

Effect of a High Electric Field on the Absorption of Light by PbI_2 and HgI_2

RICHARD WILLIAMS

RCA Laboratories, Princeton, New Jersey

(Received November 21, 1961)

High electric fields produce a shift of the optical band edge to longer wavelengths in single crystals of PbI_2 and HgI_2 . Fields in the range of 10^5 to 10^6 v/cm cause shifts of the band edge up to 30 Å. The magnitude of the shift is proportional to the square of the applied field in agreement with the theoretical prediction of Franz. Using ac fields, the frequency response of the effect has been followed up to 5 kc/sec with no observable inertia.

WHEN an insulator or semiconductor is placed in a high electric field, the wavelength of the fundamental absorption edge is changed. Theoretical treatments of the effect have been given by Franz¹ and by Keldysh.² In order to give quantitative predictions, the theory must treat a specific model for the band edge. Keldysh treated the case applying to the region of direct transitions in silicon and predicted that the band edge would shift to lower energies by an amount proportional to the two-thirds power of the applied field. Franz treated an exponential band edge and predicted that, for this case, the band edge would shift to lower energies by an amount proportional to the square of the field. On the experimental side, several observations of the effect have been reported for^{3,4} Si and CdS.^{5,6} With silicon, the effect was observed in the region of direct transitions. The band edge shifted to longer wavelengths by about 150 Å in a field of 5×10^4 v/cm and, according to Keldysh, the expected proportionality was obtained between the shift of the band edge and the two-thirds power of the field. With CdS the band edge shifted to longer wavelengths by 70 Å in fields of about 10^6 v/cm. In CdS the band edge is exponential.⁷ The observed shift⁸ was, indeed, proportional to the square of the applied field, but the interpretation was complicated by the fact that the applied field was not uniform but a function of position within the crystal. Recently, Moss⁹ has made a quantitative study of the effect in gallium arsenide and reported good agreement between theory and experiment.

In the present work, the effect of an electric field on the optical band edge has been studied for two materials having band edges which are approximately exponential over the range studied. These materials are lead iodide,

PbI_2 , and mercuric iodide, HgI_2 . For both of these materials the fundamental absorption edge lies in the visible region of the spectrum which facilitates observations. To obtain the required fields, a technique has been used which, it is believed, produces an approximately uniform field within thin single crystal specimens. A quantitative comparison of results is made with the theory of Franz and agreement is found.

EXPERIMENTAL

The fields required to observe the shift of the band edge are in the range 10^5 to 10^6 v/cm. These were obtained in this work simply by sandwiching the crystal to be studied between two thin sheets of mica and placing these between two sheets of glass having stripes of transparent conductive coating on their inner surfaces. The arrangement is illustrated in Fig. 1. The thickness of the mica sheets ranged from 10 to 25 μ . Crystal specimens were 6 to 10 μ thick with PbI_2 and 100 to 250 μ with HgI_2 . To obtain the necessary fields, required voltages of several kilovolts in some cases and special precautions were necessary to avoid air breakdown between the electrodes. These precautions led to the arrangement shown in Fig. 1. The mica sheets prevent injection of electrons into the crystal from the conducting electrodes. The squares of mica were about 2 cm on a side. They are much larger than the crystal in order to minimize breakdown in the air around the edges of the specimen. The conductive coating on the glass plates is in the form of narrow stripes as shown, in order to increase the break-

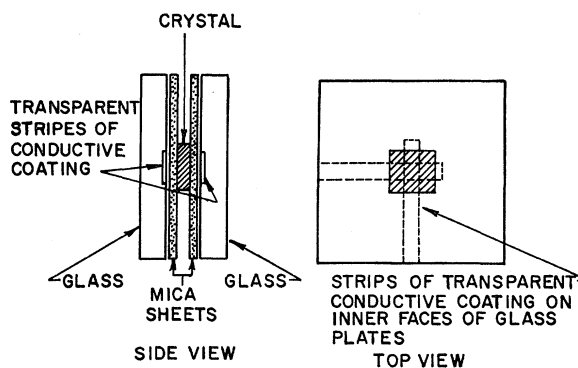


FIG. 1. Method of mounting crystals for measurement of their light absorption in a high electric field.

¹ W. Franz, *Z. Naturforsch.* **13a**, 484 (1958).

² L. W. Keldysh, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **34**, 1138 (1958) [translation: *Soviet Phys.—JETP* **7**, 788 (1958)].

³ V. S. Vavilov and K. I. Britsyn, *Soviet Phys.—Solid State* **2**, 1746 (1961).

⁴ L. V. Keldysh, V. S. Vavilov, and K. I. Britsyn, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 824.

⁵ K. W. Böer, H. J. Hänsche, and U. Kümmel, *Z. Physik* **155**, 170 (1959).

⁶ R. Williams, *Phys. Rev.* **117**, 1487 (1960).

⁷ D. Dutton, *Phys. Rev.* **112**, 785 (1958).

⁸ R. Williams, *J. Chem. Phys. Solids* (to be published).

⁹ T. S. Moss, *Suppl. J. Appl. Phys.* **32**, 2136 (1961).

down path between electrodes. The width of the stripes is deliberately made smaller than the width of the crystal specimen so that the high field does not occur in the air gap between the plates. For the experiments with HgI_2 , the crystal was pressed into melted polystyrene between the plates which solidified and further reduced the tendency toward air breakdown. The voltage source was a neon sign transformer giving a 60-cycle ac voltage up to 9 kv. In the frequency response experiment, an audio oscillator and amplifier combination was used which gave voltages of 2 kv at frequencies up to 5 kc/sec.

The crystal specimens were about 2 mm square, and the measurements of transmitted light intensity were made with the arrangement illustrated in Fig. 2. Light from a monochromator passed through the crystal and was picked up by a microscope focused on the crystal. A photomultiplier was mounted on the eyepiece of the microscope to measure the light intensity.

PbI_2 crystals were grown from water solution by slow cooling of the saturated solution from 100°C to room temperature over a period of eight hours. The crystals nucleate at the air surface and in the interior of the solution and grow to completion without coming into contact with the walls of the container. As a result many of the crystals have perfect geometric shapes and appear as thin yellow hexagonal or triangular plates, reflecting the hexagonal crystal structure¹⁰ of PbI_2 . The plates were several mm in diameter and very uniform in thickness. The average thickness was about $6\ \mu$. The hexagonal c axis of the crystals lies perpendicular to the surface of the plate, making the direction of the applied electric field coincident with the c axis. The absorption edge lies at about $5200\ \text{\AA}$ at room temperature.

HgI_2 crystals were grown by slow cooling from 80°C of a water solution having a concentration of $0.88\text{-}M$ HgI_2 and $1.2\text{-}M$ KI . The sparingly soluble HgI_2 forms a highly soluble complex with the KI , and, for this concentration ratio, the solid phase in equilibrium with the saturated solution is HgI_2 , according to the solubility data given by Seidell.¹¹ The crystals appear as bright red pyramids which can be cleaved perpendicular to the tetragonal.¹² c axis to give thin plates about $0.1\ \text{mm}$ thick. Here, also, the direction of the applied field coincided with the c axis. A room temperature absorption spectrum of HgI_2 at the band edge has been given by Bube,¹³ who gives the band gap as $2.11\ \text{eV}$.

The need for using ac voltage to apply the field to the crystals can be understood by considering the specimen and electrode arrangement shown in Fig. 1. If a dc voltage is applied to the electrodes, the potential will, in time, distribute itself so that the voltage drop across the

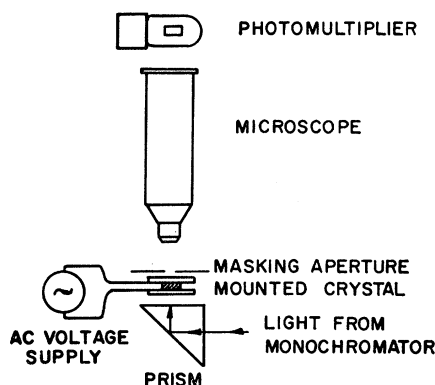


FIG. 2. Experimental arrangement for measuring transmitted light intensity.

mica sheets is proportional to their resistance and the voltage drop across the crystal is proportional to the resistance of the crystal. The volume resistivity of mica is approximately $10^{17}\ \text{ohm-cm}$, but surface leakage resistance would probably make the resistance of the sheets considerably lower than this. Still, the resistance of the mica sheets is very likely much higher than that of most crystals which might be used in this type of experiment. The dark resistivity of HgI_2 is of the order of $10^{12}\ \text{ohm-cm}$ as found by Bube¹³ and also in this work. Resistivity values around $10^{11}\ \text{ohm-cm}$ were found for PbI_2 in this work. In both cases, a dc voltage would distribute itself so that ultimately nearly all the voltage drop would be across the mica. The time required to reach this steady state is of course the rc time constant for the material which here is about $0.1\ \text{sec}$. For times short compared to this, the voltage distributes itself according to the capacitance of the mica and of the crystal. The resultant fields in the two materials are then proportional to the reciprocals of the dielectric constants. The dielectric constant¹⁴ of mica is 5.4 and that of¹⁵ PbI_2 is 6.08 , so the fields in the two materials are in the ratio $6.08/5.4$ for an ac applied voltage having a frequency appreciably greater than $10\ \text{cps}$. In addition, the field should be given by the instantaneous voltage divided by the interelectrode spacing. For HgI_2 the dielectric constant is 7.07 ,¹⁵ so the field in the crystal is $5.4/7.07$ times the field in the mica. In this work the field present in the crystal was assumed to be uniform and to be that given by these considerations. There was no evidence from the experiments to indicate polarization, barrier effects or anything which would cause a departure from a uniform field within the crystal.

The ratio, I/I_0 , shown in Figs. 3 and 5, was measured in the following way. The apparatus was arranged as shown in Fig. 2 but without the crystal or its mounting. Photocurrent, caused by the light passing through the

¹⁰ P. P. Ewald and C. Hermann, *Strukturbericht* (Akademische Verlagsgesellschaft, Leipzig, 1913–1928), p. 191.

¹¹ A. Seidell, *Solubilities of Inorganic and Metal Organic Compounds* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1940), 3rd ed.

¹² See reference 9, p. 177.

¹³ R. H. Bube, *Phys. Rev.* **106**, 703 (1957).

¹⁴ A. Von Hippel, *Dielectric Materials and Applications* (John Wiley & Sons, Inc., New York, 1954).

¹⁵ N. V. Sathe, N. L. Phalnikar, and B. V. Bhide, *J. Indian Chem. Soc.* **22**, 29 (1945).

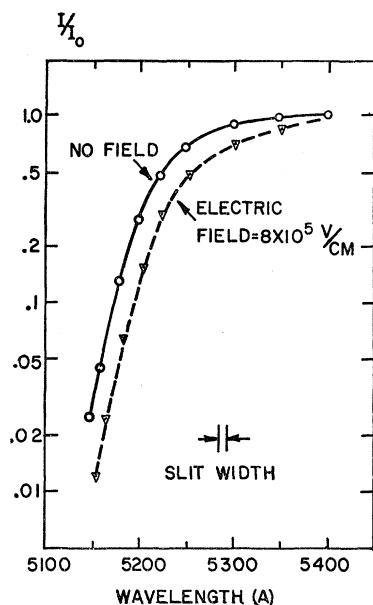


FIG. 3. Absorption edge of a PbI_2 crystal with and without an applied field. I/I_0 is the ratio of transmitted intensity to incident intensity with correction for reflectivity. The crystal thickness is 6μ .

masking aperture, was measured over the wavelength range of interest. Then the mounted crystal was inserted as shown in Fig. 2 and the monochromator was set at a wavelength longer than that of the absorption edge and sufficiently removed from the edge that there was no true absorption by the crystal. The decrease of photocurrent on placing the mounted crystal in the light path gave the losses due to reflection and scattering. Since these were primarily due to reflections at glass and mica surfaces, the losses were assumed to be independent of wavelength over the small interval of wavelengths investigated. Using this correction, the values of I_0 were obtained from the photocurrents measured above. The intensity I was then measured as a function of wavelength with the crystal fixed in position.

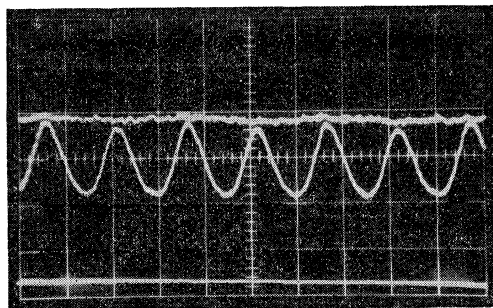


FIG. 4. Oscilloscope trace showing variation of transmitted light intensity as a function of applied field. Vertical coordinate is light intensity and horizontal coordinate is time. Top trace: light intensity transmitted with no field. Middle trace: intensity with 60-cycle ac voltage applied to crystal. Bottom trace: base line with light off. Small displacement of uppermost portion of middle trace from the top trace is due to slight heating of crystal when voltage is applied. Wavelength = 5250 Å Peak field = $7 \times 10^5\text{ v/cm}$.

EXPERIMENTAL RESULTS

More extensive experiments were done with PbI_2 than with HgI_2 because the PbI_2 crystals were thinner and more uniform than those of HgI_2 . The absorption edge of PbI_2 , with and without an applied field, is shown in Fig. 3. The curve with field is that taken with a 60-cps applied voltage and the points for the curve were obtained by measuring the transmitted light intensity at the appropriate wavelength for the instantaneous point at which the applied voltage is at a maximum. It is seen that the two curves are nearly parallel and that the band edge is shifted to longer wavelengths by about 25 Å . Curves were also taken at intermediate voltages and were also found to be parallel to the curves in Fig. 3 and to lie between them.

It is necessary to demonstrate that the shift of the band edge which is observed is not due to a heating effect since the band edge shifts to longer wavelengths with an increase of temperature. It is possible to show that, in fact, a small part of the observed effect is a heating effect but that the major part of the effect is not a heating effect. This can be seen by examination of an oscilloscope trace showing the transmitted light intensity as a function of time, using a wavelength near the band edge where application of the field has a substantial effect on the transmitted light intensity. Such a trace is shown in Fig. 4. It shows the modulation of transmitted light intensity by a 60-cps applied voltage. The modulation follows the applied voltage and is independent of the sign of the applied voltage, so there is a 120-cps ripple representing the light intensity as a function of time. A heating effect could not follow an alternating voltage of this frequency in a sample with the dimensions and thermal conductivity of the materials used. Thus, the change in transmitted light intensity with field is due primarily to a true change of the optical absorption coefficient and not to a secondary effect caused by heating of the specimen. Examination of Fig. 4 shows, however, that there is a small effect due to heating of the crystal. The highest values of transmitted light intensity reached when there is an ac voltage applied to the specimen are not quite as high as those reached when there is no voltage applied. This happens even though the applied voltage goes to zero twice during every cycle. This small displacement from the intensity for no applied voltage is apparently a heating effect in which the temperature of the crystal rises slightly but does not rise and fall with the frequency of the applied voltage. It amounts to about 10% of the total intensity modulation in the trace shown, and this is typical. The amount of the temperature rise can be estimated by assuming that the temperature coefficient of the band gap of PbI_2 is $5 \times 10^{-4}\text{ ev/deg}$ which is the order of the temperature coefficients for similar materials. On this assumption, the temperature rise which would be necessary to produce the observed heating effect would be 2°C .

In a similar way it was determined that the intensity of transmitted light follows an applied voltage having a frequency of 5 kc/sec. There was no evidence that the effect was lagging the applied voltage at this frequency. It was not possible to test the effect at higher frequencies with available equipment.

Quite similar results were obtained with HgI_2 . Fig. 5 shows the absorption edge with and without field. It was demonstrated again that the effect was not primarily a heating effect but that a small part was due to heating, as with PbI_2 . Since the crystal specimens were thicker for HgI_2 , it was necessary to apply higher voltages, up to 9 kv, to obtain fields comparable with those used to study PbI_2 . As a result, the maximum field to which measurements could be made was limited by breakdown in the air around the specimen.

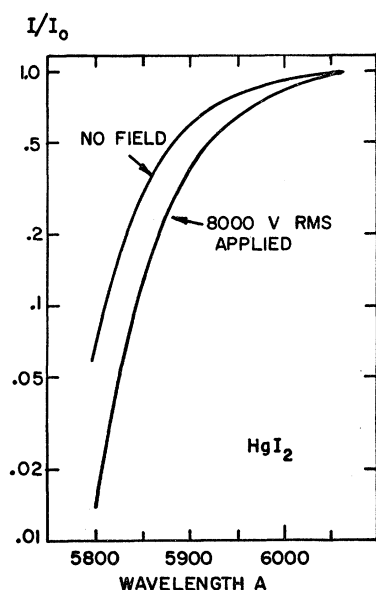


FIG. 5. Absorption edge of HgI_2 with and without applied voltage.

DISCUSSION

These observations suggest that the shift of the band edge is due to the Franz-Keldysh effect. A quantitative comparison of the data with Franz's theory has been made. For an exponential band edge the logarithm of the absorption coefficient plotted against photon energy gives a straight line. This is a good approximation for the absorption edge of PbI_2 over the range of wavelengths studied here. Figure 6 shows the absorption constant as a function of energy for one of the PbI_2 crystals used. The spectrum was taken on a Carey spectrophotometer and is for room temperature. Similar data for PbI_2 were reported by I. Imai at the Cornell International Photoconductivity Conference, 1961. The theory is compared with experiment by measuring the absorption coefficient as a function of field for light of a single wavelength. This is equivalent to a measurement

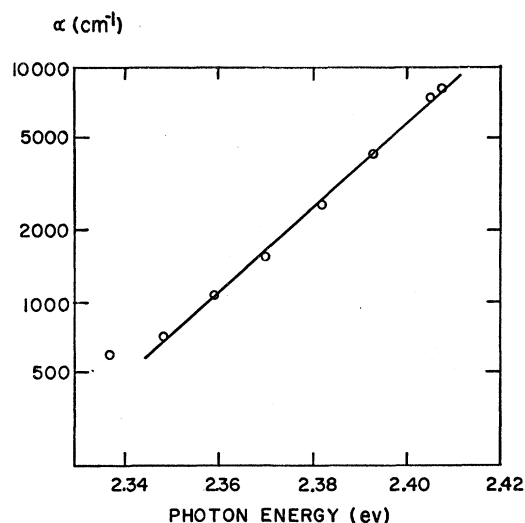


FIG. 6. Absorption coefficient vs photon energy for PbI_2 at room temperature. The definition of α as employed here is $I/I_0 = e^{-\alpha d}$ for a crystal of thickness d with correction for reflectivity.

of the band edge as a function of field, providing the wavelength chosen is in the range where the two curves shown in Fig. 3 are parallel. Data were taken from oscilloscope traces such as Fig. 4, using the change of intensity at the peak value of the applied voltage as the measured quantity. A plot of absorption coefficient versus the square of the applied field is shown for two different crystals in Fig. 7. The field was assumed to be equal to the instantaneous value of voltage divided by the interelectrode spacing as discussed above. At the lower fields there is a good proportionality between absorption coefficient and the square of the field (thus a proportionality between the shift of the band edge and

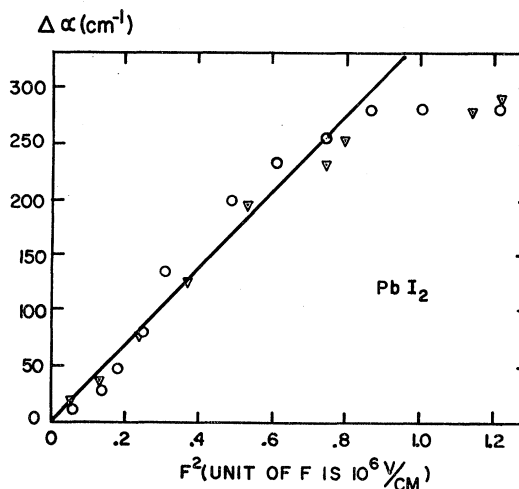


FIG. 7. Increase of absorption coefficient vs the square of the applied field. $\Delta\alpha$ is the difference between the absorption coefficients with and without the field for the wavelengths 5210 Å. \circ and ∇ represent data for two different crystals.

the square of the field). For fields above 9×10^5 v/cm, the absorption coefficient does not increase further. It is believed that this is due to a nondestructive dielectric breakdown in the PbI_2 which makes it conducting and transfers the field to the mica sheets. The dielectric breakdown field strength of mica is above 10^7 v/cm, and it would not be expected to break down at these fields. No value has been reported for the breakdown field strength of PbI_2 . For the alkali iodides, the breakdown field strengths¹⁶ range from 5×10^5 to 8×10^5 v/cm, and it is reasonable to assume that a similar value holds for PbI_2 . We interpret this data to mean that the shift of the band edge is, indeed, proportional to the square of the applied field up to fields around 9×10^5 v/cm where nondestructive dielectric breakdown of the PbI_2 prevents further increases of the field in the crystal.

The theoretical expression for the absolute magnitude of the shift of the band edge¹ is:

$$\delta\omega = \lambda^2 \omega_F^3, \quad (1)$$

where

$$\hbar\omega_F = 0.040 (m/m^*)^{1/3} (F/10^6)^{2/3}. \quad (2)$$

$\delta\omega$ is the shift of the band edge in frequency units, m is the electron mass, $1/m^*$ is the average of the reciprocals of the hole and electron effective masses and F is the applied field in v/cm. $1/\lambda$ is a measure of the steepness of the absorption edge, relating the absorption coefficient α to the frequency ν by the equation $\alpha = \alpha_0 e^{2\pi\nu/\lambda}$. From Fig. 5, $\hbar/\lambda = 0.024$ ev. The units of $\hbar\omega_F$ given by the above expression are ev. An estimate of the order of magnitude of $\delta\omega$ to be expected in the present experiments can be made.

For a field of 9×10^5 v/cm we have then $\hbar\delta\omega = 0.088 (m/m^*)$ ev, according to Eq. (1). The shift of the band edge observed for this field is 0.011 ev. The effective mass values are not yet known, but it is unlikely that m/m^* is much smaller than unity. Thus, there is a discrepancy of around eight between theoretical and experimental values for the absolute magnitude of the shift of the absorption edge.

For HgI_2 , too, there was a proportionality between the shift of the band edge and the applied voltage. The band edge is exponential in the range studied.¹³ The crystals were not as uniform in thickness as the PbI_2 crystals, and for this reason, an absolute comparison of the data with theory has not been made.

The results indicate that the Franz-Keldysh effect is a general property of crystalline insulators. There is agreement between theory and experiment for the dependence of the effect on the applied field. For the absolute magnitude of the shift, the experimental result is about $\frac{1}{8}$ the value predicted by the theory assuming m/m^* is unity. It is possible that the discrepancy is due to uncertain knowledge of the field within the crystal, since there is no simple way to measure the field independently of the method used here, and there is considerable uncertainty in the values of the dielectric constants required to obtain in the fields. On the other hand, it is probably wrong to expect agreement to better than an order of magnitude for a prediction of an absolute quantity by a theory as general as that of Franz when applied to widely different materials. In addition, there is some uncertainty introduced into the theory by the fact that the origin of the exponential band edge is imperfectly understood at present.

¹⁶ S. Whitehead, *Dielectric Breakdown of Solids* (Oxford University Press, New York, 1951).

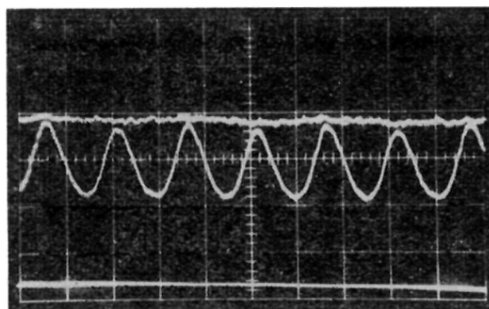


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