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Excitonic Effects in the Electroreflectance of Lead Iodide

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The reflectance and electroreflectance spectra of single crystals of lead iodide (PbI_2) were measured between 2.2 and 5.0 eV at 4.5 and 77°K, respectively. A Kramers-Kronig dispersion analysis of the data was made, and the real and imaginary parts of the dielectric constant were calculated together with their field-induced modulation. The first three lines of the hydrogenic exciton series associated with the absorption edge are well resolved in reflectivity. In the same energy range, the electroreflectance spectrum is interpreted as the Stark shift of the first exciton line from which the binding energy of the exciton is deduced. In the region of fundamental absorption, the existence of several metastable exciton states gives rise to a new and large contribution to the electroreflectance spectra.

1. INTRODUCTION

LEAD iodide PbI_2 is one of a large number of compounds which have the same crystal structure as CdI_2 (point group D_{3d}). The atomic arrangement is in form of layers of lead and iodine atoms oriented perpendicularly to the c axis. The sequence of the layers is repeated in units of I-Pb-I held together by van der Waal forces. Early optical measurements on thin films revealed the existence of a hydrogenic exciton series in front of the absorption edge at 2.5 eV.[1] In later publications fairly contradictory results as to the number and the position of the exciton lines were reported.[2,3] Excitonic structure in the fundamental optical spectra above the absorption edge has been observed in addition to one-electron interband transitions in both absorption[4,5] and reflectivity.[6,7] These exciton states have been interpreted as localized excitations of the iodine ion.[4] However, there is still little information available about the band structure of PbI_2.

Optical modulation techniques, e.g., electroabsorption and electroreflection, have recently been used in numerous investigations of the fundamental optical properties of solids. The change in optical constants induced by the electric field is interpreted in terms of the Franz-Keldysh theory which has been generalized by Aspnes[8,9] and Aymerich and Bassani.[10,11] Comparison between experiment and theory is achieved with the application of the Kramers-Kronig dispersion analysis which relates the reflectivity and electroreflectivity data to the real and imaginary parts of the dielectric constant and their field induced modulation. More recently, the electron-hole interaction has also been found to be responsible for part of the effects observed in electroabsorption.[12,13]

This paper reports results of new reflectance and electroreflectance measurements on PbI_2 single crystals. A technique similar to that of the transverse electric field method recently described by Rehn and Kyser[14] was used for the electroreflectance studies. In this technique the electric field is applied in a direction parallel to the optical surface by means of two electrodes rather than across a surface barrier[15] or an electrolyte-crystal interface[16,17] or a p-n junction.[18] One of the most obvious advantages of the transverse electric-field method is that the transverse field strength can be determined quantitatively from the known electrode geometry. It must be realized that there always exists a space-charge region at the surface of an insulator such that the longitudinal field component in the propagation direction of the light depends on the distance from the surface. In the transverse electroreflectance one measures, however, only the change in reflectance induced by the known transverse component. The method is restricted to nonconducting materials, since the application of a high electric voltage is required.

The analysis of the experimental results will show that the existence of strong electron-hole interaction in PbI_2 is the origin of a new and large contribution to the electro-optical effect in this material.

2. EXPERIMENTAL PROCEDURE

A. Sample Preparation

The PbI_2 crystals were grown either by the Bridgman method from a melt of zone-refined material or at room temperature in silica gel. The measurements, both reflectivity and electroreflectance, were carried out on

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[1] S. Nikitine and G. Perny, Compt. Rend. **240**, 64 (1955).

[2] I. Imai, J. Phys. Chem. Solids **22**, 81 (1961).

[3] M. R. Tubbs and A. J. Forty, J. Phys. Chem. Solids **26**, 711 (1965).

[4] M. R. Tubbs, Proc. Roy. Soc. (London) **A280**, 566 (1964).

[5] S. Brahms, Phys. Letters **19**, 272 (1965).

[6] D. L. Greenaway and R. Nitsche, J. Phys. Chem. Solids **26**, 1445 (1965).

[7] D. L. Greenaway and G. Harbeke, J. Phys. Soc. Japan Suppl. **21**, 151 (1966).

[8] D. E. Aspnes, Phys. Rev. **147**, 554 (1966).

[9] D. E. Aspnes, Phys. Rev. **153**, 972 (1967).

[10] F. Aymerich and F. Bassani, Nuovo Cimento **48B**, 358 (1967).

[11] F. Aymerich and F. Bassani, Nuovo Cimento **56B**, 295 (1968).

[12] Y. Hamakawa, F. A. Germano, and P. Handler, Phys. Rev. **167**, 703 (1968).

[13] R. Enderlein, Phys. Status Solidi **26**, 509 (1968).

[14] V. Rehn and D. S. Kyser, Phys. Rev. Letters **18**, 848 (1967).

[15] B. O. Seraphin and R. B. Hess, Phys. Rev. Letters **14**, 138 (1965).

[16] K. L. Shaklee, F. H. Pollak, and M. Cardona, Phys. Rev. Letters **15**, 883 (1965).

[17] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. **154**, 696 (1967).

[18] Y. Hamakawa, P. Handler, and F. A. Germano, Phys. Rev. **167**, 709 (1968).

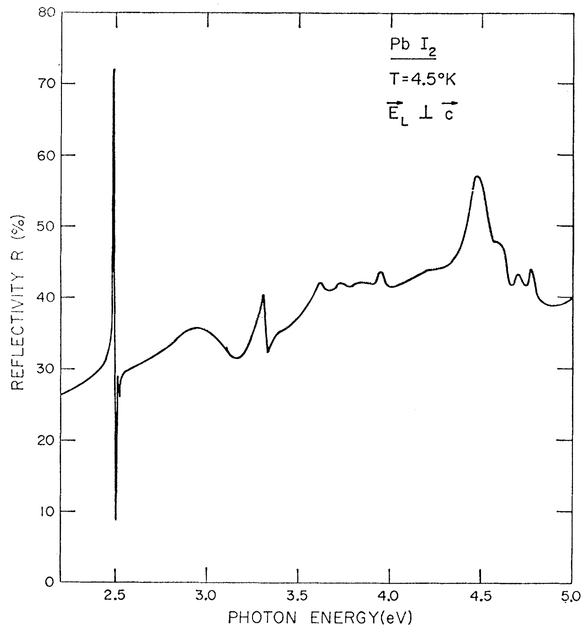

FIG. 1. Reflectivity of $2H$-PbI_2 at 4.5°K.

the faces of cleaved platelets or on as-grown faces of the silica-gel-grown crystals. Because of the large anisotropy of single crystalline lead iodide, the cleavage planes were of high optical quality, and no other treatment was given to them. The samples, about 8 mm in diameter, were mounted in a cryostat evacuated to about 10^{-6} Torr. A shield in thermal contact with the sample holder with thin quartz windows in front of the sample prevented the contamination of its surface caused by the condensation of residual gases.

The samples used for the electroreflectance measurements were provided with two gold electrodes evaporated onto the cleavage plane and an electric insulation consisting of a low-temperature adhesive (GE 7031) painted on top of each electrode. With this precaution, ac voltages up to 7 kV peak-to-peak could be applied without electrical breakdown. The monochromatic light was focused on the 1-mm-wide stripe of material between the two electrodes.

B. Apparatus

A Perkin-Elmer single-beam double-pass instrument fitted with a quartz prism and a xenon high-pressure arc as light source was used for the electroreflectance measurements. The temperature range extended from room temperature to 77°K. The reflectivity spectra were recorded on a conventional double beam spectrometer connected with a helium cryostat. All measurements have been performed under near-normal incidence. We thus measured essentially always $\mathbf{E}_L \perp \mathbf{c}$ spectra where $\mathbf{E}_L$ is the electric vector of the incident electromagnetic wave.

In the electroreflectance experiments, an ac voltage with a frequency of 1500 Hz and no superposed dc bias was applied between the electrodes. In order to measure the induced change in reflectivity, the modulation signal from the detecting photomultiplier is recovered by a PAR Model HR-8 lock-in amplifier synchronized at twice the field frequency. The signal is then amplified by an amplifier with a variable gain automatically adjusted to be inversely proportional to the dc anode current of the photomultiplier. This gain control is achieved in the feedback circuitry by a variable resistor mechanically coupled to the servomechanism of the recorder plotting the dc anode current. The feedback circuitry is such that, if the variable resistor is proportional to the anode current, the gain will be proportional to the inverse of it. Therefore, the output of this variable amplifier stage is directly proportional to $\Delta R/R$, the relative change in reflectivity induced by the electric field. The over-all linearity of the system proved to be better than 2%, even when the light intensity changes by two orders of magnitude. The sensitivity of the measurements is limited by the shot noise of the photomultiplier. Therefore, the signal-to-noise ratio is best when the light intensity is high. This was the case around 2.5 eV where the smallest detectable value of $\Delta R/R$ is about 2×10^{-6} increasing up to 2×10^{-5} at 4.5 eV, the cutoff energy of the optical system.

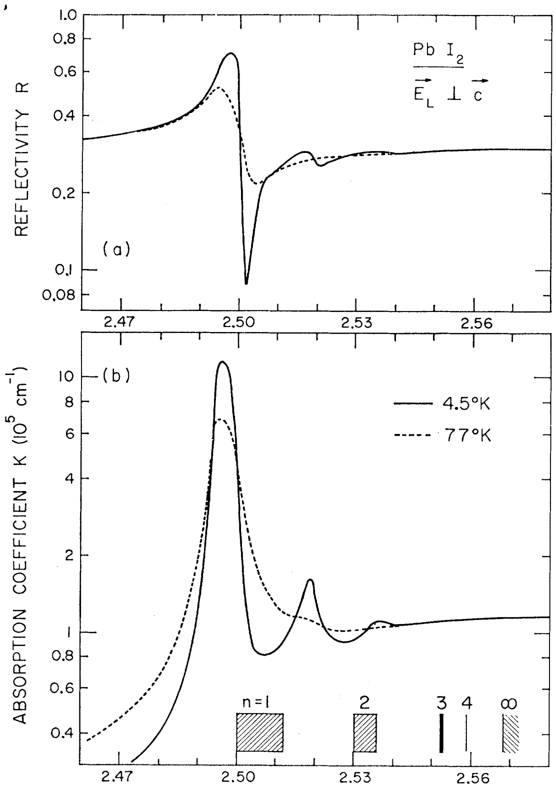

FIG. 2. (a) Reflectivity and (b) absorption coefficient of $2H$-PbI_2 at 4.5°K (solid) and 77°K (dashed) at the exciton lines in front of the absorption edge. The absorption bands reported by Nikitine and Perny (Ref. 1) are indicated on the abscissa of (b).

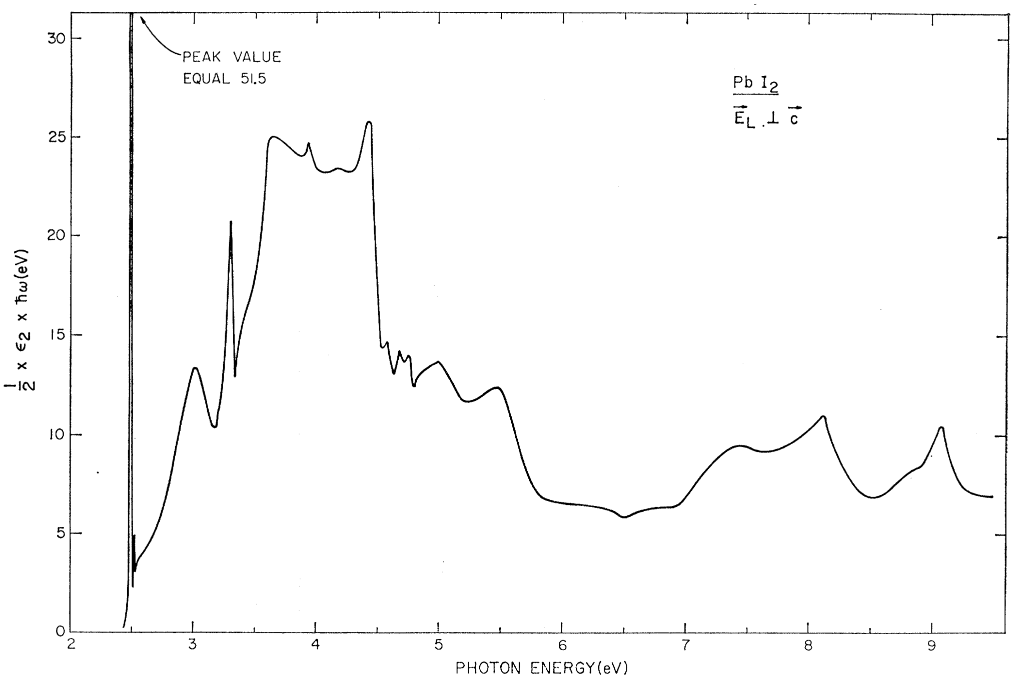

FIG. 3. Optical conductivity of PbI_2 obtained from a Kramers-Kronig analysis.

3. RESULTS

A. Reflectivity

Three different batches of Bridgman-grown PbI_2 single crystals were available, from each of which several samples were cut and measured. It appeared that the reflection spectra obtained on these samples fall into two groups. They could be characterized by the position of the first exciton line at He temperature, which was (4962±2) Å for the major group and (4942±2) Å for the minor group of samples. Occasionally a composite spectrum originating from both types has been observed but there was no continuous grading between the two characteristic positions. It was suspected that the existence of polytypism may account for such difference as in the case of CdI_2, which crystallizes in the same crystal structure as PbI_2.[6] This assumption was first supported by the fact that powder photographs taken on samples from all batches were not identical. For one type of material, all the main diffraction lines related to the D_{3d} hexagonal structure were identified. But several lines were missing on the photographs of the other type of sample. This means that the geometrical structure factor is not the same for both crystals. The identification of the missing lines clearly indicated that there is a superstructure in the lattice periodicity along the crystallographic c axis. This is typical for polytypism in case of a layer structure. However, the kind of polytypes involved cannot be identified from simple powder photographs, and in rotation photographs of Bridgman-grown crystals the polymorphic effects are partly obscured by strain. Strain-free crystals which allowed a precise structure determination have been grown in silica gel.[19] The optical spectra of the gel-grown crystals which have been identified as $2H$-PbI_2 by the Weissenberg technique are identical to those of the major group of crystals with the first exciton line at 4962 Å. The minor group has not been identified as yet, but according to the relative abundance of the polytypes reported by Mitchell[20] it is most probably the $4H$ type. All the optical data presented in this paper were taken on $2H$-PbI_2.

The reflectivity spectrum of $2H$-PbI_2 measured at 4.5°K between 2.2 and 5.0 eV on a freshly cleaved surface is shown in Fig. 1. The spectrum does not change appreciably between 77°K [7] and 4.5°K except around the narrow lines at 2.498, 3.31, 3.96, and 4.48 eV. The strong increase in the sharpness of these lines upon cooling clearly indicates that they are of excitonic nature. The excitonic peak at 2.498 eV is associated with the fundamental absorption edge and is shown in detail in Fig. 2(a). The reflectivity maximum which rises to a value greater than 70% is followed by a minimum of only 9%. This characteristic line shape has recently also been observed in the reflectivity spectra of many alkali halides by Baldini and Bosacchi[21] and by Miyata and Tomiki.[22,23]

Besides the main reflectivity peak associated with the first exciton state shown in Fig. 2(a), there are

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[19] F. P. Emmenegger (private communication).

[20] R. S. Mitchell, Z. Krist. **111**, 372 (1959).

[21] G. Baldini and B. Bosacchi, Phys. Rev. **166**, 863 (1968).

[22] T. Miyata and T. Tomiki, J. Phys. Soc. Japan **22**, 209 (1968).

[23] T. Tomiki, J. Phys. Soc. Japan **22**, 463 (1968).

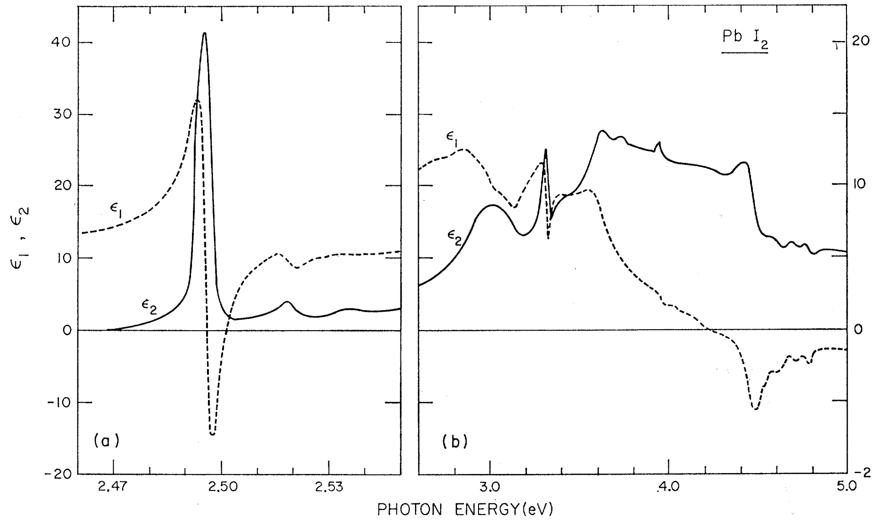

FIG. 4. Real (dashed) and imaginary (solid) part of the dielectric constant of PbI_2 obtained from a Kramers-Kronig analysis.

two other weak reflectivity maxima at 2.518 and 2.535 eV, respectively. These lines are better resolved in Fig. 2(b), where the absorption coefficient K obtained from the Kramers-Kronig analysis is plotted as a function of energy. The positions of the three peaks in absorption are 4966, 4920, and 4886 Å. The positions of the corresponding lines in a hydrogenic series reported by Nikitine *et al.*[24] (4947, 4898, and 4859 Å) are also indicated in Fig. 2(b). The separations of the lines observed in both series agree well; there is, however, a shift of about 20 Å between them. We find a halfwidth of 12 Å for the first line.

The position of the sharp reflectivity peak at 2.498 eV is very sensitive to aging effects. For instance, if the crystal is left in the open air for a few hours before measurement, the reflectivity peak is shifted to lower photon energies by an amount as large as 0.010 eV, equivalent to 20 Å. But if the sample is put into vacuum just after the cleavage operation, no change in peak position is observed with time. This is the reason why all the samples which had to be prepared for electroreflectance measurements (and which were therefore exposed much longer to the open air) always had their excitonic peak around 2.487 eV at 77°K rather than at 2.495 eV. But the position of the narrow reflectivity minimum at 2.505 eV at 77°K was the same for both freshly cleaved and aged surfaces. The sensitivity of the exciton-peak position to exposure of the

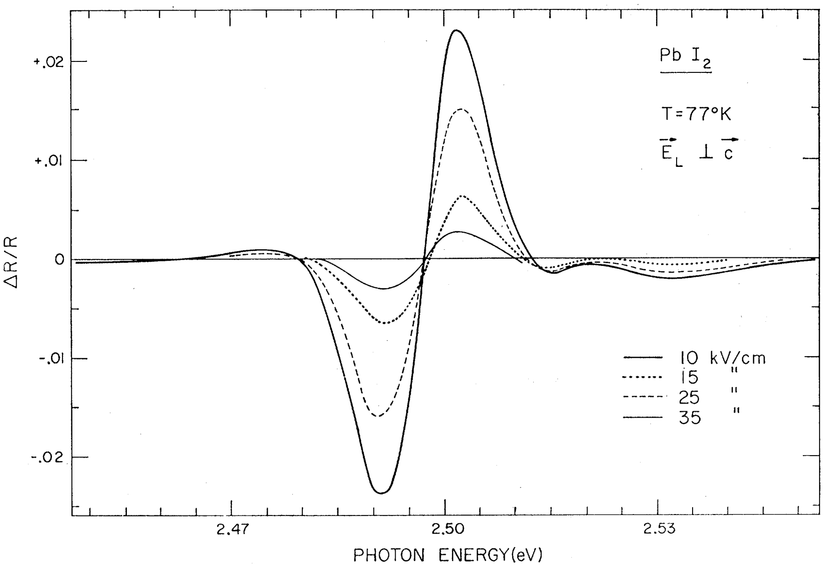

FIG. 5. Electroreflectance spectrum of PbI_2 at the exciton lines in front of the absorption edge for different field strengths.

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[24] S. Nikitine, J. Schmitt-Burckel, J. Biellmann, and J. Ringeissen, J. Phys. Chem. Solids 35, 951 (1964).

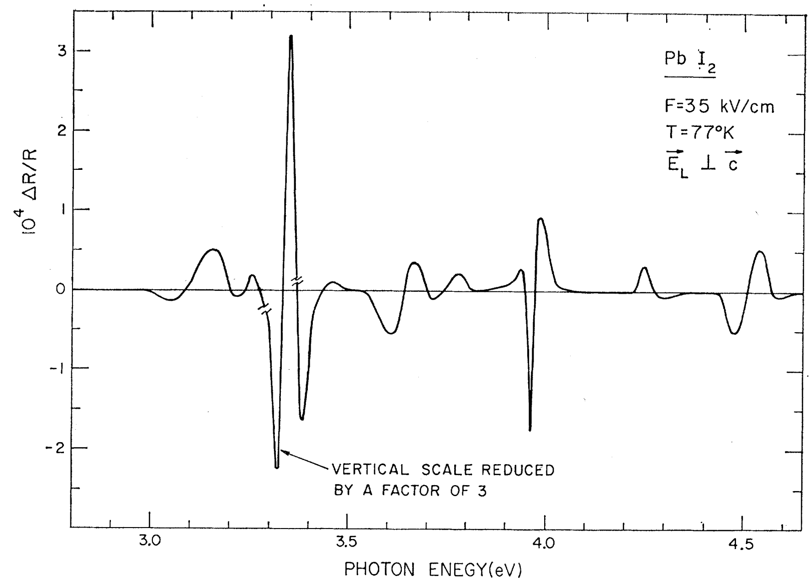

FIG. 6. Electroreflectance spectrum of PbI$_2$ in the fundamental absorption region.

sample to air may be caused by a change in the space-charge region mentioned in Sec. I which is induced by adsorption of atmospheric gases.

The other narrow and strongly temperature-dependent lines in Fig. 1 at 3.31, 3.96, and 4.48 eV correspond to exciton states associated with higher conduction bands. Therefore, they are degenerate with a continuum of states from some other bands. This will give rise to autoionization of the excitonic state and also to interference asymmetries in the fundamental optical spectra, provided the dielectric screening of the Coulomb interaction is not too strong.[25] Note, e.g., the typical asymmetric shape of the 3.31-eV line.

The real and imaginary parts of the dielectric constant ϵ_1 and ϵ_2 have been obtained by a Kramers-Kronig analysis of the reflectivity data. Since for this analysis the reflectivity R has to be known over the entire energy range, we have used the data previously measured by Greenaway and Harbeke[7] between 5 and 10 eV at 77°K. Below 2 eV, the reflectivity was calculated from the index of refraction measured by Dugan and Henish[26] on single-crystalline PbI$_2$. Between 10 and 20 eV, the data were extrapolated by a $R\propto(\hbar\omega)^{-2}$ law and above 20 eV by a $R\propto(\hbar\omega)^{-4}$ law. The criterion chosen was to obtain $\epsilon_2=0$ at all energies below the fundamental absorption edge. Figure 3 shows the quantity $\frac{1}{2}(\epsilon_2\hbar\omega)$ over the entire experimental range from 2–10 eV. We have plotted this quantity rather than ϵ_2 because it is directly proportional to the optical transition probability; this allows for a direct comparison between the different oscillator strengths over a large energy range. In Fig. 4 we have depicted ϵ_1 and ϵ_2 as functions of photon energy between 2.46 and 5.0 eV. Note that the asymmetric line shape of the 3.31-eV line is still preserved in ϵ_2 and $\epsilon_2\times\hbar\omega$.

B. Electroreflectance

The electroreflectance spectrum $\Delta R/R$ of PbI$_2$ measured at 77°K in a field $F=35$ kV/cm is shown in Figs. 5 and 6. The main feature of these spectra is the

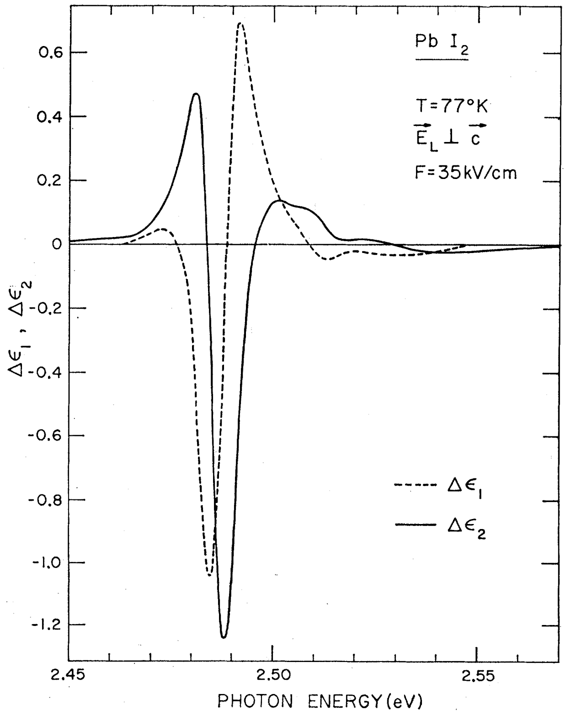

FIG. 7. Field-induced change of real part (dashed) and imaginary part (solid) of dielectric constant at the exciton lines in front of the absorption edge.

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[25] K. P. Jain, Phys. Rev. **139A**, 544 (1965).

[26] A. E. Dugan and H. K. Henisch, J. Phys. Chem. Solids **28**, 971 (1967).

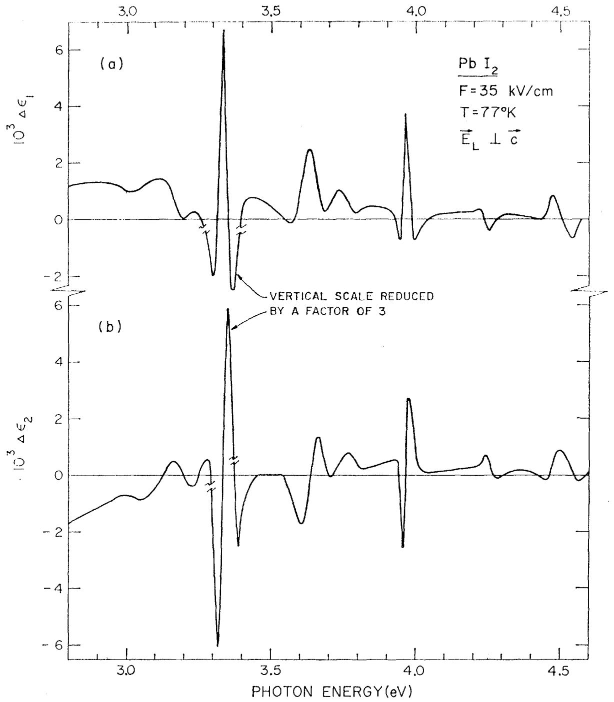

FIG. 8. **Field-induced change of (a) real and (b) imaginary parts of dielectric constants in the fundamental absorption region.**

very large contribution correlated with the exciton states at 2.50, 3.31, and 3.96 eV. A characteristic line shape is observed at these energies (and also at 4.48 eV), which consists of a negative peak followed by a positive peak of nearly equal amplitude; in addition, the position of the negative peak is almost exactly identical to the position of the corresponding reflectivity maximum. Values of $\Delta R/R$ as large as 2% are measured in a field of only 35 kV/cm around 2.50 eV, the photon energy of the exciton in front of the fundamental absorption edge. This value exceeds by one or two orders of magnitude the values usually encountered when the electroreflectance structure is of the Franz-Keldysh type.[14–18] The latter type of structure is seen, e.g., around 3.09, 3.63, and 4.25 eV in Fig. 6, and corresponds to broad and temperature-insensitive lines in the reflectance spectrum in Fig. 1.

Note in Fig. 5 also that the positions of the positive and negative peaks in $\Delta R/R$ are independent of field strength. This is characteristic of an electroreflectance structure associated with an exciton. This behavior is, in fact, the result of the field-induced broadening of the exciton peak and will be discussed later. The two other small negative peaks in $\Delta R/R$ at 2.515 and 2.532 eV are structure associated with the $n=2$ exciton line at 2.518 eV in Fig. 2(a) and possibly the $n=3$ line at 2.535 eV, respectively. The field dependence of $\Delta R/R$ around 2.50 eV is also shown in Fig. 5. $\Delta R/R$ increases linearly with field between 15 and 35 kV/cm, whereas it is proportional to the square of the field below 15 kV/cm.

A Kramers-Kronig analysis of the $\Delta R/R$ data has been performed in order to calculate the changes $\Delta\epsilon_1$ and $\Delta\epsilon_2$ induced by the electric field on the dielectric constant. Since the $\Delta R/R$ data have been taken for $\mathbf{E}_L \perp \mathbf{c}$, we obtain only the $\Delta\epsilon_1{}^{\perp}$ and $\Delta\epsilon_2{}^{\perp}$ components of the tensorial complex quantity $\Delta\epsilon$. First the change $\Delta\theta$ in phase shift is calculated using the dispersion relation

$$\Delta\theta = \frac{E}{\pi}\int_0^{\infty} \frac{\Delta R'/R' - \Delta R/R}{E'^2 - E^2}\, dE'. \tag{1}$$

Then $\Delta\epsilon_1$ and $\Delta\epsilon_2$ are evaluated from the relations

$$\Delta\epsilon_1 = \tfrac{1}{2}A\Delta R/R - B\Delta\theta,$$
$$\Delta\epsilon_2 = \tfrac{1}{2}B\Delta R/R - A\Delta\theta. \tag{2}$$

The functions

$$A = n(n^2 - 3k^2 - 1)$$

and

$$B = k(3n^2 - k^2 - 1) \tag{3}$$

are calculated from the values n and k obtained with the Kramers-Kronig analysis of the reflectivity data. For this analysis, reflectivity data measured at 77°K on the same samples as the electroreflectance were used. This is very important when the optical spectra are as sharp as around 2.50 eV where the various reflectivity and electroreflectance peaks differ in position by a few meV only. Figures 7 and 8 show the values of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ calculated from the data of Figs. 5 and 6. A main difference between the $\Delta\epsilon_2$ and the $\Delta R/R$ spectra is found only around 2.50 eV. The large positive peak in $\Delta R/R$ occurring at the minimum in reflectivity (2.505 eV) does not appear in the $\Delta\epsilon_2$ spectrum. In fact, it is the contribution of $\Delta\epsilon_1$ to $\Delta R/R$ which is the origin of this positive peak, as it is the contribution of ϵ_1 (see Fig. 4) which gives rise to the minimum in reflectivity at 2.505 eV. Based upon a calculation by Ralph,[27] Handler[28] has discussed the particular line shape of $\Delta\epsilon_2$ which is to be expected from excitonic effects.

4. DISCUSSION

A quantitative explanation of the optical modulation spectra will be attempted only around 2.50 eV where we have clearly an excitonic transition associated with the fundamental absorption edge. At higher energies, the fact that neither the band structure of PbI$_2$ nor the electron-hole interaction, which gives rise to the experimentally observed metastable excitons, has yet been studied in detail, allows us to draw only a few tentative conclusions.

A. Excitonic Transitions

A number of papers have been concerned with the band-edge excitons of PbI$_2$ in the past (see Ref. 3, for a compilation of experimental data until 1965). The

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[27] H. I. Ralph, Proc. Phys. Soc. (London) [J. Phys. C1, 378 (1968)].

[28] P. Handler, in *Proceedings of the Ninth International Conference on Physics of Semiconductors*, edited by S. M. Ryvkin (Nauka Publishing House, Leningrad, 1968).

existence of a hydrogenic series reported by Nikitine *et al.*[1,24] has not been confirmed by other authors.[2,3] Moreover, the position of the first line that has been found in all experiments varies in the range 4900–4950 Å depending on the origin and preparation of the different specimens. To our knowledge, the present results are the first ones which are definitely related to the crystalline structure of the material. We find that in $2H$-PbI_2 there exists a series of excitonic absorption lines at 4966, 4920, and 4886 Å with the separations between the lines almost identical to those reported by Nikitine *et al.*[24] but at about 20 Å longer wavelengths. The fact that we observe this series in both Bridgman- and gel-grown crystals proves that it is independent of the method of preparation. We believe, therefore, that the crystals used by other workers are of a different polytype structure. The line positions reported by Nikitine *et al.*[24] of 4947, 4898, and 4859 Å are very close to those measured on our minor group of samples (4946, 4898, and 4860 Å in absorption) which are definitely not of the $2H$ type. The lack of $n=2$ and higher lines in the work of other authors is probably caused by imperfections in the crystals or films. This conclusion is also suggested by the observed half-widths, which in most cases are considerably larger than our value of 12 Å. Energy separations of similar size between the exciton spectra of polytypes have also been reported for the layer compound GaSe by Brebner and Mooser.[29] If we fit our $n=2$ and $n=3$ lines to a hydrogenic series, in analogy to Nikitine *et al.*, we obtain $E_n=2.552-0.127/n^2$ eV with the band-gap value of 2.552 eV and a binding energy of 0.127 eV. As in many cases, the $n=1$ line is not represented by this formula.

The effect of a strong electric field upon the absorption spectrum of a Wannier-Mott exciton was first studied by Duke and Alferieff,[30] who introduced a model potential for the interaction between the positive and negative particle. More recently, Ralph[27] and Blossey[31] have solved the effective mass equation numerically. Their results show the shift and the broadening of the exciton line induced by the electric field. However, in the limit of weak electric fields, the theory is formally identical to the theory of the Stark effect in atomic hydrogen. According to Landau and Lifshitz,[32] the quadratic shift of the $1s$ hydrogenic state in an electric field F is equal to

$$\Delta E=-(9/4)a_B{}^3F^2\,, \tag{4}$$

where a_B is the Bohr radius. For a $1s$ exciton state, this relation becomes

$$E=-(9/4)a_E{}^3\epsilon F^2\,. \tag{5}$$

Here $a_E=a_B\epsilon m/\mu$ is the exciton Bohr radius, ϵ the appropriate dielectric constant screening the Coulomb interaction between electron and hole, m the electron mass and μ the reduced mass of the exciton. The relation (5) provides an independent way to calculate the exciton Rydberg (i.e., the binding energy)

$$R_E=e^2/2a_E\epsilon \tag{6}$$

(e = charge of an electron) if the energy shift ΔE for a given field and the dielectric constant are known.

The energy shift ΔE has been determined from the measurements in the following manner: First an analytical expression which combines a Gaussian on the low-energy side and a Lorentzian on the high-energy side of the peak is fitted to the data representing $\epsilon_2(0)$ as a function of energy around the exciton peak. According to Toyazawa,[33] a Lorentzian is to be expected for weak exciton-lattice coupling and a Gaussian for strong coupling, but in our case a combination turned out to give the best fit. An analytical curve for $\epsilon_2(F)$ in the electric field is then obtained by changing the parameters of the curve fitting $\epsilon_2(0)$ so that $\epsilon_2(F)-\epsilon_2(0)=\Delta\epsilon_2$. This is done by a least-squares fit which gives the change in peak position of the ϵ_2 curve as well as its broadening due to the electric field. In Fig. 9(a) we have plotted the experimental values of $\epsilon_2(0)$ obtained from the Kramers-Kronig analysis together with the fitting curve for $\epsilon_2(0)$ and $\epsilon_2(F)$ for 35 kV/cm. Figure 9(b) shows the experimental points for $\Delta\epsilon_2$ and the calculated difference $\epsilon_2(F)-\epsilon_2(0)$. The fit is so accurate that the shift ΔE, which turns out to be as small as $\Delta E=(-0.25\pm0.05)$ meV, can be determined with sufficient precision.

For the dielectric constant of PbI_2, we use the value $\epsilon=n^2=6.25$ measured by Dugan and Henisch[26] on single crystals. This value, which is the same for both parallel and perpendicular directions relative to the c axis, is very close to the quasistatic dielectric constant measured at a frequency of 10^4 cps. From Eqs. (5) and (6), we obtain $a_E=14$ Å and $R_E=0.10\pm0.01$ eV, while the effective mass becomes $\mu=0.24m$. The new value for the exciton Ry has to be compared with the value $R_E=0.127$ eV determined by fitting the higher-order exciton lines $n=2$, 3 with a hydrogenic series. There is a good agreement between the results obtained from the electroreflectance measurements at 77°K and the observation of an hydrogenic exciton series at 4.2°K.

In the calculation we have assumed that the applied electric field is small compared to the field strength at which ionization of the $1s$ exciton state will be induced. This critical field is of the order of 1 Ry per Bohr radius, which in the case of PbI_2 corresponds to roughly 700 kV/cm, a value much larger than the maximum value used in the experiments (35 kV/cm). For the same reason the oscillator strength of the $1s$ exciton tran-

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[29] J. L. Brebner and E. Mooser, Phys. Letters **24**, A274 (1967).

[30] C. B. Duke and M. E. Alferieff, Phys. Rev. **145**, 583 (1966).

[31] D. Blossey (private communication).

[32] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics: Non-Relativistic Theory* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 251.

[33] Y. Toyazawa, Progr. Theoret. Phys. (Kyoto) **20**, 53 (1958).

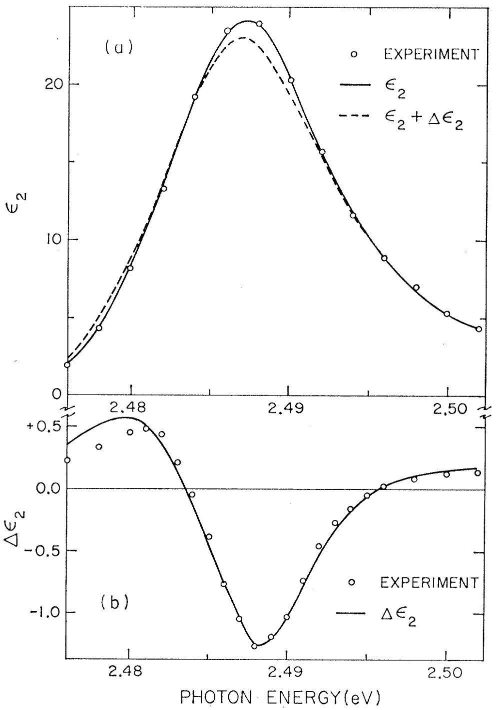

FIG. 9. (a) Analytical curves $\epsilon_2(0)$ (solid) and $\epsilon_2(F)$ for 35 kV/cm (dashed) and (b) their difference $\Delta\epsilon_2$ to fit the experimental points (circles) obtained from the Kramers-Kronig analysis at the $n=1$ exciton line.

sition should not be reduced by the application of the electric field.[34] The oscillator strength f is related to the imaginary part of the dielectric constant by the equation

$$f=\frac{2mV_0}{e^2h^2}\int \epsilon_2 E dE, \tag{7}$$

where the integration is taken over the exciton peak. V_0 is the volume of the unit cell, and m, e, and h have their usual meaning. We have calculated f from Eq. (7) by using the analytical expressions for ϵ_2. We obtain the same value $f=6.02\times10^{-2}$ (within 0.3%) in both cases, with and without electric field. This result is further evidence for the 1s character of the excitonic transition at 2.496 eV (4.5°K).

The satellite structure which is seen in the $\Delta\epsilon_1$ and $\Delta\epsilon_2$ spectra (Fig. 7) around 2.518 eV can be attributed to higher-excited exciton states. The line shape strongly suggests a considerable broadening of the $n=2$ line in the electric field which results in a negative contribution to $\Delta\epsilon_2$ at this energy. There is probably also a splitting of the $n=2$ state caused by the removal of its degeneracy in the electric field as it is observed, for example, in CdS at 1.6°K.[35] Thermal broadening prevents us from seeing a similar effect on lead iodide at 77°K. No structure is seen in the electroreflectance spectrum between 2.55 and 2.60 eV where a contribution from the optical transition at the energy gap is expected. Such a contribution, which would be of the order of a few times 10^{-4} in $\Delta R/R$, is probably masked by the tail arising from the excitonic transitions. Measurements at lower temperature and with higher field would certainly resolve more structure in this energy range.

The effect of an electric field upon the metastable exciton states has not yet been investigated theoretically. However, the experimental results indicate that, as in the case of a Wannier exciton, there is a large broadening of the excitonic peak caused by the electric field. This appears as a negative peak in the $\Delta\epsilon_2$ spectrum exactly at the position of the corresponding maximum in ϵ_2. Because of this behavior, one can make a distinction between the modulation of ϵ_2 correlated with the existence of exciton states and the modulation predicted by the Franz-Keldysh effect.

B. Band Structure

Because no energy-band calculation for PbI_2 has yet been reported, it is not possible to achieve a detailed analysis of the optical transitions. However, a model of the band structure has been proposed[3,36] which will be extended in the following discussion.

The outer electronic configurations of the lead ion is $6s^2$, $6p^2$ while for the iodine it is $5s^2$, $5p^5$. This gives a total of 18 electrons per unit cell to be located on the different valence bands. To a first approximation, we may assume the lowest conduction band to be a combination of $6p$ states of the lead ion, and the valence bands combinations of iodine $5s$, $5p$ with lead $6s$ states. Because of its position in the lattice, the iodine ion is situated in a strong crystal field parallel to the c axis. This will cause a considerable splitting of the $5p$ states placing the $5p_z$ level energetically higher than the $5p_x$, $5p_y$ levels which correspond to binding states within the layer of iodine atoms. Therefore, it is likely that the upper valence bands are mixed bands of iodine $5p_z$ and lead $6s$ states, a combination favored by the crystal field. Optical transitions from the $5p_z$, $6s$ energy bands to the lower conduction band with $6p$ character are allowed, while they are not from pure $5p$ valence bands. Additional splitting of the valence bands will be due to spin-orbit interaction and to overlap integrals between the wave function of neighboring ions.

The different exciton states have been considered by Tubbs[4] as localized excitons of the iodine ion in analogy to the exciton levels reported for the isoelectronic xenon. These considerations led to a band gap of 3.1 eV. This is in contradiction to the existence of an exciton series at 2.50 eV of the Wannier-Mott type associated with

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[34] This is actually true only for an allowed, nondegenerate excitonic transition, the oscillator strength of which will not be partly transferred to other new transitions previously forbidden in the field-free case.

[35] D. G. Thomas and J. J. Hopfield, Phys. Rev. **124**, 657 (1961).

[36] A. E. Dugan and H. K. Henisch, J. Phys. Chem. Solids **28**, 1885 (1967).

the fundamental absorption edge. Therefore, we assign a value $E_g=(2.552\pm0.005)$ eV to the band gap of $2H$-PbI_2. Dugan and Henisch[36] also assume a similar value, and explain the optical transition at 3.02 eV which they observe in the photoconductivity of PbI_2 as a transition from a lower subband to the lowest conduction band.

The energy bands obtained from the combination of the (I) $5p_z$ and (Pb) $6s$ atomic orbitals can be occupied by 6 electrons for each molecule of PbI_2. This fact should appear in the dependence of N_{eff}, the effective number of electrons in a unit cell, upon photon energy. The quantity N_{eff} is related to the optical constants by the relation

$$N_{\text{eff}}=\frac{2mV_0}{e^2h^2}\int_0^{E_0}\epsilon_2 E dE, \qquad (8)$$

which is identical to Eq. (7) except for the integration interval. Figure 10 shows a plot of N_{eff} versus energy. There is indeed a tendency for N_{eff} to saturate at a value of six or seven electrons around 6 eV before it increases again at higher energies. But this experimental evidence for the $5p_z$, $6s$ character of the upper valence bands can only be justified if the next deeper valence bands do not contribute appreciably to the optical transitions between 2.5 and 5 or 6 eV. Accordingly, it has to be proved that the upper valence bands are flat (which is likely because of the low carrier mobility) and that the lower located bands (with $5p_x$, $5p_y$ characters) have a large negative curvature at the center of the Brillouin zone.

As can be seen from Fig. 8, the electroreflectance spectrum around the critical point at 3.63 eV is particularly well resolved. Furthermore, the same $\Delta R/R$ spectrum was obtained for several orientations of the electric field within the cleavage plane perpendicular to the c axis. Such a result strongly suggests that the optical transition at 3.63 eV occurs at the center of the Brillouin zone rather than at a zone boundary. It is therefore possible to compare the experimental line shape of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ with those calculated by Aspnes,[9] which are graphically summarized in a paper by Hamakawa *et al.*[18] Among the four different cases, it is most likely that the critical point at 3.63 eV is an M_1-type saddle point. However, the presence of another optical transition at 3.74 eV observed at 4.5°K (Figs. 1 and 4) might also give a contribution to $\Delta\epsilon_2$ in this energy range, so that some ambiguity remains in the above assignment.

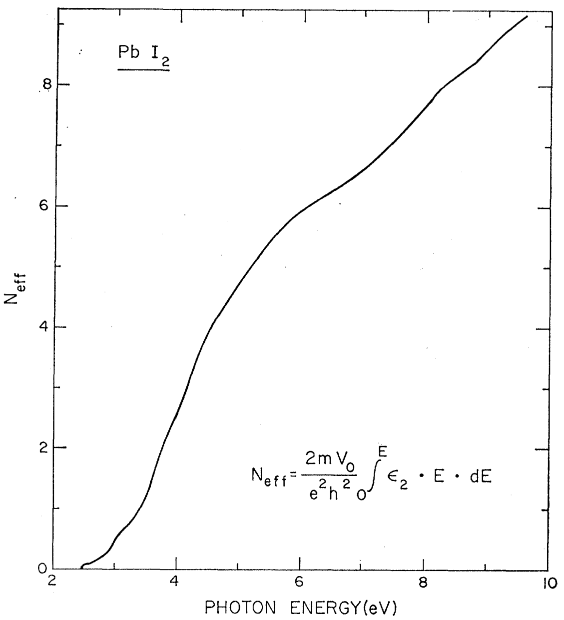

FIG. 10. Effective number of electrons per unit cell versus photon energy obtained from the numerical integration of the optical conductivity.

5. CONCLUSIONS

Reflectance and electroreflectance spectra of PbI_2 single crystals have been investigated at very low temperature in the visible and near ultraviolet portion of the spectrum. In front of the absorption edge, two additional lines are seen in the reflectivity besides the very sharp exciton lines at 2.498 eV. They correspond to the next higher excited states $n=2$ and $n=3$ of an hydrogen-like excitonic series. In the same energy range the electroreflectance spectra have been interpreted in terms of the Stark effect of the hydrogenic exciton states. The experimental determination of the shift of the first exciton line provides an independent way to evaluate the different exciton parameters. In the region of the fundamental absorption, two different effects contribute to the observed electroreflectance structure. The dominant one is the broadening of several lines associated with transitions into metastable exciton states; the other is the Franz-Keldysh effect. Considering the importance of these effects in PbI_2, it seems very desirable to continue both experimental and theoretical investigations in order to determine the band structure of this material and to gain a better understanding of the mechanism which leads to the formation of the metastable exciton states.

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