out that the emission is observed at the silver electrode and only when the silver electrode is the positive electrode, as shown in Fig. 2. Even in the case where an ac field was applied, the emission appeared to be brightest in the neighborhood of the silver electrode. This suggests that the emission results from recombination of injected carriers and is explained on the basis of the model shown in Fig. 11. Here it is proposed that the lower levels are occupied by electrons while the crystal is in the dark. This results in the Fermi level being in a position unfavorable for hole injection. Now, when the crystal is exposed to light, the electrons are excited to the conduction band and holes are trapped at the impurity level. The fact that storage occurs indicates that the holes remain trapped in an equilibrium condition. The readjustment of the Fermi level to the new charge distribution then makes it possible for hole injection to occur and thus recombination radiation is observed in much the same manner as for uv excitation.

Since only the characteristic CdS green fluorescence was observed in the field-induced emission spectra, it was felt that there was not an appreciable diffusion of the Ag electrode into the lattice. If there had been an appreciable diffusion of Ag into the lattice, the crystals should have shown a characteristic red fluorescence along with the green emission, but such was not the case. It is well known that Cu in CdS gives rise to a red fluorescence, and it has also been shown that, in CdS, Cu has a rather high thermal diffusion coefficient¹⁹; it is, in fact, several orders of magnitude higher than Ag. In a simple experiment, where Cu was substituted for the Ag electrode (Cu and In electrodes on the crystal), it was impossible to induce a visible emission from a tap-effect crystal when an electric field of reasonable intensity (<2000 v/cm) was applied. From this it appears that there is not an appreciable field-induced diffusion of the Cu electrode into the tap-effect CdS lattice. Also, unlike a Ag electrode, the Cu electrode appears not to inject carriers into the crystal when the electric field is applied.

¹⁹ R. L. Clarke, J. Appl. Phys. **30**, 957 (1959).

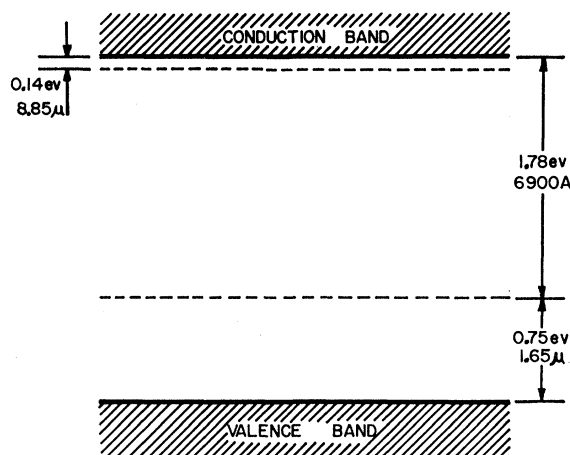


FIG. 11. Energy model for edge emission in "tap-effect" CdS.

V. SUMMARY

(1) CdS crystals that show mechanical stimulation of green edge emission are very good current storage crystals. Optically stimulated crystals have been observed to store for long periods of time while maintained at liquid nitrogen temperature in a darkened room.

(2) The edge emission spectrum of a "tap-effect" CdS crystal is different from that of a normal crystal. The first edge emission peak (zero-phonon) is always the most intense in normal CdS, while the second peak (first-phonon) is the most intense in tap-effect crystals. Also, the emission peaks are broader in tap-effect crystals.

(3) The temperature dependence of edge emission in tap-effect crystals is observed to be the same as that in normal CdS. The incompatibilities of a simple shallow-trap model with CdS edge emission, for both normal and tap-effect crystals at 4.2°K, are pointed out. Hopfield's shallow-trap model¹² was fitted to the edge emission spectrum from a tap-effect crystal; from this the mean number of phonons for the spectrum was determined to be 1.2.

(4) In a tap-effect CdS crystal, it is possible to induce the characteristic green edge emission by application of an ac or dc electric field, but line structure has not been observed in the emission spectrum. The emission intensity generally increases with increasing current up to a saturation point. In order to induce an emission of detectable intensity, it was necessary to use an In and a Ag electrode, with the positive potential applied to the Ag electrode.