Exciton Effects in the Electroabsorption of Cadmium Sulfide

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Optical-absorption and electroabsorption spectra of cadmium sulfide have been measured in the vicinity of the fundamental absorption edge at temperatures from 4.2–300°K, using thin-film samples. The optical-absorption spectra show the features characteristic of the single-crystal exciton spectrum. Comparison of the electroabsorption with optical absorption for applied fields up to 5×10^4 V cm^{-1} shows that exciton states are responsible for the electroabsorption. No electroabsorption structure which can be associated unambiguously with band-to-band transitions can be seen for photon energies in the range of 2.4–2.7 eV. Effects associated with bound excitons dominate the electroabsorption at 77°K and below.

I. INTRODUCTION

THE application of electric, magnetic, or stress fields to a solid produces changes in the optical properties which can be related to the energy-level structure of the material. The largest changes are expected to occur at energies corresponding to critical points in the energy-band structure[1] or at other singularities in the electronic density of states, such as excitons.[2] By utilizing synchronous detection techniques which are sensitive only to changes in the optical properties produced by a field, very small effects can be observed experimentally. Optical effects produced by the application of electric fields (electroabsorption[3,4] and reflectance[5,6]) and stress (piezoreflectance[7]) have proved to be very useful in determining critical-point energies and symmetries for a variety of materials. The spectra observed by these techniques have generally been interpreted in terms of optical transitions at critical points in the joint interband density of states.

Handler[8] has suggested that exciton effects may play a significant role in the electroabsorption experiments and should be taken into consideration in the interpretation of such measurements. Changes in the exciton optical absorption resulting from the application of an electric field have been considered from a theoretical standpoint by Seitz[9] and by Tharmalingam.[10] More recently, the problem has been discussed in detail by Duke and Alferieff.[2] Gross[11] and co-workers have studied the Stark effect of the exciton lines in Cu_2O, and Thomas and Hopfield[12] have reported investigation of the Stark

effect of several of the exciton lines in CdS. Other than these experiments, very little investigation of the exciton Stark effect, or electroabsorption, has been performed.

This paper reports measurements of optical absorption and electroabsorption in the exciton region of the CdS absorption spectrum. Cadmium sulfide is particularly suitable for a study of this type since the CdS exciton spectrum has been the subject of extensive investigation[13] and is well understood. The experiments to be described were performed in the temperature range 4.2–300°K with thin-film samples. This facilitates low-temperature measurements and enables high fields to be obtained with low applied voltages. The difficulties associated with the use of electrolytes[6] and p-n junctions[3] are avoided.

Electroabsorption in the long-wavelength tail of the CdS absorption has previously been observed by Boer et al.,[14] Williams,[15] Gutsche and Lange,[16] and Kireev et al.[17] These authors interpreted their results in terms of the photon-assisted tunneling model of electroabsorption considered by Franz[18] and Keldysh.[19] On the basis of this model, Gutsche and Lange[16] deduced an electron effective mass from experiments on CdS at 300°K which is consistent with previously published values. The experimental results of Gutsche and Lange for measurements at 77°K were not consistent with the model of Franz and Keldysh, however. The discrepancy was attributed to exciton effects not considered in the theory.

In addition to the spectral region previously investigated, the present experiments extend the electroabsorption measurements to energies greater than the highest-energy exciton. On the basis of these measure-

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ments it is concluded that the electroabsorption in CdS is dominated by exciton effects, especially bound excitons at low temperatures.

II. EXPERIMENTAL

A. Sample Preparation

The experimental samples were in the form of thin films 0.8–2 μ thick prepared by vacuum evaporation of Eagle-Picher UHP grade CdS upon conducting glass (Nesa) substrates. After evaporation the layers were annealed in sulfur vapor at a pressure of one Torr or in H_2S at atmospheric pressure at 400–500°C for 1 h. The resistivity of these samples was found to be 10^8–10^{10} Ω cm with very little photosensitivity. The x-ray diffraction pattern of samples prepared in this way showed that the films, though polycrystalline, had the wurtzite structure and were oriented with the C axis normal to the substrate. This result is in agreement with the observations of Behringer and Corrsin[20] and Foster,[21] who studied the orientation of evaporated CdS films.

The thickness of the films was determined from the wavelength difference between optical-interference maxima and minima by standard techniques. The refractive-index data of Cyzak et al.,[22] were used in this measurement.

Sample preparation was completed by the evaporation of a 150 Å transparent gold film on the surface of the CdS, to form a sandwich structure. The gold film and the Nesa coating of the glass served as electrodes for the application of an electric field to the CdS.

B. Apparatus

The experimental arrangement used was similar to that described by Chester and Wendland.[3] The sample was placed in an Andonian Associates variable-temperature optical Dewar system. Optical-absorption spectra were obtained with a Cary Model 14 Recording Spectrophotometer. A Leiss double monochromator with flint prisms was used as the light source for the electroabsorption measurements. The change in optical transmission resulting from the application of a unidirectional square-wave voltage at a frequency of 10^2–10^4 Hz between the Nesa and gold electrodes was measured. An EMI Type 6592B photomultiplier tube was used as the photodetector, with signal recovery performed by a Princeton Applied Research Model HR-8 lock-in amplifier synchronized to the electric field. The photomultiplier-tube supply voltage was adjusted automatically by a feedback circuit to keep the dc anode current of the photomultiplier tube constant as the monochromator swept through regions of varying absorption coefficient. The anode current was measured with an electrometer. The

output signal from the lock-in amplifier was thus directly proportional[4] to $\Delta\alpha$, the change in absorption coefficient resulting from the application of the electric field. The $\Delta\alpha$ signal was plotted on a strip chart recorder with wavelength markers supplied by the monochromator.

Measurements were performed alternately with the sample at the entrance and exit slits of the monochromator, i.e., with white-light or monochromatic illumination, for comparison. It was hoped in this manner to determine whether the measurements were being influenced by photoconductivity. No significant difference in the results obtained by the two methods was observed.

III. RESULTS

A. Optical Absorption

The valence band of CdS is divided into three two-fold-degenerate levels by the spin-orbit interaction and crystal-field splitting.[23] The conduction band at $k=0$ is simple and has S-like symmetry. Optical dipole transitions from the uppermost valence band to the conduction band, or exciton states formed from conduction-band wave functions at $k=0$, are allowed only if the electric-field vector of the light is perpendicular to the crystalline C axis $(E{\perp}C)$.[13] Dipole transitions originating from the lower two valence bands are allowed for either $E{\perp}C$ or $E{\parallel}C$.[13]

The optical-absorption spectra were measured with the crystalline C axis parallel to the propagation vector of the incident light, since the films are formed with the C axis normal to the sample substrate. For this geometry the electric-field vector of the light is perpendicular to the C axis and the absorption spectrum characteristic of $E{\perp}C$ is observed. The absorption spectra were measured with films of 1000, 4000, and 8000 Å thickness. The latter thickness was the maximum for which optical-absorption data could be obtained and yielded the best-defined spectra. Although the absorption peak energies for the thinner films were in agreement, only the data for the 8000 Å films are presented.

The absorption spectra measured at 300, 195, 77, and 4.2°K are shown in Fig. 1. The effects of thermal broadening on the structure are clearly evident. The lines observed in the 77 and 4.2°K spectra are assigned the designations used by Thomas and Hopfield.[13] A, B, and C are the so-called intrinsic, or free, exciton lines, and the subscripts on these letters denote the principal quantum numbers of a hydrogenic series. The three series arise from exciton transitions originating in each of the three valence bands. The lines designated by an I with a subscript correspond to the energy levels of exciton states bound to various types of crystalline defects.[24]

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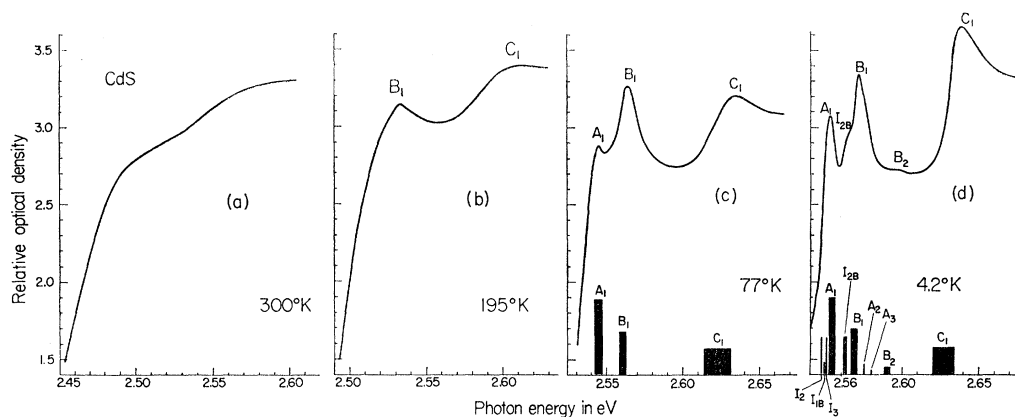[24] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).

FIG. 1. Optical-absorption spectra of an 8000 Å film of CdS, showing exciton lines observed at several temperatures. The lines along the abscissa of curves (c) and (d) give energies, widths, and relative intensities of the lines studied by Thomas and Hopfield in single crystals. The lines are labeled according to the notation of Thomas and Hopfield.

For comparison, the exciton linewidths and relative intensities observed by Thomas and Hopfield[13] in reflectivity measurements with single crystals are indicated by the widths and heights of the lines plotted along the abscissas of the 77 and 4.2°K data. The bound-exciton lines were observed by Thomas and Hopfield[24] and Gross[11] to be much narrower than the intrinsic lines. The bound-exciton lines in the thin-film samples seem to be considerably broader and less well-defined than those observed in the single crystals. The broadening is real and is not a consequence of the slit width used in making the absorption measurements. The absorp-

tion spectra of the films exhibited a long-wavelength tail, which lies below the minimum energy of the abscissas in Fig. 1, which is not characteristic of the single crystals. These effects are probably the result of imperfections associated with the surfaces and with grain boundaries.

It was difficult to estimate the absorption coefficients at the spectral peaks since the optical density of the films was greater than 3.5. Consequently, a very small amount of stray light resulting from scattering within the optical Dewar or microscopic pinholes in the film can easily invalidate such measurements. However, it is possible to conclude that the absorption coefficient at the intrinsic exciton absorption peaks is greater than 10^5 cm^{-1}. Since the peak height cannot be determined accurately, it is also difficult to measure the linewidth. Observed linewidths for the A_1, B_1, and C_1 lines in Figs. 1(c) and 1(d) seem to be consistent with those measured by Thomas and Hopfield,[13] however.

The absorption spectrum measured at 300°K is very similar to that obtained by Dutton[25] for a single crystal. In the 4.2°K absorption spectrum, some structure at the energies corresponding to the I_1 and I_2 lines[24] is observed. If the linear portion of the low-energy tail of the A exciton absorption is extrapolated to a low absorption coefficient, the structure of the I_1 exciton line becomes visible. The absorption associated with this line is estimated by taking the difference between the measured absorption and the extrapolated tail, and is plotted in Fig. 2. The energy at the absorption peak, 2.539 eV, is at slightly higher energy than the value of 2.536 eV measured by Thomas and Hopfield[24] for single crystals.

It is possible to estimate the total number of states involved in the I_1 absorption by application of Smakula's[26] formula to the absorption peak of Fig. 2. On assuming an oscillator strength $f=1$, an index of refraction $n=2.5$,[22]
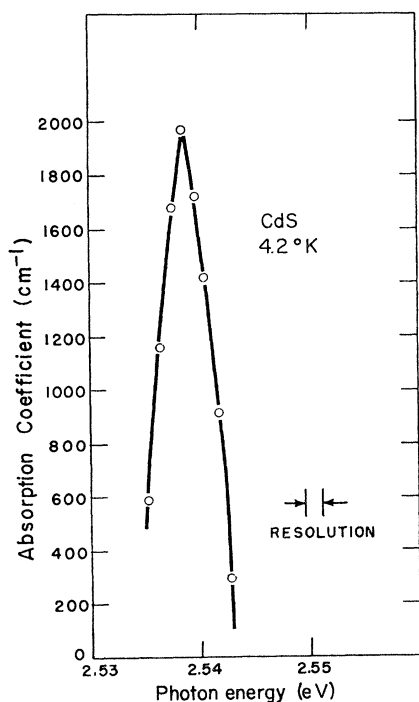

FIG. 2. Absorption spectrum of the I_1 line at 4.2°K in an 8000 Å film of cadmium sulfide.

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a peak absorption coefficient $K_{max}=1970$ cm^{-1}, and a half-width $H=0.005$ eV, we calculate a density of centers

$$N=\frac{1.29\times10^{17}n}{(n^2+2)^2 f}, \quad K_{max}H=4.8\times10^{16} \text{ cm}^{-3}.$$

Thomas and Hopfield[24] have suggested that the I_1 absorption line is associated with an exciton bound to a cadmium vacancy. Annealing the films in an atmosphere with a high sulfur pressure should produce cadmium vacancies and enhance the I_1 absorption line. A density of cadmium vacancies of the calculated magnitude could reasonably be produced during the annealing process.

Some optical absorption associated tentatively with the I_{2b} and the $n=2$ level of the B exciton is also observed at 4.2°K. This assignment is made on the basis of comparison with the data of Ref. 24. The B_1 and C_1 peaks lie at slightly higher energies than those measured by Thomas and Hopfield, whereas the observed A_1 peak lies approximately 1.5 meV below their value. Gross[11] observed that crystalline strain tended to shift the CdS exciton lines toward higher energy. The thin-film samples are probably strained as a result of differential contraction between the substrate and the CdS upon cooling, and this could result in a discrepancy between the energies of the exciton lines in the films and single crystals.

B. Electroabsorption

The electroabsorption measured at 300°K is shown in Figs. 3(a) and 3(b) for applied fields of 1.3×10^4 and 6.5×10^4 V/cm, respectively. The three-line spectrum is very similar to that predicted by Seraphin[27] for an allowed transition between parabolic energy bands, i.e.,
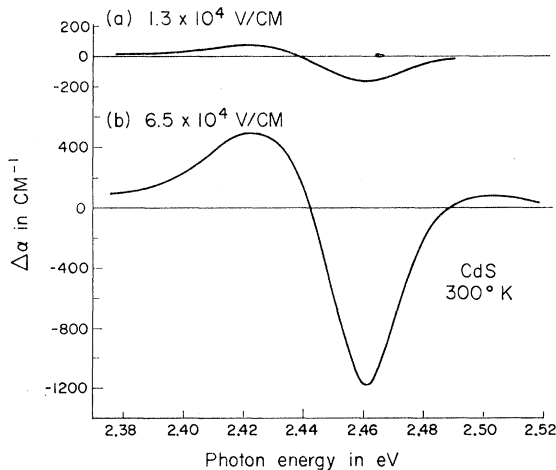
a type M_0 critical point[1] in the joint density of states, if the measurement is performed at a temperature high enough for lifetime broadening to be effective. However, the energy of the negative peak does not shift with field as expected for an M_0 absorption edge. For such a transition Chester and Fritsche[28] have shown that the energy at the negative peak should increase as the $\frac{2}{3}$ power of the electric field. Instead, the observed energy of the negative peak is nearly independent of field. Furthermore, the peak width does not exhibit the field broadening expected for an M_0 absorption edge, since the peak width is nearly independent of field strength. Thus, the electroabsorption does not seem to be associated with band-to-band transitions at a type M_0 critical point. However, the peak position and width should be expected to be independent of field for exciton electroabsorption. This is so because the negative electroabsorption peak will occur at the exciton peak and should have approximately the width of the original exciton-absorption line.[2]

As the temperature is decreased, the electroabsorption spectrum develops additional structure, as shown in Figs. 4–6, which illustrate the results at 195, 77, and 4.2°K, respectively. The exciton energies obtained from the absorption data of Fig. 1 are indicated on the curves by arrows. On the basis of the photon-assisted tunneling model of the band-to-band electroabsorption, the negative peak would be expected at approximately the energy of the band gap.[27] The energy of the band gap can be estimated by assuming a temperature-independent binding energy for the A and B excitons of 0.028 eV, the value measured at 4.2°K by Thomas and Hopfield. The gap energy is then approximately 0.011 eV above the B_1 peak, giving values of 2.54, 2.57, and 2.58 eV at 195, 77, and 4.2°K, respectively. For all three temperatures, the large negative peak is at a significantly lower energy than the band gap. A comparison of the peak positions with the exciton energies obtained from Fig. 1 shows that the electroabsorption is
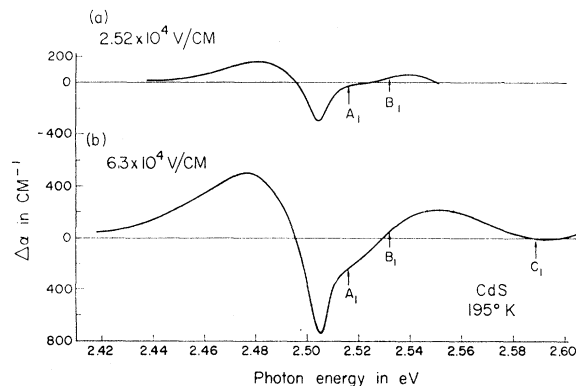

FIG. 3. Electroabsorption spectrum of 1.55-μ cadmium sulfide film at 300°K for applied electric fields of (a) 1.3×10^4 V cm^{-1}, and (b) 6.5×10^4 V cm^{-1}.
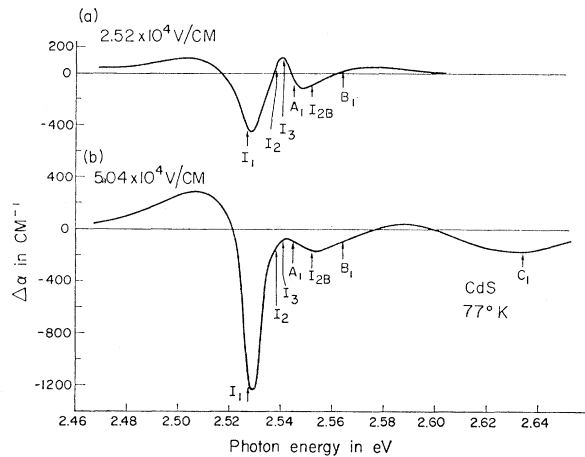

FIG. 4. Electroabsorption spectrum of 1.59-μ cadmium sulfide film at 195°K for applied electric fields of (a) 2.52×10^4 V cm^{-1}, and (b) 6.3×10^4 V cm^{-1}.

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[28] M. Chester and L. Fritsche, Phys. Rev. **139**, A518 (1965).

FIG. 5. Electroabsorption spectrum of 1.59-μ cadmium sulfide film at 77°K for applied electric fields of (a) 2.52×10^4 V cm^{-1} and (b) 5.04×10^4 V cm^{-1}. Exciton energies deduced from the thin-film optical absorption spectra are indicated by the arrows.

associated with the excitons rather than with the band-to-band absorption. This is especially evident in the 4.2°K electroabsorption spectrum of Fig. 7. The band gap energy at 4.2°K, 2.582 eV,[13] is not associated with the prominent electroabsorption structure. That there is no structure in the electroabsorption spectrum at the gap energy is not so surprising since there is no apparent structure in the optical absorption which can be related to the gap energy as seen in Fig. 1.

The large negative peak in the 4.2°K electroabsorption spectrum agrees very closely in energy with the I_1 exciton line, as seen by comparison with Fig. 3, and is therefore quite probably related to it. The linewidths of the I_1 absorption and electroabsorption spectra also agree very closely at 4.2°K. At 77°K the energy of the I_1 line, as indicated by the arrow in Fig. 5, is deduced
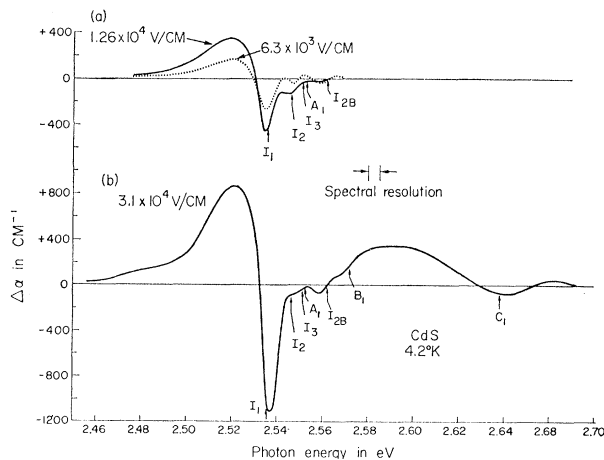

FIG. 6. Electroabsorption spectrum of 1.59-μ cadmium sulfide film at 4.2°K, with applied electric fields of (a) 1.26×10^4 V cm^{-1} (solid curve) and 6.3×10^3 V cm^{-1} (dashed curve), and (b) 3.1×10^4 V cm^{-1}. Exciton energies deduced from the thin-film optical absorption spectrum at 4.2°K are indicated by the arrows.

from the data of Thomas and Hopfield[13] by assuming the energy difference between the A_1 exciton and I_1 exciton to have a temperature-independent value of 0.017 eV. Structure associated with the I_2 and I_{2b} lines is also seen in the 4.2°K electroabsorption spectra. No prominent structure associated with the intrinsic A_1 and B_1 lines is observed, although there is a broad negative peak at the energy of the C_1 exciton at 4.2, 77, and 195°K. In studies of the Stark effect in Cu$_2$O, Gross[11] observed very little effect on the $n=1$ and 2 lines of the "yellow" exciton series for fields less than 5×10^4 V/cm. The binding energy of the $n=2$ line in Cu$_2$O is 0.022 eV compared with 0.028 eV for the A_1 and B_1 lines of CdS. Since the Stark shift of the absorption
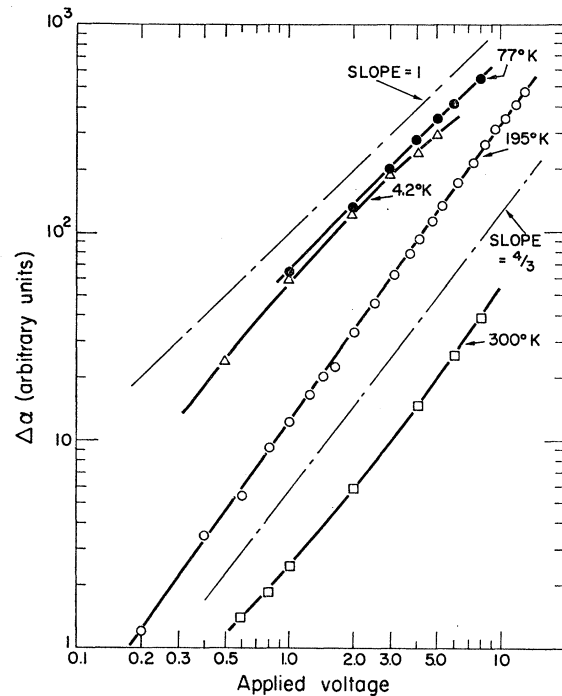

FIG. 7. Magnitude of the low-energy positive electroabsorption peak as a function of applied electric field at several temperatures: (a) $T=300°K$; (b) $T=195°K$; (c) $T=77°K$; (d) $T=4.2°K$.

line is expected to vary as the reciprocal square of the exciton binding energy,[9] a proportionately smaller effect would be expected for A_1 and B_1 lines CdS than for the $n=2$ lines of Cu$_2$O.

The strong electroabsorption of the I_1 line can be understood in terms of the model (deduced by Thomas and Hopfield[24]) in which a bound exciton is responsible for the I_1 absorption. These authors attributed the I_1 absorption to an A_1 exciton bound to a neutral acceptor, i.e., an acceptor state containing a hole. This entity can absorb a photon to produce a complex consisting of an electron and two holes trapped at the acceptor site, a complex analogous to a H$_2^+$ molecular ion. If it is assumed that the electron binding energy is the same

as for the free exciton, 0.028 eV, the binding energy of the highest energy hole is approximately the energy difference between the A exciton and the I_1 exciton, 0.013 eV, as deduced from the optical-absorption data of Fig. 1(d) and Fig. 2. It might be expected that the exciton would be destroyed by the tunneling of the hole into the valence band with an applied field lower than that required to ionize the free exciton due to the lower binding energy of the hole.

A detailed interpretation of the experimental results in terms of the theory of exciton electroabsorption has not been successful. The theories based upon a hydrogenic model[2,29] do not yield the proper electric-field dependence for the dominant peaks of the electroabsorption spectrum. The electroabsorption linewidths and energies have already been shown to be inconsistent with the predictions of the photon-assisted tunneling model of the band-to-band electroabsorption process. Since the dominant observed structure is associated with the I_1 exciton, a three-body excitation, the hydrogenic model could not be expected to apply. The qualitative features of the hydrogenic model, line broadening and quenching, should still be observed, however, as they are.

The electric-field dependence of the low-energy positive electroabsorption peak height is shown in Fig. 7 for several temperatures. At 300 and 195°K, the peak height is seen to obey a nearly $\frac{4}{3}$-power dependence upon electric field. The peak height increases approximately linearly with field at 77 and 4.2°K. The 300°K result is in disagreement with the nearly square-law dependence noted by Gutsche and Lange[16] in single crystals. These authors, however, observed at 77°K that the field dependence of the positive $\Delta\alpha$ peak magnitude was less than the square law observed at room temperature. They attributed this to an exciton contribution to the optical absorption.

Cadmium sulfide exhibits an Urbach-rule[30] absorption edge in the temperature range 90–340°K.[25] It has been proposed by Segall[31] with both theoretical and experimental support that the Urbach-rule edge in CdTe can be accounted for in terms of phonon-assisted direct exciton transitions. Thomas *et al.*[32] have presented some evidence for the occurrence of this process in CdS as well.

In their consideration of the electroabsorption of phonon-assisted band-to-band transitions, Tharmalingam,[10] Penchina,[33] and Yacoby[34] have predicted a $\frac{4}{3}$-power field dependence of the low-energy positive electroabsorption peak. That these theories should also

apply to phonon-assisted exciton transitions has not been demonstrated. However, the observed dependence of the low-energy electroabsorption peak upon field in the Urbach-rule temperature region is not inconsistent with the explanation of this absorption behavior in terms of phonon-assisted direct excitons.

Since the electric field is applied in the direction of the C axis, a piezoelectric strain will be produced in the cadmium sulfide which, in turn, produces a shift in the energy of the band gap and exciton energies. An effect similar to the observed electroabsorption would result if the energy-gap change were of the order of the exciton binding energy. The magnitude of such an effect can be estimated and compared with the 4.2°K electroabsorption. Langer[35] has measured the change in refractive index of crystalline CdS with hydrostatic pressure and has found the shift in absorption-edge energy with pressure to be given by $\Delta\mathcal{E}=K_1T$, where T is the hydrostatic pressure (stress) and $K_1=4.45\times10^{-12}$ eV cm²/dyn. It will be assumed that the change in the energy of the absorption with uniaxial stress along the C axis is of the same order of magnitude. Uniaxial stress and strain are related by $T_3=c_{33}S_3$, where T_3 and S_3 are the C-axis stress and strain, respectively, and c_{33} is the elastic constant relating a C-axis strain to a C-axis stress. The C-axis strain can be calculated from the known value of electric field and the appropriate piezoelectric constant[36]:

$$S_3 = -\epsilon_3 E_3/e_{33},$$

where ϵ_3 is the dielectric constant, E_3 is the electric field in the direction of the C axis, and e_{33} is the piezoelectric constant. From these relations we have the change in energy gap $\Delta\mathcal{E}$ resulting from the application of an electric field E_3:

$$\Delta\mathcal{E} = -K_1 c_{33}\epsilon_3 E_3/e_{33}.$$

Using the values $K_1=4.45\times10^{-12}$, $c_{33}=9.39\times10^{11}$ dyn/cm²,[37] $\epsilon_3=10.22$, $e_{33}=0.49$ C/m², and $E_3=3.6\times10^6$ V/m—the value of the electric field from Fig. 7(b)— we find that $\Delta\mathcal{E}\cong2.5\times10^{-3}$ eV.

If it is assumed that the exciton energies shift by the same amount, such a shift is too small to account for the observed changes in absorption spectrum. It is concluded that the major change in absorption results from the electric field and not from the piezoelectrically induced strain.

IV. CONCLUSION

At 300°K, the electroabsorption spectrum of CdS exhibits a line shape very similar to that expected for an interband optical transition. However, the field independence of the linewidth and the position of the

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[37] W. P. Mason, *Crystal Physics of Interaction Processes* (Academic Press Inc., New York, 1966), p. 67.

dominant negative peak of the electroabsorption spectrum do not agree with the theory for the band-to-band electroabsorption process. Instead, the behavior is more nearly that expected for the electroabsorption of an exciton state. Measurements performed at lower temperatures, 195, 77, and 4.2°K, display spectra with the same field-independent linewidth and position of the dominant negative peak. Comparison of the electroabsorption with optical absorption shows clearly the correlation of the exciton-absorption and electroabsorption peaks. On this basis it is concluded that the electro-optical properties of cadmium sulfide are dominated by exciton effects at temperatures below 300°K.

Note added in proof. Recently published work of Gutsche and Lange[38] has also demonstrated a relationship between exciton states and the electroreflectance spectra of CdS and CdSe single crystals.

Piezoabsorption of Germanium Thin Films above the Fundamental Energy Gap*

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Reported here are measurements at 300 and 80°K of the stress-modulated absorption between 2 and 5 eV of thin polycrystalline films of Ge deposited directly on quartz transducers. Changes in the index of refraction and extinction coefficient as well as changes in the real and imaginary part of the dielectric constant due to the applied periodic strain are calculated. Strong polarization effects are observed for polarizations parallel and perpendicular to the strain axis. These effects are explained in terms of different contributions of the piezo-optic tensor components to the change in the real and imaginary parts of the dielectric-constant tensor. Temperature coefficients of the Λ spin-orbit-split transitions and the Σ-X transitions are reported. A transition at 3.1 eV which has a temperature coefficient of $(-2.3\pm0.4)\times10^{-4}$ eV/°C is also discussed.

I. INTRODUCTION

I N recent years, optical-modulation experiments have become increasingly important in the study of weak optical structure. The main techniques used have been electric field modulation and stress modulation, though energy[1] and temperature[2] modulation have also been reported. Here we report for the first time the stress-modulated absorption of polycrystalline germanium films in the 2–5 eV spectral region and determine the temperature coefficients of several peaks. Stress-modulated *reflection* experiments on germanium,[3,4] silicon,[4,5] and the noble metals[3] have been described previously, as well as stress-modulated absorption near the funda-

mental absorption edge in germanium and silicon using bulk samples.[6] Except for energy modulation, which under proper experimental conditions is essentially a differential technique, these techniques require a periodic variation of a physical parameter of the solid. Since the optical properties are affected differently by the various modulation methods, interpretation of the resulting data is not straightforward, and considerable care in data reduction is generally required to obtain information about the band structure from the experimental results. In the piezoabsorption experiments reported here, we find that far above the fundamental absorption edge, the observed signal $\Delta I/I_0$ is to a reasonable approximation directly related to the change in the extinction coefficient k and hence to the change in the absorption coefficient α.

Band parameters are, however, more directly related to ϵ_2, the imaginary part of the dielectric constant, which for a given interband transition is proportional to the product of the oscillator strength of the transition and the interband joint density of states. In Sec. III we calculate the changes due to strain in the real and

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