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# Fundamental Absorption Edge in Cadmium Sulfide*

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The absorption and reflection spectra of CdS have been determined in the temperature range 90°–340°K by photoelectric measurements on single crystals, using polarized light. The temperature and frequency dependence of the absorption coefficient in the edge, over a substantial range of absorption magnitudes, are well described by expressions of the form $\alpha(\nu)=\alpha_0\exp[-\beta(E_{00}-CT-h\nu)/kT]$, where the energy $(E_{00}-CT)$ is closely associated with the position of an absorption peak. For light polarized with $E$ vector parallel to the crystalline $c$ axis, there is one such peak, at λ4844 A at 90°K; for light polarized with $E$ vector perpendicular to the $c$ axis, the 4844 A absorption is again present in about equal strength and a stronger line appears at λ4874 A, shifting the absorption edge toward longer wavelengths by a corresponding amount. These absorption lines, or sharp bands, are observed in the reflectance spectrum, and correspond to absorption lines observed photographically by Gross and others. These results are discussed in the light of the present theoretical picture of absorption in insulating crystals, and it is noted that an exponential absorption edge of this kind, characteristic also of other ionic crystals, cannot be adequately explained in terms of existing models.

## 1. INTRODUCTION

THE fundamental absorption of CdS is especially interesting in view of the importance of this material as a "model" photoconductor and phosphor, and is the subject of a considerable experimental literature.[1–14] The main purpose of the work reported in this paper was to determine in some detail the shape of the absorption edge, particularly the dependence of the edge shape on the polarization of the incident light, since the dichroism[7,8] of CdS had not been taken into account in previous quantitative absorption measurements. Because of the apparent close correspondence of the thresholds of intrinsic photoconductivity and optical absorption, it has been widely assumed that absorption in the edge is due to band-to-band transitions; on this basis Dresselhaus[15] has suggested, as a possible interpretation of the absorption dichroism, direct transitions which are symmetry allowed or symmetry forbidden, depending on the orientation of the polarization vector, the two processes being distinguishable in principle by the frequency dependence of the absorption coefficient. On the other hand, the discovery by Gross and coworkers[9–14] of complex structure in the strong-absorption region, which they attribute to excitons, and observations by Balkanski and others[16] of possible exciton diffusion, raise the possibility that exciton transitions comprise part or all of the familiar absorption in the neighborhood of 5100 A. Information about the strong-absorption structure has been obtained by photographic methods which give only a rough idea of the relationship of this structure to the absorption "tail" which defines the fundamental absorption edge in crystals of the thicknesses normally employed for photoconductivity and luminescence studies. A detailed knowledge of the frequency dependence of the absorption coefficient, covering a wide magnitude range and extending as far as possible into the fine-structure region, would clarify this relationship and perhaps provide useful clues to the nature of the edge absorption mechanism and the actual magnitude of the band gap.

For photoelectric measurements of absorption in the strong-absorption region extremely thin samples are required, and evaporated samples[1] of CdS usually do not duplicate too closely the spectrum detail characteristic of good crystals. However, crystals grown from the vapor phase can occasionally be obtained in thicknesses of 1 μ or less and can be used for optical measurements without further grinding or polishing treatments. The vapor-phase growth technique also produces samples of thickness greater than ~100 μ which preserve the crystal habit most convenient for optical measurements, i.e., platelets with surfaces parallel to the crystalline $c$ axis. The material is thus particularly amenable from an experimental point of view for ab-

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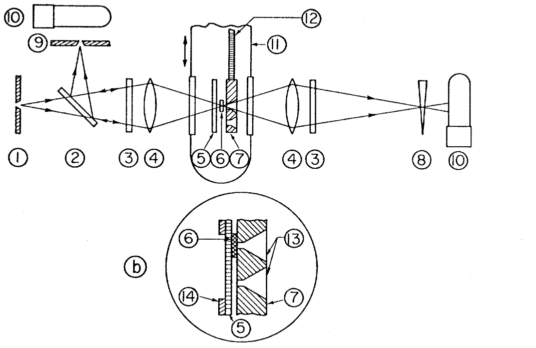

FIG. 1. Optical system and crystal mounting arrangement of low-temperature apparatus (schematic diagram, not to scale). The slit image in the sample plane has dimensions roughly 10×100 $\mu$. The entire cryostat assembly is supported on an accurate vertical slide and moves up to allow the beam to pass through the reference aperture. (1) Monochromator exit slit 1.0×0.04 mm; (2) beam splitter: glass cover slip coated with Evaporated Metal Films 2-630; (3) Polaroid film polarizers; (4) objectives: Elgeet 13 mm $f/1.5$; (5) glass cover plate 100 $\mu$ thick; (6) crystal specimen 1 to 40 $\mu$ thick; (7) cooled copper mounting block; (8) wedge interference filter ($B$ and $L$); (9) diaphragm with aperture roughly equal to exit slit size; (10) detector: 1P21 photomultiplier; (11) cryostat outer jacket of Pyrex with fused quartz windows; (12) stainless steel coolant container tube. (b) Detail of crystal mounting: (13) symmetrical 0.013 in. diam holes, counterbored; (14) copper clamping plate.

sorption measurements, and for studies of reflection and refraction correlated with the absorption behavior.

Relatively little attention has been given to interpretation of the edge shape in CdS. Seiwert discussed his 1949 data[3] in terms of a linear dependence of absorption coefficient on frequency, and the same data have been analyzed from a different point of view by Cheeseman.[17] Urbach[18] has called attention to the exponential dependence of the absorption coefficient ($\alpha \propto e^{h\nu/kT}$) manifested by several materials, among which he included CdS on the basis of Klick's data.[5] Seiwert's data[3] also appear to fit such an exponential law fairly well.

A fresh experimental examination of the "edge shape" problem, for analysis in the light of more recent theoretical work,[15,19,20] seemed appropriate at this time, and this paper reports the results of such an investigation; data have also been obtained, chiefly from observations of the reflectance spectrum, which give some indication of the relationship of the exciton-like absorption fine structure to the absorption "tail" at liquid-nitrogen temperatures and above.

## 2. EXPERIMENTAL PROCEDURE

The absorption data reported here were obtained by point-by-point photoelectric transmittance measurements on single crystals. Samples from several different laboratories (see Sec. 7) were measured; they were grown by the Frerichs technique[21] or modifications of it. Since for part of the absorption range extremely thin samples were required, and since the thinner specimens were often quite small, a microscopic technique was employed throughout. For measurements at room temperature, the samples were mounted on the stage of a polarizing microscope in which the substage condenser was replaced by a strain-free achromatic objective. Light from a monochromator, after passing through a polarizing prism, was focused on the crystal by this objective, collected by a symmetrical objective above the sample, and passed through a second polarizer, set parallel to the first, into the detector, a 1P21 photomultiplier. The beam was modulated at 15 cps, and a Ballantine Model 310A voltmeter served as the measuring instrument. Optical flare in the system was obviated by placing a small aperture, completely covered by the specimen, in the image plane. A symmetrical blank aperture was provided for the reference beam, the sample mount being shifted alternately between the two positions. Samples of dimensions ~100×150 $\mu$ could be used, and the arrangement proved quite convenient for larger specimens also, since a narrow region of accurately measureable thickness could be selected even in a striated or wedge-shaped crystal.

The monochromator employed was a Leiss double-dispersion instrument with flint prisms, capable of about 1 A resolution at 5000 A, and quite free from stray radiation. At 5000 A, with tungsten illumination, stray light of longer wavelengths was too faint to be detected, i.e., less than 0.01%. With this system, using the minimum band width obtainable from the monochromator, optical densities up to 4.0 were measureable to a precision of about 0.01 density unit.

For measurements above and below room temperature, the samples were mounted vertically in a cryostat and the analogous optical system consisted of symmetrical objectives preceded and followed by Polaroid film polarizers. To obtain sufficient aperture and working distance, cinematographic lenses were used (Elgeet $f/1.5$ 13 mm f.l.) stopped down slightly to improve image definition and to keep the incident cone angle relatively small (about 10°). The cryostat was mounted on the carriage of a vertical slide which permitted the sample to be moved out of the beam and returned with position reproducibility of about 0.02 mm. The more cumbersome mounting arrangement of this apparatus required samples of somewhat larger dimensions, of the order of 350 $\mu$ square. Provision was also made in the latter apparatus for reflectance measurements, as shown in the schematic optical system of Fig. 1. Light reflected from the crystal, and from the thin glass supporting plate in front of it, returned through the lens and converged after 90° deviation by a partially

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reflecting mirror to form an image of the monochromator exit slit at the point (9) in Fig. 1. A small aperture was placed in the image plane to pass this beam and discriminate against light reflected from other elements in the system. The intensity at this point was first measured with the crystal in the beam ($I_1$), then with the cryostat shifted so that reflection occurred only from the cover plate and other stationary elements ($I_2$). The quantity $(I_1-I_2)/I_2$ was taken as proportional to the ratio of the reflectance of the crystal to that of the glass plate, the latter a slowly varying function of wavelength. Absolute reflectance values were obtained by normalization to the computed reflectance at some wavelength where the index of refraction was known. The necessary data were quickly and easily obtained by automatic recording.

Sample thicknesses less than $\sim 40\ \mu$ were determined from the multiple-beam interference pattern, obtained by automatic recording of the transmitted or reflected intensity as a function of wavelength, using values of the index of refraction given by Reynolds *et al.*[22] Thicker samples were measured by focusing a shallow-field microscope successively on top and bottom surfaces, or by micrometer calipers. The over-all precision of thickness determination is estimated at $\sim 3\%$. The thickness values measured at room temperature were used for reducing the data at low temperatures also; the coefficient of thermal expansion in the appropriate direction ($\perp$ to $c$ axis) at room temperature, according to Seiwert,[3] is $6.5\times 10^{-6}$/deg C. It was assumed that the average coefficient between room temperature and $-180$°C is no larger than this value, which gives a negligible thickness correction.

Corrections for reflection were based on computed values, for the wavelength range in which the index of refraction was known, and on the measured reflectance at shorter wavelengths. In nearly all cases the measured optical density, in the region of transparency, was identical to that computed from reflection losses, and no further corrections were necessary; in a few instances a small additional constant correction was made for vignetting effects. The magnitude of the reflectance correction ranged from 0.15 to 0.30 density unit.

For the low-temperature measurements, cooling of the sample occurred primarily by conduction to the copper block on which it rested, and there were apt to be variations from sample to sample in the equilibrium temperature achieved (e.g. from $\sim 81$°K to $\sim 105$°K). In most cases direct measurement of the sample temperature by attachment of a thermocouple was impracticable because of the small sample size; the procedure finally adopted for temperature measurement consisted of a careful observation of the wavelengths of the peaks in the reflectance spectrum, the temperature shift of the latter having been previously determined on a larger crystalline specimen to which a thermocouple could be directly attached. Temperatures could be measured in this way to within about 3°K.

For intermediate temperatures, small quantities of coolant were introduced into the cryostat as required, the thermal inertia of the system being high enough so that measurements could be made at a known temperature. In such cases, care was taken to prevent deposition of condensable vapors on the crystal surface, i.e., measurements were made during the cooling cycle so that the sample always remained somewhat warmer than its surroundings.

Most of the specimens investigated showed green "edge" luminescence at low temperatures. The optical geometry was such that during absorption measurements the fluorescence intensity was below the threshold of the detector and did not interfere with the measurement of the sample transmittance. When it was necessary to verify that the detected radiation was actually transmitted light of the appropriate wavelength, a Bausch and Lomb wedge interference filter could be inserted before the detector for rough spectral analysis. This system also proved a convenient one for some simple observations of the fluorescence, which have been reported previously.[23]

## 3. RESULTS

### A. Absorption

The complete absorption data are given in Fig. 2 for two different polarizations of the incident light, i.e., with $E$ vector parallel to or perpendicular to the crystalline $c$ axis (referred to hereafter as $\|$ and $\perp$ polarizations) and with the direction of incidence in all cases normal to the $c$ axis (within the incident cone angle of 10°). The room temperature data were obtained on some 22 specimens, ranging in thickness from 0.89 to 165 microns. There was virtually no variation, from sample to sample, in the absolute values of the absorption coefficient above $10^3$ cm$^{-1}$. Below this range, two samples showed deviations from the curve of Fig. 2, both in the direction of stronger absorption; in one case, with an exponential frequency dependence like that of Fig. 2 but with lower slope, and in the other case a very flat absorption tail extending far out toward longer wavelengths. For the remaining specimens, absolute absorption values were consistent from sample to sample within experimental error. There is thus good reason to believe that the data below $10^3$ cm$^{-1}$, which follow the same law as the data above, do in fact represent the intrinsic absorption of CdS. Most of the samples used for this part of the curve were RCA Type I crystals[24]; no variation was observed among these down to the smallest measureable absorption values, about 20 cm$^{-1}$.

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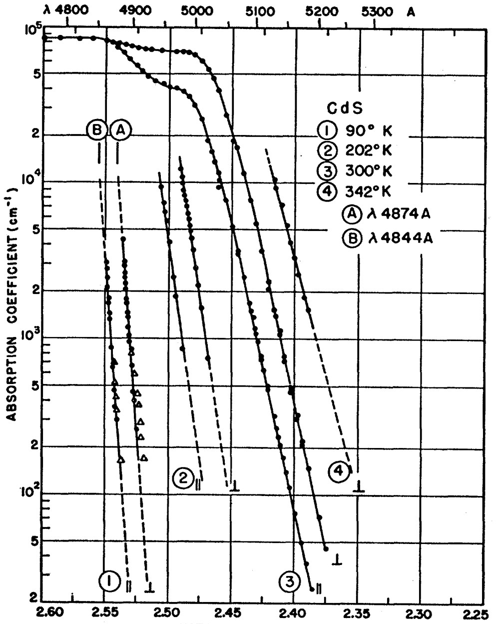

FIG. 2. Absorption coefficient of crystalline CdS. The linear portions of the solid curves are plots of the form $\ln\alpha = \beta h\nu/kT + \text{const}$, where $\beta = 2.17$. The vertical lines $A$ and $B$ are the positions of absorption peaks inferred from the reflection spectrum at 90°K. ∥ and ⊥ indicate absorption for polarized light with **E** vector parallel or perpendicular, respectively, to the crystalline $c$ axis. Absorption coefficient $= (1/t)\ln(\mathcal{T}^{-1})$, where $\mathcal{T}$ is the optical transmittance corrected for reflection, and $t$ = sample thickness.

Absolute values of the absorption coefficient, at room temperature, are considered accurate within ±10%. The low-temperature data are subject to considerably greater error, due to the steepness of the edge, an instrumental uncertainty of ±1 A in the absolute wavelength scale, and the difficulties of exact temperature measurement. Error due to the use of a finite measuring band width can be estimated from a relation due to Moser and Urbach,[25] appropriate for cases in which the absorption coefficient varies exponentially with frequency or wavelength. The relative error in the absorption coefficient $\alpha$, where $\alpha = \alpha_0 \exp(-c\lambda)$, is given approximately by[25]

$$\frac{\Delta\alpha}{\alpha} = \frac{c^2(\Delta\lambda)^2}{24}(1-\alpha t),$$

where $\Delta\lambda$ is the measuring band width and $t$ the sample thickness. For CdS the parameter $c$ is approximately $4.2\times10^6$ cm$^{-1}$ at room temperature, and $13\times10^6$ cm$^{-1}$ at 90°K. The resulting errors, computed for a band width of 1 A and an optical density of 3.0, and corresponding to measured values of the absorption coefficient lower than the true values, are respectively 0.045% and 0.42%.

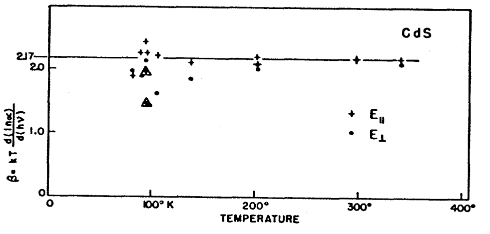

FIG. 3. Experimental values of the parameter $\beta$ at various temperatures.

The solid curves in Fig. 2, in the linear portions, are plots of the function $\ln\alpha = (\beta h\nu/kT) + \text{constant}$, where $\beta = 2.17$. Such a function describes the frequency dependence of $\alpha$ and the low-temperature sharpening quite well. Figure 3 shows various experimental values of $\beta$ as determined on individual specimens. The scatter at 90°K is partly, but not entirely, instrumental. There does not seem to be any systematic trend toward lower values of $\beta$, i.e., the absorption edge is apparently continuing to steepen with decreasing temperature at 90°K.

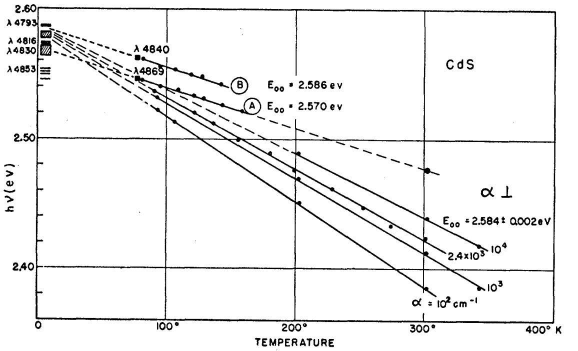

FIG. 4. Temperature shift of the absorption spectrum. The photon energy $h\nu$ at which the ⊥ absorption coefficient $\alpha_\perp$ has a given value is plotted on a linear scale against absolute temperature. Curves $A$ and $B$ denote the positions of absorption peaks as inferred from the reflection spectrum. The points 4840 and 4869 A are the positions of absorption lines reported by Gross. The line absorption spectrum at 4°K, after Gross,[10] is shown by the rectangular boxes on the left. The point at 300°K on curve $A$ is taken from the room-temperature absorption spectrum (see Fig. 8).

The largest variation among the samples measured at low temperature is indicated by the triangular experimental points in Figs. 2 and 3.

The temperature shift of the edge as well as the steepening can be described over most of the temperature range 90°–340°K by an expression of the form

$$\alpha = \alpha_0 \exp\left[-\frac{\beta}{kT}(E_0 - h\nu)\right], \tag{1}$$

where $E_0 = (E_{00} - CT)$. This is illustrated in Figs. 4 and 5, in which the photon energy at which the absorption coefficient has a given value is plotted against the temperature. From (1) the temperature dependence should be

$$h\nu|_\alpha = E_{00} - \left[\frac{k}{\beta}\ln\frac{\alpha_0}{\alpha} + C\right]T. \tag{1a}$$

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[25] F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956).

This linear relationship holds for absorption values $10^2$ cm$^{-1}$ and below to nearly $10^4$ cm$^{-1}$.

The assignment of numerical values to $E_0$ and $\alpha_0$ is to some extent arbitrary. $E_0$ may be taken as the position of an absorption peak, in which case $\alpha_0$ and $C$ are determined. The dichroism can be described for temperatures above 160°K by the function (1) with different values of $E_{00}$ for $\perp$ and $\|$ polarizations, but with the same values of $\alpha_0$, $\beta$, and $C$; below this temperature, the $\|$ absorption appears to shift a little less rapidly than the $\perp$ absorption, so that the energy separation of the two absorption edges is somewhat less at 90°K than at room temperature.

## B. Reflection

The reflection spectrum is shown in Figs. 6 and 7, for an untreated crystal surface at 81°K. Figure 6 is plotted directly from recordings of the reflected light intensity *vs* wavelength, uncorrected for a slow variation of the incident intensity with wavelength, and is included here to illustrate the polarization dependence of the reflectance at normal incidence. The fine structure is first perceptible at a temperature of about 160°K, and it sharpens and shifts to shorter wavelengths as the temperature is reduced. This shift can be compared with that of the absorption edge. The wavelength midway between a reflectance maximum and a minimum should correspond very closely with the position of an absorption peak. The positions of absorption lines, inferred in this way, are plotted as functions of temperature in Figs. 4 and 5. On the same plot are shown the positions of absorption lines as reported for 77°K by Gross *et al.*,[10,14] at 4869 and 4840 A. The line positions at 90°K, as inferred from the reflection spectrum, fall at 4874 and 4844 A, and extrapolate to Gross's values at 77°. The shift with temperature is very nearly linear, and if the positions are linearly extrapolated to 4°K there is again fairly close correspondence with lines or narrow bands observed by Gross,[10] namely, the bands (4820-4836 A+4815, 4816, 4817 A) and (4791-4793 A) respectively. It would be remarkable if a linear shift of this kind continued to so low a temperature as 4°, and it is possible that this apparent behavior is an accidental coincidence; there are, however, in the 90° reflection spectrum, no further reflectance anomalies at shorter wavelengths which could be identified with the strong (4815 A etc.) and (4791 A) 4° lines. Gross identifies[10] a 4°K (4854.2 A, 4853.3 A) doublet with the 77° (4869 A) line. Details of his extrapolation procedure are not given, and no measurements of the strong-absorption spectrum at intermediate temperatures have yet been published.

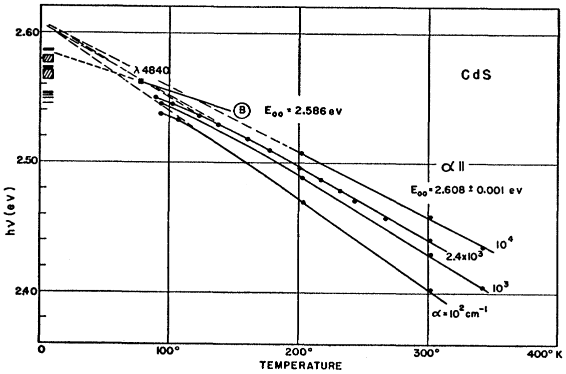

FIG. 5. Temperature shift of the absorption spectrum. A plot similar to Fig. 4 for the $\|$ absorption.

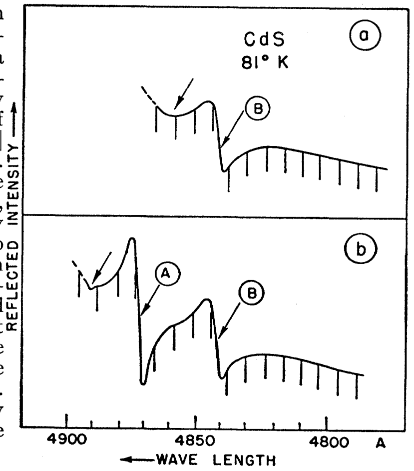

FIG. 6. Reflection spectrum. Reproductions of original data records giving reflected light intensity as a function of wavelength, (a) for $\|$ light, (b) for $\perp$ light. The upturn at the left of each curve, marked by heavy arrows, is due to additional reflection from the second surface, since the crystal becomes transparent at these points. The vertical pips are wavelength markers. Note the similarity of anomaly $B$ in the two polarizations.

The absorption line positions at 90°K are shown also on Fig. 2. The lines coincide very closely with the two absorption edges.

Figure 7 shows similar reflectance data for the $\perp$ polarization, corrected and normalized by the procedure described in Sec. 2 to give absolute values of the reflection coefficient, good probably within a relative error of 10% (in the magnitude of the reflection coefficient).

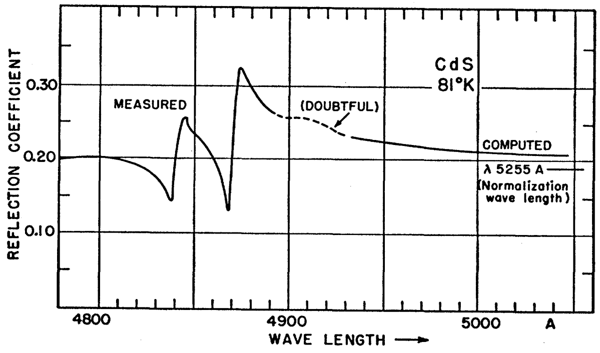

FIG. 7. Reflection coefficient. Data similar to those of Fig. 6, reduced to give approximate absolute values of the reflection coefficient at 81°K, for $\perp$ light. The "computed" part of the curve is based on values of the index of refraction measured from the interference pattern at low temperature.

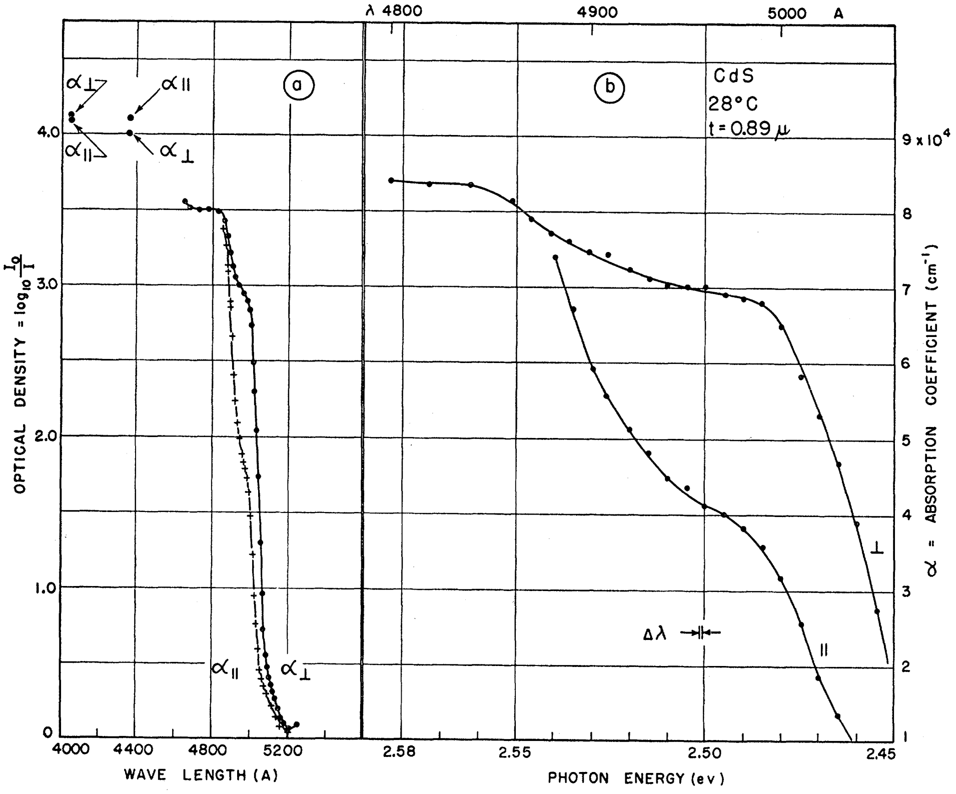

FIG. 8. (a) Absorption spectrum at room temperature, based on measured transmittance of a single specimen 0.89 μ thick The apparent structure at λ 5100 A is an interference effect. (b) Detail of 8(a).

The absorption spectrum at 90°K, near the edge, can be described in summary as follows: an absorption line occurs at λ = 4844 A, about equally strong in both ∥ and ⊥ polarizations, and the ∥ absorption edge appears as the "tail" of this line, with the frequency and temperature dependence of the absorption coefficient given by Eq. (1). A stronger line appears at λ = 4874 A in the ⊥ polarization, is completely absent in the ∥ polarization, and the ⊥ absorption edge appears as the "tail" of this line, again with the frequency and temperature dependence of Eq. (1).

Careful efforts were made to observe additional absorption fine structure at longer wavelengths, for example, by automatic recording of the transmitted light intensity as a function of wavelength in the absorption edge, in crystals of varying thickness. No evidence for any additional structure was found, indicating that any absorption lines present must be orders of magnitude weaker or else very narrow compared to 1 A.

There is some trace of fine structure in the room-temperature absorption spectrum. Figure 8 is a plot of the absorption coefficient on a linear scale, as obtained from a single specimen of thickness 0.89 μ. The slight bump near 5000 A is significant, and the instrumental wavelength resolution is ample to define the shape accurately [Fig. 8(b)]. A linear extrapolation of the λ = 4874 A, 90°K line to room temperature coincides roughly with the position of this bump. A rather interesting feature of the room-temperature spectrum is the wide region from λ = 4840 A to 4660 A in which the ⊥ absorption is constant. Due to instrumental limitations, the ∥ absorption was not measured in this region. A slight further rise occurs toward shorter wavelengths. At λ = 4358 A the ∥ absorption appears to be slightly stronger than the ⊥ absorption.

### C. Miscellaneous Observations

Reflectance measurements were made at low temperature on one large crystal which had been given a good optical polish. The polished surface showed strong specular reflection, but no trace of the fine structure observed on untreated CdS surfaces. This is not too surprising, since the lattice disorder introduced by polishing could easily be equivalent to that produced by warming to 160°K, which also washes out the fine structure.

Attempts were made to observe an effect noted by Gobrecht and Bartschat,[7] namely, a shift of the absorption edge toward longer wavelengths during prolonged illumination, also an apparent shift induced by simultaneous illumination in the infrared around 1 μ. No effects of this kind were observed. In the experiments of Gobrecht and Bartschat, the samples were illuminated by imaging a tungsten filament upon them, and it is possible that the incident radiant flux was sufficient to raise the sample temperature and produce an apparent shift of the edge. A change in the absorption edge subsequent to illumination with green light has been reported by Halperin and Garlick[26]; this is a different effect, presumably associated with the population of impurity levels. It was not observed during the present experiments.

## 4. DISCUSSION

Recently developed analytical models for absorption due to band-to-band transitions[15,19] predict an absorption coefficient varying with frequency essentially as $(h\nu-E_G)^n$, where $n=\frac{1}{2}$ for direct, symmetry-allowed transitions, $n=\frac{3}{2}$ for direct, symmetry-forbidden transitions, and $E_G$ is the band gap. A distinction of this kind has been suggested by Dresselhaus[15] as a possible mechanism for the dichroism of CdS. These edge shapes are based upon a simple $E^{\frac{1}{2}}$ density of states dependence, and would be expected to describe only the weak absorption region where $(h\nu-E_G)$ is small. Indirect transitions, according to the Hall-Bardeen-Blatt theory,[19] lead to a frequency dependence which is essentially $(h\nu-E_G)^2$ or $(h\nu-E_G)^3$ depending on the symmetry of the appropriate wave functions. Elliott[27] has shown that a similar shape might be expected for indirect exciton transitions. Edge shapes of this kind have been observed in several semiconductors, e.g., PbS.[28] In the case of CdS, none of the above functions provides even a partial fit to the experimental data.

The exponential frequency dependence of the absorption coefficient shown by CdS is characteristic of a number of other ionic crystals; there is in fact a striking similarity to the behavior of KBr, which has recently been measured over a wide absorption range by Martiennsen.[29] In each case there is a sharp absorption line with an exponential tail extending over several decades of the absorption coefficient. (One difference which should be noted is that while in KBr the position of the absorption peak, extrapolated to 0°K, agrees with the parameter $E_{00}$ of the absorption tail, this is not quite true for CdS. A better knowledge of the line shape near the peak is required before the significance of this point can be assessed.) No very detailed or satisfactory theory of this property has yet appeared in the literature. Dexter[20] has offered a semiquantitative suggestion of a possible mechanism, based on statistical consideration of the local fluctuations in the band gap energy due to lattice dilatations associated with thermal vibrations. If these fluctuations are taken into account, an absorption tail arises on the long-wavelength side of the band gap, and the shape of this tail resembles an exponential over two decades or so. In principle, the magnitude of the parameter $\beta$ would depend on the magnitudes of the deformation potential constant and of appropriate crystal elastic constants. A similar argument might be expected to apply in the case of exciton transitions. Major difficulties in the quantitative application of this model arise from the necessity for treating lattice dilatations of wavelengths comparable to the Bloch wavelengths of the excited electronic states.

The origin of the absorption dichroism is not clear. A test of the mechanism proposed by Dresselhaus[15] is not possible in this case since the frequency dependence of $\alpha$ predicted by the model is masked by the thermal processes which create the exponential tail. Dexter[20] has suggested that the polarization dependence be accounted for by a difference in the matrix elements for $\perp$ and $\parallel$ transitions; in this case, one would expect the ratio of $\alpha_\perp$ and $\alpha_\parallel$ to be more or less independent of temperature. The experimental results indicate that a more apt description would be the assignment of two different characteristic energies to $\perp$ and $\parallel$ transitions, since the $\alpha_\perp/\alpha_\parallel$ ratio gets very much larger at low temperatures, while the energy separation of the two absorption edges remains almost the same.

From the appearance of the absorption spectrum at 90°K, one is inclined to attribute the fundamental absorption near the edge to exciton transitions very much analogous to those of the alkali halides. The exciton spectrum at this temperature is relatively uncomplicated, consisting of one or two lines depending on the polarization of the light. This viewpoint must be reconciled with the efficient occurrence of photoconductivity on the one hand, and on the other with the spectral dependence reported by Balkanski *et al.*[16] for their exciton diffusion effects, the pertinent feature of the latter being the presence of a prominent excitation band in the yellow red which is not observable in the intrinsic absorption spectrum.

## 5. FURTHER WORK

A number of interesting problems remain to be investigated. The line absorption spectrum becomes considerably more complex at 4°K,[10] with a number of longer-wavelength lines which show variability in strength depending on the sample history.[12] Quantitative measures of the peak absorption coefficients would be of considerable value, and it is hoped that the present investigation can be extended along these lines. It would be interesting to know whether the marked sharpening of the absorption structure continues down to liquid-helium temperature, as presently available data would suggest.

The birefringence of CdS is also of some interest. The most recent measurements of the refractive index[30] show the extraordinary ray $(\mathbf{E}\parallel c)$ as having the larger index, while the stronger absorption is associated with $\mathbf{E}\perp c$. Index measurements made during the present in-

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vestigation by observation of the interference pattern, at shorter wavelengths than those covered by Czyzak *et al.*,[30] show a steeper rise, toward the absorption peak, than that predicted by the Cauchy dispersion formula given by those authors. These observations indicate that some stronger short-wavelength absorption process, perhaps the ultraviolet band observed by Hall,[1] plays a dominant role in the dispersion of CdS, and that the sense of the polarization dichroism is reversed in this region.

The absorption dichroism is probably closely associated with the fluorescence anisotropy observed[23] in the 5205 A emission bands. This emission is thought to arise from a luminescence center which is very weakly bound, so that it is probably the lattice anisotropy, rather than the structural symmetry properties of the center itself, which is responsible for the effect. In this connection, it would be interesting to study the dichroism associated with discrete impurity absorption. Recognizable color centers have not been observed in CdS, but a close analog is the infrared photoconductivity quenching bands[31] which are observable by electrical means.

In their 1955 paper,[10] Gross and Iakobson describe a dependence of the absorption strength on the direction of propagation of the radiation. It is not entirely clear to what extent this effect is related to a polarization dependence. A propagation-vector effect distinct from polarization dichroism has been predicted for certain molecular crystals by Fox and Yatsiv.[32] The effect arises from the possibility of exciton excitation coherent over large volumes of the crystal. This point appears to merit further investigation in CdS.

## 6. SUMMARY

The absorption edge in CdS, over a wide magnitude range of the absorption coefficient, has the frequency and temperature dependence given by the formula

$$\alpha=\alpha_0 \exp-\left[\frac{\beta}{kT}(E_{00}-CT-h\nu)\right].$$

The energy $(E_{00}-CT)$ is closely associated, at least at low enough temperatures, with the position of a sharp absorption line. For light polarized with its $E$ vector parallel to the crystalline $c$ axis, there is one such line, which falls at $\lambda=4844$ A at 90°K. For light polarized with its $E$ vector normal to the $c$ axis, the 4844 A line is again present in about the same strength, and a stronger line appears at $\lambda=4874$ A, shifting the absorption edge toward longer wavelengths. The shape of the absorption edge cannot be interpreted in any detail within the existing theoretical framework of optical absorption in insulating crystals.

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