inverse Auger or auto-ionization transition. In the case of electron scattering by the hydrogen atom, this corresponds to a doubly excited state of the negative hydrogen ion which can undergo auto-ionization.

In actual calculations, one usually replaces $\Psi^{\pm}(1, 2)$ in the integrand of (4) by the single term corresponding to one electron in the atom and an incident plane wave (Oppenheimer approximation), or by a finite number of terms from (5).[1, 4] In either case, the use of symmetrized approximation wave functions in (4) implies symmetrized asymptotic conditions in the manner discussed above.

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Luminescence and Photoconductivity in Cadmium Sulfide at the Absorption Edge

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Measurements of optical transmission, photoconductive response, luminescent edge emission, and excitation spectrum for edge emission have been made on single crystal specimens of CdS at 77°K and 4°K. At the lowest temperature there is an energy gap of more than 0.1 electron volt between the absorption edge and the onset of emission. Coupled with information from the emission spectrum and the infrared properties of CdS, this observation suggests that edge emission in this material may occur at a special center and not be characteristic of the pure lattice.

INTRODUCTION

LUMINESCENT edge emission occurs in cadmium sulfide at the long wavelength side of the absorption edge when the material is cooled to liquid nitrogen temperature (77°K) and excited with ultraviolet light.[1] At liquid helium temperatures (4°K) the emission spectrum of single crystal materials sharpens into a series of equally spaced "lines" with a width at half-maximum of approximately 10A.[2] This luminescent emission is less broad than that of impurity activated materials with the exception of activators, such as the rare earths, in which the electronic transition occurs in an inner electronic shell.[2] One explanation is that either free electrons and holes or excitons recombine in the pure lattice so that this emission is "lattice" emission. The successive luminescent peaks would correspond to the excitation of increasing numbers of vibrational quanta, and the spacing of the peaks would correspond in energy to the principal infrared vibrational frequency. This simple explanation faces theoretical objections since the probability of electron-hole or exciton recombination in the pure material is relatively small.

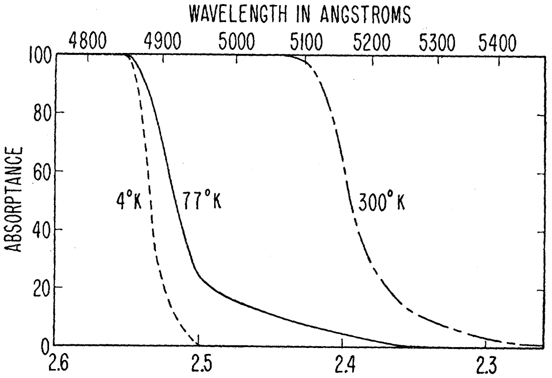

FIG. 1. Absorptance (100 minus percent transmission) of CdS as a function of wavelength for temperatures of 4°K, 77°K, and 300°K. The sample is approximately 0.004 cm thick.

The experiments on the electrical and optical properties of CdS at the absorption edge was undertaken primarily to investigate whether edge luminescence was characteristic of the pure lattice. Also, since the large photoconductivity in CdS is technically and scientifically of great interest,[3] it was felt that the measurements would aid in understanding this phenomenon. Finally, an understanding of edge emission in CdS might suggest explanations of edge emission in such varied materials as the silver halides[4] and germanium.[5]

EXPERIMENTAL ARRANGEMENT

The cadmium sulfide investigated here was single crystal material grown from the vapor by the Frerichs technique.[6] Photoconductivity was measured on a rod-like specimen approximately 1 mm in diameter and 4 mm long. The other measurements were on thin flaked specimens approximately 4 mm×1 mm×0.1 mm. For the emission and excitation measurements the samples were held between quartz plates. Because of this, the

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[2] C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

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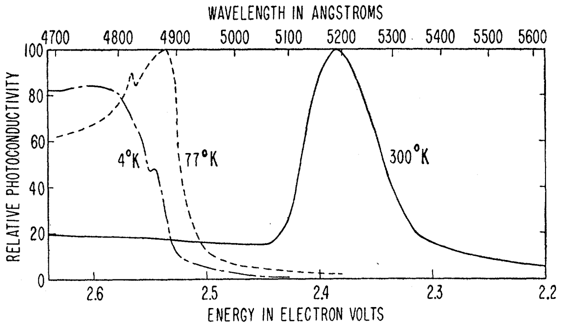

FIG. 2. Relative photoconductivity of CdS as a function of wavelength. The ordinate scale for each curve is set independently.

flakes broke into smaller pieces; there was, however, no grinding of the material. Although excitation and emission measurements were made on the same specimens, other samples were used for the photoconductivity and transmission measurements. In order to minimize effects due to inclusion of silver in the material, specimens whose luminescence was low at room temperature were chosen.

In all measurements temperature control was obtained by immersing the samples directly in either liquid nitrogen (77°K) or liquid helium (4°K) exposed to atmospheric pressure.

All optical measurements were made with the same monochromator and the same slit widths in order to facilitate comparison of the various data. The trace of the emission spectrum of the mercury 5461A line given in Figs. 4, 5, and 6 indicates that the energy band pass of the instrument at its half-maximum points is 0.015 electron volt. The change in dispersion with wavelength of the monochromator is such as to maintain this band width approximately constant over the narrow wavelength range investigated. In each measurement the monochromator was motor-driven and a continuous record obtained.

EXPERIMENTAL RESULTS

A. Absorption

Figure 1 presents the results of measurements on the absorptance (100 minus percent transmission) of a flake of CdS 0.004 cm thick. An absorptance of 90 in this case corresponds to an absorption coefficient of 600 cm^{-1} neglecting reflection losses; an absorptance of 10 corresponds to an absorption coefficient of 25 cm^{-1}. Between 300°K and 77°K the absorption edge shifts to the short wavelength by about 1A/°K; between 77°K and 4°K the shift continues at a slower rate—approximately 0.5A/°K. It also appears that the absorption edge is sharper at 4°K than at the higher temperatures. Both the 300°K and the 77°K curves show a decided long wavelength tail; the 4°K curve is drawn without this tail, but the data here is not conclusive because of the light scattering in the arrangement used. Data from measurements on photoconductivity and excitation indicate that there is probably also a long wavelength tail in the 4°K absorptance curve.

B. Photoconductivity

The photoconductivity of a single crystal of CdS as a function of the wavelength of the incident light is given in Fig. 2 for temperatures of 300°K, 77°K, and 4°K. The curves are drawn for equal numbers of incident quanta. For 50 volts applied to the crystal, the photocurrents at 4700A were 2.5×10^{-10} amp at 300°K, 1.5×10^{-9} amp at 77°K, and 2.5×10^{-10} amp at 4°K. At all temperatures the growth and decay of the photocurrent was slow with as much as a minute being required for equilibrium to occur. Point-by-point measurements were used to check the results of a continuous record.

At 300°K the well-known photoconductivity peak appears at the absorption edge. The peak shifts to shorter wavelengths as the temperature is decreased and is reduced in size relative to the short wavelength response until at 4°K the peak essentially disappears.

C. Emission

The emission spectrum of single crystal CdS is presented in Fig. 3 where the results are given in units of relative number of emitted quanta as a function of wavelength. Although excitation was by the 3650A Hg line, the emission spectrum has been found to be independent of the exciting wavelength. In going from 77°K to 4°K, the main portion of the emission shifts to long wavelengths and small emission bands appear at short wavelengths. These small bands were also found at 77°K by Kröger[1] in powdered materials prepared in the usual way by firing with flux. Since they appear to the short wavelength side of the absorption edge, Kröger attributed them to surface emission. At the lowest temperature there is a considerable sharpening of the main emission peaks; spectra taken with higher resolution[2] indicate that the width at half-maximum is 10A. The spacing of the main emission lines is uniform in energy and the energy difference between two suc-

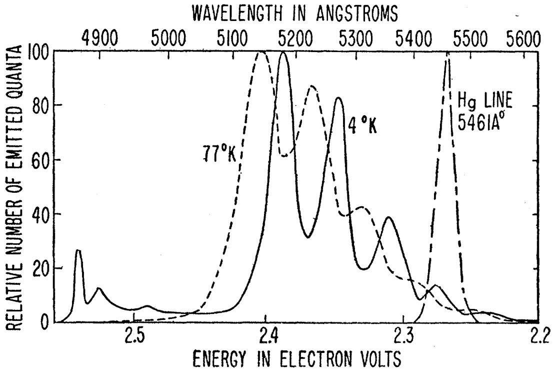

FIG. 3. Relative number of emitted quanta of CdS as a function of wavelength. Excitation is by the Hg 3650A line.

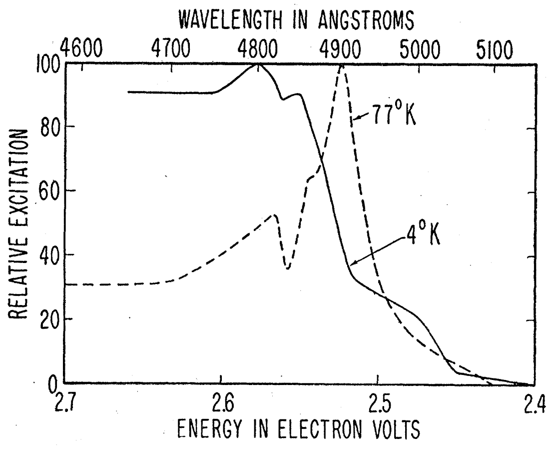

FIG. 4. Relative quantum efficiency of excitation for edge emission in CdS as a function of wavelength. Emission filtered through Corning No. 3484 glass transmitting wavelengths longer than 5300A.

cessive peaks corresponds to a quantum of infrared light with a wavelength of 32 microns.

D. Excitation

Relative quantum efficiency for the excitation of the main edge emission is shown as a function of the wavelength of the exciting light in Fig. 4 for temperatures of 77°K and 4°K. As in the photoconductivity and absorptance results there is a shift to short wavelengths as the temperature decreases. At 77°K there is a large peak in the excitation spectrum as there is in photoconductivity at the same temperature; in both measurements these peaks disappear at 4°K. In contrast with the photoconductivity measurements, however, the rise and decay of luminescence with the application or removal of excitation occurs in less than a second.

E. Summary of Experimental Results

In order to facilitate comparison of the data taken at each temperature, the results for 4°K have been collected in Fig. 5 and those for 77°K in Fig. 6. At 4°K the excitation spectrum has a peak at 2.48 ev which is approximately 0.1 ev below the highest points of the photoconductivity and excitation spectra. This peak is not accompanied by a photoconductivity maximum. In general, the absorptance and excitation edges at 4°K are found on the long wavelength side of the photoconductivity edge. At 77°K the separation of these curves is less than at 4°K. The distinct gap between the absorption edge and the onset of emission at 77°K is increased to more than 0.1 ev at 4°K.

DISCUSSION

As mentioned above, the uniform spacing of the emission lines in CdS is suggestive of interaction with a vibrating system the frequency of which corresponds to a 32 micron infrared quantum. It has been found by Plyler[2] that an absorption band at 34μ exists at room temperature. The absorption coefficient at the peak of this band is only of the order of 100 cm^{-1} and cannot correspond to the main infrared absorption peak. From data on the infrared absorption of ZnS, it is possible to estimate that the main CdS band is in the range of 40–45 microns; experimentally, it is found not to be less than 37 microns. These results suggest that the vibration system with which the electronic transition responsible for edge emission is coupled is not characteristic of the pure lattice. Further evidence is found in the data of Fig. 5 discussed above. The energy gap between the absorption edge and the onset of emission also implies that this is not a case of simple lattice emission corresponding to some type of resonance radiation.

One explanation of these experiments is that the emission corresponds to electron-hole or exciton recombination but that two effects occur. First, the emitting system is coupled closely enough to the lattice so that there is observed the normal Stokes' shift in absorption and emission wavelengths. Second, the coupling of the emitting system with the lattice causes an increase in the lattice vibrational frequency near the emitting system.

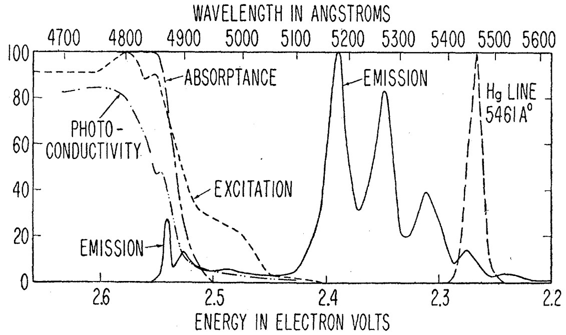

FIG. 5. Absorptance, photoconductivity, emission, and excitation of CdS at 4°K.

Another explanation is that edge emission in CdS occurs at points in CdS containing specific lattice defects. The emission energy would then be characteristic of the defect as would be the vibrational frequency. A conclusive choice between these explanations is not possible at present. However, there appear to be several arguments which favor the second explanation. First, the probability of an exciton radiating appears to be small compared with the probability that it will be annihilated at a lattice defect. Second, the change in lattice frequency appears to be quite large to be caused by an electrically neutral system of coupled hole and electron. Calculations of this effect would, of course, be instructive. Finally, the observed infrared band at 34μ is understood as arising from the vibrational frequency of the defect in its ground state on the second explanation above. The first explanation of edge emission offers no interpretation of this band which is observed under conditions where neither free electrons nor holes are formed.

If defects are responsible for edge emission in CdS, their nature is unknown, but they are almost certainly not due to the inclusion of foreign ions. The commonly known activators for CdS give an emission to the long wavelength side of the edge emission both at high and low temperatures. Also the intentional inclusion of impurities tends to weaken the edge emission rather than enhance it. Finally, it seems improbable that a trace of impurities could produce as bright and consistent a luminescence as is observed. From the infrared data it is apparent that the vibrational frequency of the luminescent center is higher than that of the pure material. This suggests that the center is in a region of lattice compression as may occur near an interstitial atom or ion.

There are two explanations for the excitation peak which is not accompanied by photoconductivity and occurs at 2.48 ev in the 4°K curve. The first is that this is an exciton level. A relation derived by Seitz[7] predicts that the lowest exciton level for CdS would be 0.17 ev below the conduction band. Since the approximations used in deriving this expression are worst for the lowest level, the difference between the theoretical value of 0.17 ev and the experimental value of approximately 0.10 ev may not be significant. The second explanation is that the excitation peak corresponds to absorption directly in the luminescent center so that luminescence occurs without the transport of charge. Supporting evidence for this view is the low value of the absorptance in this region as contrasted with high values in bands normally ascribed to excitons.

This investigation touches upon the complicated problem of conductivity in CdS in two respects. The first is that the large peak in conductivity occurring at the absorption edge at 300°K is reduced in size as the temperature decreases and finally disappears at 4°K. Thus it is distinctly a temperature dependent phenomenon. The second is the general similarity of the wavelength response of excitation and photoconductivity coupled with their widely different response times. It has been suggested that the large photoconductivities observed in the sulfides originate in small special volumes of the crystal such as *n-p* junctions,[8] *n-p-n* junctions,[9] or surface layers.[10] The data here is consistent with this view if the luminescence originates throughout the crystal. A model in which both the slow response photoconductivity and fast response luminescence are characteristic of the whole crystal has been suggested by Kallman and Kramer.[11]

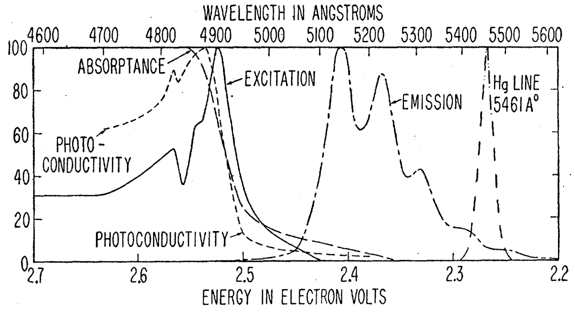

FIG. 6. Absorptance, photoconductivity, emission, and excitation of CdS at 77°K.

The emission spectrum of CdS is also of considerable interest because it presents evidence for the interaction of the electronic transition with only a single mode of vibration of the luminescent center. Should there be more than one vibrational mode of importance or a spectrum of interactions, one would expect a smearing out of the lines in the long wavelength side of the emission or at least a distinct loss of resolution. That this is not apparent lends support to the procedure used in computing configurational coordinate curves for luminescent impurities[12,13] where interaction is considered with only a single mode of vibration. A detailed discussion of the approximations involved in this procedure is contained in recent work by Lax.[14]

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