We can formally add to this expression all analogous terms arising from the other symmetrized valence wave functions $\psi_{nl}{}^{\beta}$ with $\beta \neq \alpha$ since their cross product with $S_i{}^{\alpha}$ is zero, and then because of the unitary property of the transformation on the Y_{lm}'s this last equation can be written

$$(S_q{}^{\alpha},\psi_{nl}{}^{\alpha})(\psi_{nl}{}^{\alpha},S_p{}^{\alpha}) = [O_{nl}{}^{\alpha}(\mathbf{k})]^{-1}\sum_i\sum_j a_{qi}{}^{\alpha *}a_{pj}{}^{\alpha}A_{nl}A_{nl}(|\mathbf{k}+\mathbf{h}_i|)^* \times A_{nl}(|\mathbf{k}+\mathbf{h}_j|)[4\pi/(2l+1)] \times\sum_m Y_{lm}(\theta_j,\varphi_j)^*Y_{lm}(\theta_i,\varphi_i). \quad \text{(A7)}$$

From the addition theorem of spherical harmonics this becomes

$$(S_q{}^{\alpha},\psi_{nl}{}^{\alpha})(\psi_{nl}{}^{\alpha},S_p{}^{\alpha}) = [O_{nl}{}^{\alpha}(\mathbf{k})]^{-1}\sum_i\sum_j a_{qi}{}^{\alpha *}a_{pj}{}^{\alpha} + A_{nl}(|\mathbf{k}+\mathbf{h}_i|)^*A_{nl}(|\mathbf{k}+\mathbf{h}_j|)P_l(\cos\omega). \quad \text{(A8)}$$

In (A8) ω is the angle between $\mathbf{k}+\mathbf{h}_i$ and $\mathbf{k}+\mathbf{h}_j$.

Formula (A8) has been given by Herring for the particular case of nonoverlapping core states $[O(\mathbf{k})=1]$.

The present derivation makes use of the symmetry of the lattice from the beginning and allows one to treat orthogonalization to valence states in the same way as orthogonalization to nonoverlapping core states. This procedure can be made more general to include the case of mixing of wave functions with different angular quantum numbers in the valence states.

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A Magneto-Stark Effect and Exciton Motion in CdS*

D. G. THOMAS
Bell Telephone Laboratories, Murray Hill, New Jersey

AND

J. J. HOPFIELD†
Laboratoire de Physique, Ecole Normale Superieur, Paris, France, and Bell Telephone Laboratories, Murray Hill, New Jersey

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Exciton absorption occurs, for weak exciton lines, at an energy which is the energy of an exciton having a wave vector equal to that of the light in the medium. These excitons have a finite wave vector, and therefore, a finite velocity. In a uniform magnetic field, the Lorentz force on the electron and hole due to the center-of-mass velocity produces a magnetic perturbation in addition to those ordinarily considered. The measurement of such a perturbation measures the velocity of an exciton of known wave vector, and therefore determines the total exciton mass. In addition, the measurement of this effect which depends on the exciton velocity provides a positive distinction between exciton absorption lines and absorption lines due to impurities. It is shown that this perturbation can be measured by the measurement of the Stark effect on excitons in the presence of a uniform magnetic field. The exciton mass for the $n=2$ states of excitons formed from the top valence band in CdS was measured by this technique, and found to be 0.92 ± 0.18 in reasonable agreement with the mass calculated from independent experiments. The Stark effect in the absence of a magnetic field was also studied to ensure an understanding of the effect in the presence of a magnetic field. The stark effect in a magnetic field sometimes exhibits peculiar behavior which was attributed to an extraneous Hall field. This interpretation gives an estimate of $\omega_c\tau_r\approx 2$ for electrons in "good" CdS crystals at 1.6°K and at 31 000 gauss.

I. INTRODUCTION

THE optical absorption of insulating crystals having a direct band gap is often dominated, at energies near the band gap, by the absorption due to excitons. These bound electron-hole pairs cause a series of discrete absorption lines below the band gap. Many experiments have been performed to try to demonstrate exciton motion or the current-free transport of energy by excitons. These experiments have, by and large, been marginal and ambiguous.

Recent work by Hopfield and Thomas[1,2] in CdS and by Gross[3] in Cu_2O has shown that the finite wave vector of light having band-gap energies can produce easily observed effects on the selection rules for exciton transitions. Although both experiments could be most easily interpreted on the basis of exciton states, the finite wave vector of the light can produce similar effects on the absorption due to impurity atoms.

The present experiments describe the measurement of the *velocity* $\mathbf{v}$ of an exciton of known wave vector. The possibility of such experiments[1] and early experimental work[4,5] has been previously reported. The experiments

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† Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

[1] J. J. Hopfield and D. G. Thomas, Phys. Rev. Letters **4**, 357 (1960).

[2] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

[3] E. F. Gross and A. A. Kaplyanskii, Fiz. Tverdoga Tela USSR **2**, 379 (1960) [translation: Soviet Phys. Solid State **2**, 353 (1960)].

[4] D. G. Thomas and J. J. Hopfield, Phys. Rev. Letters **5**, 505 (1960).

[5] J. J. Hopfield and D. G. Thomas, Proceedings of the International Conference on Semiconductors, Prague, 1960 [Czech. J. Phys. (to be published)].

demonstrate that the absorption lines studied represent excitons, not impurities (for the effect depends on the velocity of the exciton). The experiments also measure the effective mass of the exciton through the measurement of the relation between the velocity and the momentum of an exciton. The following section shows the theoretical possibility of such a measurement.

II. THEORY

Consider a bound electron-hole pair in the effective-mass approximation for a band structure having non-degenerate bands and a vertical band gap. The electron and hole motion can be factored into the reduced-mass motion and the center-of-mass motion. The exciton states are characterized by a center-of-mass wave vector $\mathbf{k}$ and orbital quantum numbers representing the internal motion. Each internal state generates a band of states having all possible $\mathbf{k}$ and a parabolic dependence of the energy on $\mathbf{k}$ for small k. The energy of the ith level is thus

$$E_i(\mathbf{q})=E_i+\hbar^2k^2/2M_{\text{ex}};\ M_{\text{ex}}=m_e+m_h,$$

with suitable trivial modifications for the case of non-spherical bands. m_e and m_h are the electron and hole effective masses, respectively.

A uniform magnetic field produces three different perturbations on the exciton energy levels. The first is the ordinary Zeeman effect, and the second the ordinary diamagnetic shift of the energy levels. There exists, also, a third effect (there is a derivation of this perturbation in reference 2) due to the center-of-mass motion of the exciton in the magnetic field. This perturbation is equivalent to the effect of an electric field, E_q,

$$\mathbf{E}_q=(\hbar\mathbf{k}/M_{\text{ex}}c)\times H=\frac{1}{c}\mathbf{v}\times\mathbf{H} \qquad (1)$$

on an exciton at rest. This perturbation represents the effect of the oppositely directed Lorentz forces on the electron and hole due to the center-of-mass motion.

Conservation of wave vector demands that light of wave vector $\mathbf{k}$ can directly create only excitons of the same wave vector. In the case of excitons coupled very weakly to the light (i.e., excitons which cause very weak absorption lines), the index of refraction and the wave vector of the light are well defined at the exciton absorption line. The energies of the absorption lines will therefore be the energies of excitons which have the wave vector $\mathbf{k}$ of light of the absorption-line energy in the crystal. In the magneto-optics of excitons, the perturbing quasi-field E_q is always present due to the finite wave vector of the light.

The perturbation produced by $\mathbf{E}_q$ is normally by far the smallest of the three magnetic perturbations, and it is quite difficult to isolate the effect from the other magnetic perturbations by analyzing the exciton energy levels in a magnetic field. To avoid this difficulty and the necessity of a detailed analysis of the energy levels, we have made use of an electric balancing technique.

The Stark effect on excitons is dominated by the simple "hydrogenic" Stark effect in the effective-mass approximation. For an exciton of zero wave vector, all Stark-effect energy shifts should thus be a function only of the absolute value of the electric field. All energy levels will be the same for an applied laboratory field $\mathbf{E}$ and for $-\mathbf{E}$, and the exciton energy level spectrum will be symmetric about $\mathbf{E}=0$. The same argument holds even in the presence of a uniform magnetic field, and follows from the inversion symmetry of the effective-mass Hamiltonian. An exciton of finite wave vector $\mathbf{k}$ feels in addition to the applied external electric field $\mathbf{E}$ the quasi-field $\mathbf{E}_q$. If $\mathbf{E}_q$ and $\mathbf{E}$ are arranged to be collinear, E_q can be directly measured as follows. The Stark shift is plotted against the applied electric field $\mathbf{E}$; in the absence of a magnetic field the figure will have a plane of symmetry at $\mathbf{E}=0$. In the presence of a magnetic field the plane of symmetry occurs not at zero applied field but at a value E_s, and $E_s=-E_q$. The quasi-field E_q can thus be measured without the need for an analysis of the energy level spectrum.

III. EXPERIMENT AND EXPERIMENTAL RESULTS

Observations were made at 1.6°K on the second main quantum state ($n=2$ state) of the exciton derived from the top valence and conduction bands of hexagonal CdS. CdS was chosen because its exciton level structure is well understood, and because it has sharp exciton absorption lines corresponding to states of suitable radius for the measurement of the Stark effect. The states are observed as weak absorption lines in light polarized parallel to the hexagonal axis. The spectra were recorded photographically using a Bausch & Lomb spectrograph having a dispersion of 2 A/mm; microphotometer traces of the spectra were made from the photographic plates. The crystals were immersed in the refrigerant between the pole pieces of a magnet $\frac{5}{8}$ in. apart. As the effects observed were not large it was essential to use crystals which gave sharp $n=2$ exciton lines; the crystals were 5–10 μ thick. Only a few crystals were found to be suitable; some of these came from outside laboratories and some were grown at the Bell Telephone Laboratories. Crystals were grown at the Bell Laboratories by passing argon at one liter/min over purified CdS held at about 1140°C; the crystals formed farther down the quartz tube in a region at about 1000°C. The quality of the crystals, which were stuck with a minimum quantity of glue to small glass plates, could be judged from the spectra taken at 4.2°K. Although efforts were made to produce good quality crystals consistently, no satisfactory method was found. The use of pure starting material appeared to help, but the physical conditions during growth seemed to be more important since, when good crystals were found, they occurred in the same batch among many poor crystals.

Subsequent annealing of the crystals in an inert atmosphere made little difference, and high temperature treatment in sulfur vapor decreased the quality, both broadening the lines and increasing the background absorption.

As explained in Sec. II the quasi-electric field can be detected by opposing it with an applied electric field. Initial attempts were made to apply this field by evaporating contacts onto the crystal and passing a dc current through it while the crystal was illuminated and photoconductive (the dark conductivity of the crystals is very low). A Stark effect was observed using this method. This arrangement, however, was not satisfactory; strain associated with the contact area broadened the lines, there appeared to be an uneven distribution of the field along the crystals, and the contacts were not always Ohmic. Consequently a method was used in which no contacts were made to the crystal. The crystal was held between two metal plates 0.61 cm in diameter and 0.43 cm apart. (See Fig. 1.) A potential difference between the plates formed an electric field E. The crystals were several millimeters long and about 10 μ thick; they were held on glass plates which were of similar length and were 0.023 cm thick. The long dimensions were parallel to E so that near the center of the crystal the distortion in E produced by end effects could be neglected, provided that electrostatic shielding due to the crystal conductivity is eliminated. Since the crystals are photoconductive it is necessary to apply a square-wave voltage to the plates with a time interval less than the effective dielectric relaxation time of the crystal to avoid polarization. Since it is necessary to observe the effects separately for the electric field in both negative and positive directions, the light falling on the photographic plate is shuttered for one phase of the square wave. This was done by revolving a single

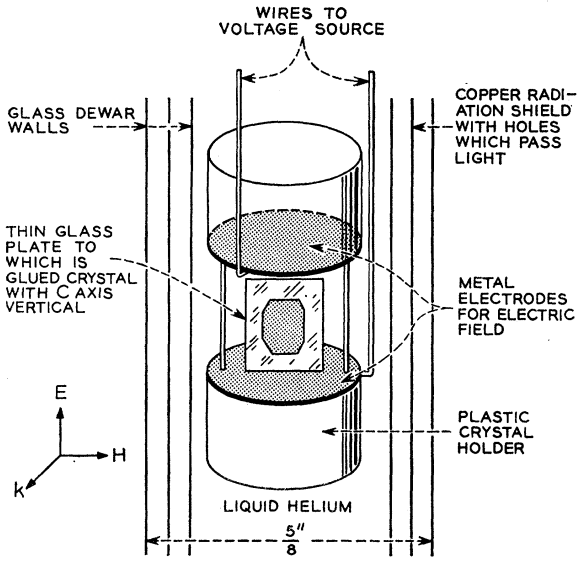

FIG. 1. Detailed view of crystal holder assembly.

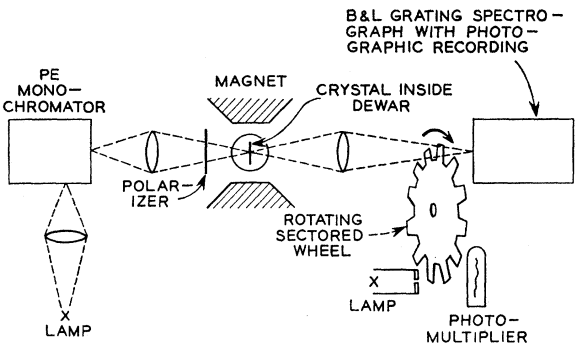

FIG. 2. Schematic diagram of the apparatus used. The signal from the photomultiplier is used to control the voltage applied to the crystal electrodes shown in Fig. 1.

sectored disk immediately in front of the entrance slit of the spectrograph; a commutator on the same shaft switched the voltage. A pulse length of 2 msec was reached by this means. However, higher frequencies were necessary and these were obtained by using a disk nine inches in diameter revolving at speeds up to 10 000 rpm, in which were cut near its periphery 16 rectangular holes. (See Fig. 2.) The holes allowed the light to fall on the entrance slit and allowed another beam of light to fall onto a photomultiplier. The signal from the photomultiplier was amplified and used to vary the grid potential on a 6293 tube. The square wave signal for the condenser plates was obtained from a 2400-ohm load resistor in the output circuit of the 6293. The wave shape was improved by adjusting the inductance of the load resistance. The speed of the rotating disk set a limit of 200 μsec on the square wave duration.

In other experiments, a variable rectangular pulse generator was used to provide the electric field, and the light was not chopped. By adjusting the relative lengths of the two halves of the rectangular wave the quasi-field can be measured, though less directly than in experiments with chopped light. Using this system, it was possible to apply to the condenser plate a rectangular waveform having a period as short as 6 μsec and a potential as high as 600 v.

The crystal was illuminated with a narrow spectral band of light from a Perkin-Elmer double-pass quartz prism spectrometer, centered on the exciton wavelength. In addition a polarizer passing light with its E vector parallel to the hexagonal c axis was placed in front of the crystals. These measures were necessary to keep the photoconductivity produced in the crystal at a minimum, so that the dielectric relaxation time should be as long as possible. A schematic diagram of the apparatus is shown in Fig. 2.

Results

Figure 3 shows the exciton spectrum of CdS which is relevant to the present work as seen in transmission for

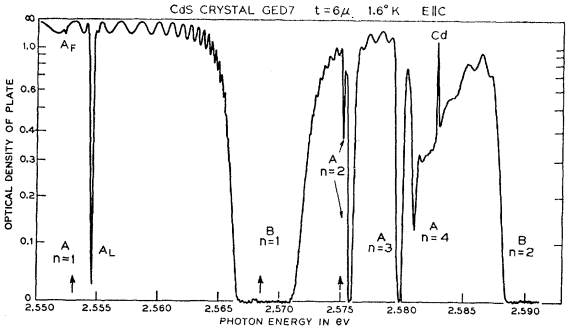

FIG. 3. A microphotometer trace of a photographic plate showing the exciton spectrum of a CdS crystal 6 μ thick at 1.6°K as seen in transmission for $E\|C$. There is absorption in the crystal when the optical density of the plate decreases. The arrows mark the approximate transition energies as deduced from the reflection spectrum seen with $E\perp C$. Interference effects occur where the crystal is transparent. The line marked "Cd" is a Cd emission line used for calibration purposes.

light with $E\|C$. Exciton series A, made up from an electron in the conduction band and a hole from the top valence band, is strongly active for light with $E\perp C$,[2] and in $E\|C$ the comparatively weak and sharp lines shown in Fig. 3 are seen. The contrasting width of the $n=1$ state of exciton B which is active in both modes of polarization is apparent from this figure. The two lines which occur at the $n=1$ position of series A have been called[2] A_F and A_L since one is a strongly forbidden transition and the other marks the formation of a "longitudinal" exciton. They occur at 2.5524 and 2.55455 ev, respectively. In fields of up to 1000 v/cm these lines were shifted by less than 10^{-5} ev, the limit of detection. The same is true for various "impurity" or "bound" excitons[6] which occur at longer wavelengths. The $n=3$ and $n=4$ states of the same exciton series merge into a continuous absorption at fields above about 200 v/cm. Consequently none of these states lend themselves to Stark effect experiments.

The $n=2$ state was thus found to be the one most suitable for study. In general the lines tended to broaden even for this state as an electric field was applied, although the effect was usually more marked when a magnetic field, H, causing a large Hall field was present (see Sec. IV). The $n=2$ state consists, for $H=0$, of a strong (and so apparently wide) line and a much weaker and sharper line at a photon energy 6.45×10^{-4} ev less than that of the strong line. The weak line has been termed the $2P_z$ state[2] and represents the $n=2P$ state with zero orbital angular momentum about the c axis; it is split off from the other $n=2$ states, which merge into the strong line, by the crystal anisotropy. As an electric field is applied parallel to the c axis, the strong line remains approximately unchanged, although at the highest fields a line splits off from it toward higher energies. The $2P_z$ state, however, is shifted to lower energies. These results are shown in Fig. 4. At a particular applied field the shift of the $2P_z$ line was studied as a function of the duration of the applied square wave; the results are shown in Fig. 5 for a light level approximately the same as that used in Fig. 4. It is seen that at low frequencies there is no Stark effect since the field is screened out by accumulation of charge near the ends of the crystal; at higher frequencies the Stark shift occurs and saturates as the frequency exceeds that of an effective dielectric relaxation time. When an external lamp was focused onto the crystal, thus producing a considerably larger photoconductivity, the Stark shift vanished as expected. The frequency used to obtain the data for Fig. 4 is in the saturation range. The Stark effect described here for zero magnetic field was generally reproducible from one crystal to another and is in reasonably good agreement with the theoretically predicted effects.

The most interesting part of this work is concerned with the Stark effect in the presence of a magnetic field, when there is in addition a Zeeman splitting of the lines. Either the geometry $H\|c$ or $H\perp c$ may be chosen. The orientation $H\perp c$ was chosen because the lines which fell at the extremities of the Zeeman pattern were strong and well resolved for $H=31\,000$ gauss, which was not the case for $H\|c$. A complication arises using

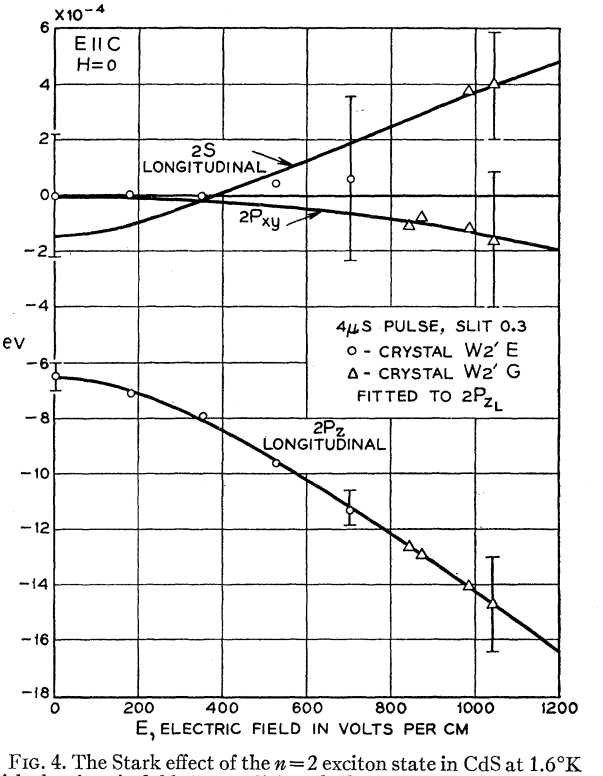

FIG. 4. The Stark effect of the $n=2$ exciton state in CdS at 1.6°K with the electric field, E, parallel to the hexagonal c axis. Energies have been measured from the energy of $2P_{xy}$ at $E=0$. The lines are theoretical taking the position of $2S_L$ at $E=0$ to be -1.45×10^{-4} ev. The points marked Δ are from a run in which the electric field although high was not known precisely. The values of E used for these points were obtained by fitting the $2P_z$ points to the $2P_z$ theoretical line. Some approximate line half-widths are indicated, and show why $2S_L$ cannot be resolved at low electric fields.

[6] D. G. Thomas and J. J. Hopfield, Phys. Rev. 116, 573 (1959).

$H \perp c$ in that the absorption spectrum is different for the two directions of the magnetic field.[1,2] The pair of lines at the low-energy side of the multiplet consist of the spin doublet of the $2P_z$ state, and the pair of lines on the high-energy side consist of the spin doublet derived from the $2P_y$ state (the magnetic field is taken to be along the x direction). In one of the spectra the low-energy line of each spin doublet is strong and observed (these are the P_z^+ and P_y^+ states), and in the other spectrum the high-energy line of each spin doublet is observed (the P_z^- and P_y^- states). The energy difference between the lines P_y^+ and P_z^+ is almost identical to that between P_y^- and P_z^-. It is the changes in these energy differences which are used to measure the Stark effect for it was found that in an electric field these lines moved in opposite directions. The individual Zeeman lines become less distinct as the electric field is applied; at sufficiently high fields the pattern is expected to be essentially a Stark pattern rather than that of the Zeeman effect. Thus our measurements which follow the individual lines are made when the Stark shifts are comparable with or smaller than the zero electric field splittings.

The results of such measurements on crystal $W2'E$ are shown in Fig. 6 taken at a certain light level indicated by the slit opening of the Perkin-Elmer monochromator. The two curves refer to the results for the magnetic field in each direction. At the higher electric fields the lines become broadened, and the fields are apparently less than expected. This may be caused by some sort of breakdown or multiplication in the crystal. At lower fields the curves are approximately symmetrical but their symmetry planes are displaced from the $E=0$ line. This displacement is the result expected if there exists a quasi-electric field, E_q, as described in Sec. II. The value of the displacement, about 95 ± 10 v/cm, should equal the quasi-field. Furthermore knowing the direction of **H** and **q** the sign of E_q can be predicted and in this and in all other crystals examined the observed sign agreed with the predicted value.

If the light were not chopped off for one phase of the

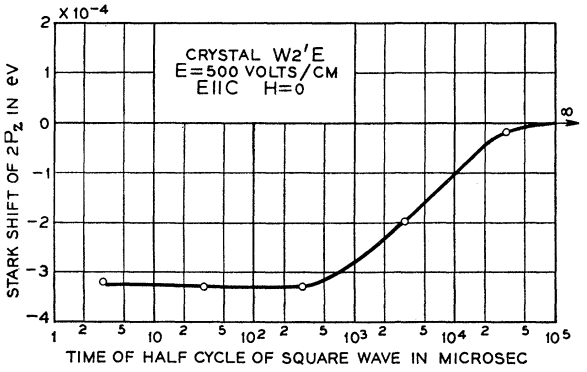

FIG. 5. The shift of the $2P_z$ line at 1.6°K as a function of the frequency of the applied square wave at a level of illumination approximately equal to that used in Fig. 4.

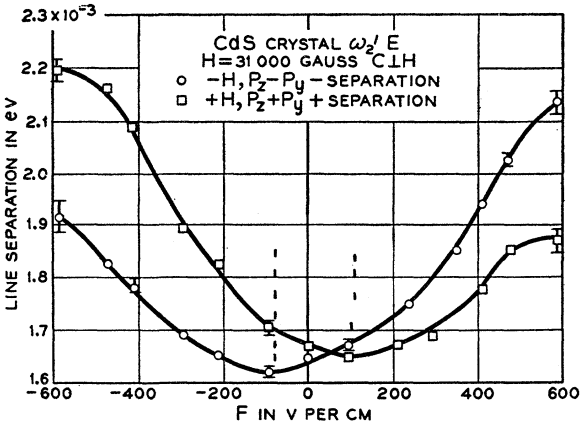

FIG. 6. The separation between two pairs of lines in the Zeeman spectra of the $n=2$ exciton state in CdS as a function of the applied electric field. The pair of lines P_z^-, P_y^- are two lines in the absorption spectrum with H in one direction, and the pair of lines P_z^+, P_y^+ are two analogous lines for H in the other direction. The half-cycle square-wave duration is 200 μsec. The temperature is 1.6°K. The monochromator slit width is 0.2 mm.

applied field then the lines would be expected to be broadened since for fields of $+E$ and $-E$ v/cm the line separations are not equal as a result of the displacement just described. If, however, the duration of the alternate phases of a rectangular wave of applied voltage are altered then the polarization of the crystal will adjust so that the product of the field strength and duration in one direction equals the same product for the other direction. It is therefore possible to adjust the ratio of the durations so that the unequal fields in each direction will produce equal Stark shifts and the lines should then become sharp. This effect was observed for the $n=2$ exciton state in CdS and gave a value of E_q compatible with the value just quoted, and again of the correct sign. Precise quantitative data could not be obtained by this method because of the following difficulty. If the total field applied to the crystal is only a few hundred v/cm, then in order to introduce fields which differ by about 100 v/cm a large duration ratio must be employed. If, however, the pulse durations are widely different then they produce unequal darkening of the photographic plate and the effects become hard to distinguish. On the other hand if the total applied field is too large the lines become broadened.

The Stark shift in a magnetic field was measured as a function of the square-wave frequency. For pulse lengths greater than 200 μsec the square-wave generator had to be used and the light was not chopped; as a consequence of the E_q field the lines are broadened. The results obtained were not entirely consistent but they indicated that for the conditions used in Fig. 6 the 200-μsec pulse length was short enough to eliminate appreciable relaxation screening of the field.

Behavior like that just described for crystal $W2'E$ was observed in a number of crystals, but in some crystals a much larger Stark effect occurred when a

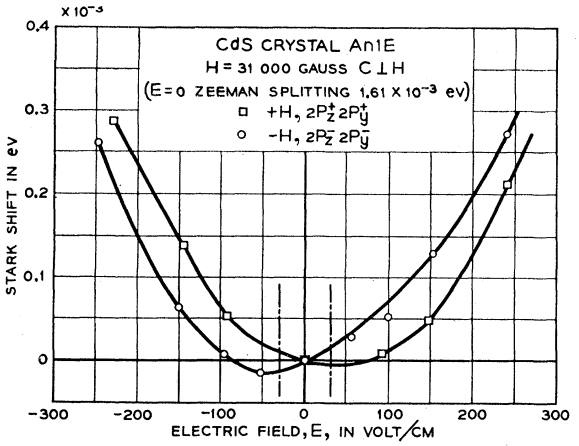

FIG. 7. A plot similar to that of Fig. 6 showing the Stark shift for a different crystal. Notice that the Stark shifts are much larger than in Fig. 6 but that the minima are now only about 30 v/cm from the origin. The half-cycle duration of 200 μsec was used.

magnetic field was present; simultaneously the minimum was displaced a smaller amount from the origin. This is illustrated in Fig. 7 for crystal *An1E* where the displacement is only about 30 v/cm. The behavior of such crystals as a function of frequency in a magnetic field was again somewhat erratic, but the result of one experiment is shown in Fig. 8. This and other experiments again indicated that sufficiently high frequencies were used to determine the displacement of Fig. 7. Crystals showing the abnormally large Stark effect in a magnetic field showed the normal effect for $H=0$. In addition it was found that if the light was directed parallel to H then a normal, much smaller Stark effect was observed, although of course in this geometry there is no displacement effect since $\mathbf{H}\times\mathbf{v}=0$. This experiment was performed by having two small angle mirrors positioned between the condenser plates so arranged that each turned the light beam through 90°. The distortion of the electric field by these mirrors was minimized by cutting horizontal lines on the mirrors; by performing the experiment with $H=0$ it was found that the distortion was not important since the results now agreed with those obtained without using the mirrors.

IV. DISCUSSION

Stark Effect in Zero Magnetic Field

The Stark effect of the $1S$ exciton state can be adequately estimated from the known radius (28.7 A) and binding energy (0.027 ev) of the $1S$ state[2] using the hydrogenic model. One calculates from the well-known expressions for the Stark effect of a hydrogen atom[7] an energy shift of -4×10^{-6} ev for the $n=1$ state in an electric field of 1000 v/cm. The experimental shift of the $1S$ state in a field of 1000 v/cm was found to be less than 10^{-5} ev, the limit of detection in the present experiments. The "impurity excitons" were also found to shift by less than 10^{-5} ev, and are therefore probably derived from the $n=1$ exciton states also. The change in the energy gap for a field of 1000 v/cm must also be less than 10^{-5} ev, in spite of the fact that the crystal is piezoelectric. One can therefore associate unambiguously all observed Stark effects with the Stark shifts of the exciton states themselves.

For an electric field parallel to the c axis, the Stark shift of the $2P_{xy}$ excitons can be calculated directly from the formulas of reference 7 and the known exciton parameters. The Stark shift of the $2P_z$ and $2S$ states is more complicated, since the degeneracy of the $2P_z$ and $2S$ states which gives rise to the linear Stark effect for these states in the hydrogen atom has been lifted by the anisotropy of the reduced mass and dielectric constant for the excitons in CdS. The actual energy levels are further complicated by the fact that the $2P_z$ state has a fourfold spin degeneracy, while the corresponding degeneracy for the $2S$ states has been lifted by a longitudinal-transverse energy difference of the $2S$ exciton states. Fortunately, an electric field parallel to the hexagonal axis does not alter the symmetry of the crystal. In the absence of an electric field, only the states $2P_z$ (Γ_5 longitudinal) and $2S$ (Γ_5 longitudinal) are observable. Since these states will be mixed with each other (but not with any of the other $2S$ or $2P_z$ states) by an electric field in the z direction, the observed Stark levels should contain but two lines from the $2S$, $2P_z$ states. The Stark effect can be satisfactorily estimated by assuming that the wave functions of the $2S$ and $2P_z$ states are not appreciably altered by the anisotropy which lifts the $2S$–$2P$ degeneracy, and calculating the modification in the hydrogenic Stark effect due to the lifting of the degeneracy. The terms leading to the first- and second-order Stark effects of the hydrogen atom are included in our calculation. The only parameter needed for this calculation which was not previously well known was the energy position at zero field of the $2S$ (longitudinal) state, which lies directly under part of the $2P_{xy}$ line. This energy value, previously known to within $\pm2\times10^{-4}$ ev, was determined within these limits to fit the data.

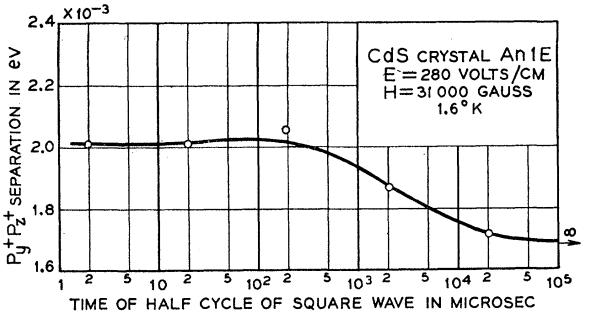

FIG. 8. A plot showing the Stark shift at a field of 280 v/cm as a function of frequency of the applied square wave under conditions similar to those used in Fig. 7.

[7] H. E. White, *Introduction to Atomic Spectra* (McGraw-Hill Book Company, Inc., New York, 1934), p. 402.

Figure 4 shows the experimental and theoretical energy levels of the $n=2$ states in an electric field. At low fields, the Stark effect is dominated by the quadratic Stark effect which would be linear if the $2P$ and $2S$ states were degenerate. At higher fields, this effect becomes linear, and the ordinary quadratic Stark effect becomes observable. The agreement between experiment and theory confirms the exciton energy level assignments previously made.

The $n=3$ and higher exciton states are observed to broaden and merge into the continuum at quite low electric fields. This is not unexpected. The $n=3$ state has a diameter of about 500 A. The potential energy difference in a field of 500 v/cm across an $n=3$ state is thus about 2.5 millielectron volts. The binding energy of this state is about 3 millielectron volts. Electric field ionization of the $n=3$ state will thus be extremely rapid and the lines will broaden. The simple Stark effect of the $n=3$ and higher levels should therefore disappear at fields well below 500 v/cm.

Stark Effect in a Magnetic Field of 31 000 Gauss

The $n=2$ exciton level structure in a magnetic field of 31 000 gauss in the x direction is shown in Fig. 9.[2] In addition to the six "P" states and two S states which have been previously identified, there are two unobserved S states which lie somewhere between the two observed S states. Each "P" state is doubly degenerate. The Stark effect is very complicated due to the complex structures of the four S levels, and its calculation is rendered essentially impossible. In the low-field range, where the Stark effect is quadratic, it can be roughly calculated (within an error of perhaps 20%) and within this error, is the same for the states P_{y+} and P_{y-}, and for P_{z+} and P_{z-}. The calculated displacement of the minima can be obtained from Eq. (1), the known electron and hole masses perpendicular to the hexagonal axis (0.20 and 0.7, respectively), and the index of refraction at the energy of the excitons ($2.2\pm10\%$), as determined by an analysis of the reflection spectrum.

In the data of Fig. 6, the shift of the minima from $E=0$ is 95 ± 10 v/cm, and the low-field line separation increases with electric field (as measured from the minimum) as AE^2, where $A=1.4\times10^{-9}$ electron volt/(v/cm)^2. The theoretical calculation gives a shift of 115 ± 20 v/cm for the shift, and a value of A of $(0.9\pm0.2)\times10^{-9}$. The data of Fig. 7 yields values of the shift and of A of 30 ± 5 v/cm and 4.2×10^{-9} electron volt/(v/cm)^2, respectively. The same theoretical values should, of course, hold for all crystals in the same geometry. Finally, in the geometry $\mathbf{k}\|H$, the same crystal which displayed the large Stark effect (large A) for $k\perp H$ showed a very small Stark shift of the $2P_z$ line, this line shifting as αE^2, where $\alpha=0.58\times10^{-9}$ electron volt/v/cm. The theoretical value for α is $(0.68\pm0.15)\times10^{-9}$. (The experimental and theoretical relation between α and A is approximately $\alpha=\frac{3}{4}A$.) In this geometry, no shift of the plane of symmetry is expected ($\mathbf{E}_q=0$ since $\mathbf{k}$ is parallel to H), and this was experimentally verified.

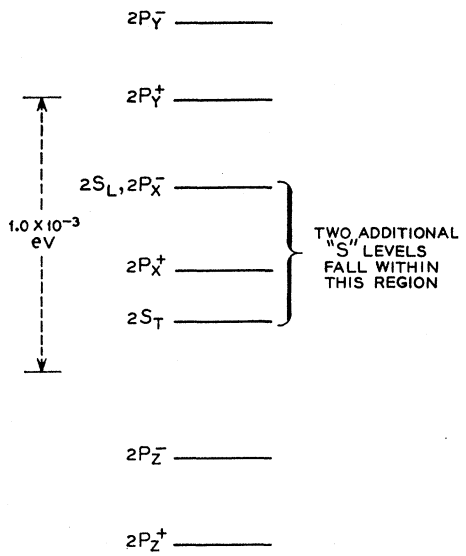

FIG. 9. A schematic drawing of the $n=2$ exciton level structure of CdS in a magnetic field in the x direction of 31 000 gauss.

Effect of the Hall Field

Consider an ellipsoidal cylinder of dielectric having a major axis a and a minor axis b. Let the complex dielectric constant of the cylinder be $\epsilon(\omega)=1+4\pi\alpha+4\pi\sigma/i\omega$, σ representing the conductivity (in cgs units) of the dielectric and $1+4\pi\alpha$ the background dielectric constant. When an external electric field E is applied at $t=0$ parallel to the major (or minor) axis, an internal field

$$E(1+\gamma\alpha)^{-1}$$

exists in the sample at $t=0$. The depolarization factor γ depends on the geometry. For $a/b\gg1$, γ is 4π for an external field parallel to the minor axis, and is π^2b/a for an external field parallel to the major axis. The relaxation time τ for the internal electric field decay to $1/e$ of its original value is given in either geometry by

$$\tau=(1+\gamma\alpha)/\gamma\sigma. \tag{2}$$

The crystals used in the present experiments are platelets having a thickness-to-length ratio of about 1/500. In CdS, α is about $\frac{2}{3}$. The geometry is not really ellipsoidal, but one would nevertheless expect from Eq. (2) an average relaxation time for an electric field parallel to the platelet ($\tau_{\|}$) to be about 100 times the normal dielectric relaxation time $\tau_0=\epsilon/4\pi\sigma$, which will apply to an electric field perpendicular to the platelet.

The fact that $\tau_{\|}$ is 100 times longer than might have been anticipated in the geometry in which the electric field lies in the plane of the platelet means that in this

geometry (the geometry used throughout), the condition $\omega\tau_0 > 10^{-2}$ is all that need be fulfilled in order to avoid screening the applied electric field.

In the presence of a magnetic field parallel to the minor axis of the elliptic cylinder, an electric field E parallel to the major axis will introduce a Hall field also parallel to the minor axis. This Hall field will establish itself in a time τ_0, and exist as long as a current flows parallel to the major axis (τ_{II}). This Hall field will have the approximate value $\omega_c\tau_r E$ (where ω_c is the cyclotron resonance frequency of the carriers responsible for the current and τ_r the relaxation time of the carriers) independent of the actual carrier density. No measurements of the mobility of electrons in CdS has been made in such pure specimens at low temperatures. If, however, one extrapolates Hutson's formulas[8] for the mobility of electrons in CdS to 1.6°K, one finds $\omega_c\tau_r$ of the order of 5 for the electrons in a magnetic field of 31 000 gauss. It is thus quite possible to have an electric field due to the Hall effect several times larger than the actual applied electric field. This field establishes itself rapidly. In the presence of a magnetic field, one must perform the experiments at chopping frequencies such that $\omega\tau_0 > 1$, in spite of the fact that without a magnetic field, $\omega\tau_0 > 1/100$ is adequate.

The Stark shifts shown in Fig. 6 yield a value of the coefficient A which is 20 to 50% greater than the value expected from the parameters which give excellent agreement with experiment for A in zero magnetic field (compare Fig. 2). The data of Fig. 7 give a value of A four times the expected value. These disagreements we attribute to the Hall field. In the presence of a Hall field, the theoretical expression for the Stark-induced energy shift between the lines of Fig. 6 or 7 is

$$\Delta = A(E-E_q)^2 + B(\omega_c\tau_r)^2E^2. \tag{3}$$

The coefficient B should be of the same order of magnitude as A.

There are several experimental reasons for believing that this additional Stark effect due to the Hall field exists.[9] First, in spite of the fact that in the absence of a magnetic field all crystals exhibit a Stark effect (such as that in Fig. 4) which agrees with theory, great variability between crystals and disagreement with theory exists as indicated earlier for the geometry $\mathbf{k}\perp\mathbf{H}$ in the presence of a magnetic field. This variability and the size of the observed quadratic Stark effect can be explained if $\omega_c\tau_r$ varies from crystal to crystal, and has values as large as one or two for the "best" crystals. Second, if the Stark separation at small applied fields is given by Eq. (3), then the relation between the electric field E_S at the minimum energy separation in a magnetic field and E_q is

$$AE_q = [A + B(\omega_c\tau_r)^2]E_S. \tag{4}$$

A and E_q are the same for all crystals, so the right-hand side of Eq. (4) should be a constant for all crystals. The quantity $[A+B(\omega_c\tau_r)^2]$ is obtained by knowing E_q, A, and E_m, and using Eq. (4). The quantity $[A+B(\omega_c\tau_r)^2]E_S$ is the same for all crystals within experimental accuracy (for example, this product has the value $1.3_2\times10^{-7}$ and $1.2_6\times10^{-7}$ for the data of Fig. 6 and Fig. 7, respectively, although the values of E_m differ by a factor of three). Finally, a crystal which showed a Stark effect four times too large in the geometry $\mathbf{k}\perp\mathbf{H}$ exhibited a normal Stark effect in the geometry $\mathbf{k}\|\mathbf{H}$. The explanation of this experiment has nothing to do with the direction of propagation of the light, but concerns the orientation of the sample. The crystal is always turned so that the direction of propagation of the light is normal to the platelet. In the geometry $\mathbf{k}\perp\mathbf{H}$, the Hall field is therefore perpendicular to the platelet, and the relaxation time for the establishment of the Hall field is about $10^{-2}\tau_{II}$. A Hall field can thus be observed. In the geometry $\mathbf{k}\|\mathbf{H}$, the Hall field would lie in the plane of the platelet, and the formation time of the Hall field would be τ_{II}. Since all experiments are performed at frequencies larger than $1/\tau_{II}$ to avoid screening, no Hall field can be established in this geometry.

In view of the nonideal geometry, the unknown dependence of the crystal conductivity on electric field and previous history, the nonsimple electric field wave form, and other such complications, a detailed analysis of the Hall field and relaxation times is impossible. The fact that Fig. 8 shows a "large Stark effect" constant over three orders of magnitude of the frequency rather than dropping after two orders of magnitude is not understood. The qualitative broadening of the exciton lines when the Hall field is present is probably due to the distortion of the wave form in the Hall field.

The anomalously large Stark effect has the expected geometry dependence, while the magnitude of the "small" Stark effect observed in many crystals is in rough agreement with the calculated Stark effect. We thus feel justified in accepting the "small" Stark effect as that relevant to the simple analysis of the experiment. Unfortunately, the value of $A+B(\omega_c\tau_r)^2$ cannot be measured very accurately, since at small fields the energy shifts are small, and at large fields, the Stark effect is no longer quadratic. It is not possible to calculate A with high precision. In view of these two difficulties, it is not possible to make a reliable correction for the effect of the Hall field. The analysis leads one to believe that the actual E_q is larger than the largest shift of the plane of symmetry measured, and that the experiments which represent most nearly the ideal experiments are those (performed, of course, at sufficiently high frequencies) which show the smallest Stark effect in the presence of a magnetic field.

[8] A. R. Hutson, Phys. Rev. Letters 4, 505 (1960).

[9] The existence of a Hall field resulting from the transient flow of current in the crystal may be compared with A. G. Redfield's method of measuring the Hall effect in insulating photoconductors [Phys. Rev. 94, 526 (1954)].

V. SUMMARY AND CONCLUSIONS

There exists a magnetic perturbation on the energy levels of excitons which have a center-of-mass velocity $\mathbf{v}$ in a uniform magnetic field due to the Lorentz force on the electron and hole. Since the excitons observed in optical absorption have the wave vector of the exciting light, they will in general have a nonzero velocity and a finite magnetic perturbation of their energy levels due to this velocity. This perturbation can be measured by balancing the Lorentz electric field $(1/c)\mathbf{v}\times\mathbf{H}$ against an applied electric field. The measurement of this perturbation determines the velocity of an exciton of known wave vector, and therefore determines the total exciton mass.

The effect of this quasi-electric field has been observed in CdS. The experiment is made difficult by the conflicting requirements of measuring the optical absorption at high resolution of a nearly perfect unstrained small crystal (which is also a good photoconductor) in known uniform electric and magnetic fields at liquid helium temperatures. Systematic difficulties arose in the experiments when both electric and magnetic fields were present. As a result of these difficulties, the measured quasi-electric field of 95 v/cm due to the exciton velocity is probably 0–50% lower than the true quasi-field. The measured quasi-field can be interpreted as due to an exciton of total mass (in the direction perpendicular to the c axis) of $1.1m_e$ (or up to 33% smaller). This mass compares favorably with an independent estimate of $0.9m_e$ for this mass based on elec tron and hole masses deduced from other experiments.

To aid in understanding the Stark effect in the presence of a magnetic field, the Stark effect in the absence of a magnetic field was investigated. This study provided a confirmation of the previously suggested energy level scheme in CdS.

The difficulties which arose in connection with Stark effect experiments in the presence of a magnetic field were thought to be caused by an extraneous Hall field. This interpretation suggests that in the best crystals which could be found, $\omega_c\tau_r$ for electrons in CdS is approximately 2 at 1.6°K for a magnetic field of 31 000 gauss.

The quasi-electric field is always present in ordinary exciton Zeeman effect measurements. Failure to account for this field can lead to systematic errors in the interpretation of the Zeeman effect on excitons of high quantum number and large radius.

The basic effect studied in the present experiments, the effect of the quasi-field E_q, is in no way specific to CdS. Exciton mass spectrometry experiments of this general variety should be feasible in many substances. The experiments determine the exciton mass which, in the case of weakly bound excitons (the only excitons for which the experiments are feasible), is directly related to the electron and hole effective mass tensors. The experiments provide also a positive method of identifying absorption lines as being due to excitons rather than impurities, because the observed effect depends explicitly on the fact that excitons move.

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