

Ac Impedance Measurements on Insulated CdS Crystals*

HARTMUT KALLMANN, BERNARD KRAMER,† AND GRACE MARMOR SPRUCH
Department of Physics, New York University, New York, New York

(Received June 4, 1959)

In order to study the induced conductivity in CdS crystals without charge injection at the electrodes, the crystals were insulated with Mylar and ac impedance measurements were made. The capacitance and resistance of the crystals were studied as functions of intensity and wavelength of excitation, and frequency and voltage of the ac field. The crystal-Mylar combination was found to behave in a manner similar to that of powdered samples in like experiments. With a model that treats the crystal as a capacitor shunted by a light-sensitive resistance, the capacitance was found to increase with intensity of excitation, and to decrease with voltage and frequency. The resistance of the crystal increased by factors of 4 or 5 as the intensity of excitation decreased by factors of 10. The limitations of the model are discussed, and conclusions drawn regarding whether trapped electrons or only conduction electrons contribute to the impedance.

INTRODUCTION

THE induced conductivity in materials of the ZnS type has been investigated by many laboratories, but the actual behavior of the current carriers has been masked by "side-effects" in many cases.

When these materials are used in powder form, dc measurements depend strongly upon the grain boundaries and electrode pressure. With ac measurements these effects can be reduced, but quantitative conductivity data is still difficult to obtain.

When these materials are in the form of single crystals, other difficulties arise. The electrodes may introduce unknown effects because of blocking layers, for example, or because at high field strengths charge injection (or ejection) may occur. Blocking layers can be reduced by cleaning (glow discharge) or by a suitable choice of electrodes (i.e., indium, gallium, or gold). Still a third difficulty concerns geometry. If a crystal of several millimeters to several centimeters in length has electrodes at the ends, the inhomogeneity of the crystal may be such as to cause the measured conductivity to be determined by the least conductive region. This difficulty can be partially overcome in flat crystals by glow discharging the surface thoroughly and evaporating transparent gold electrodes on the flat surfaces, so that the effective thickness of the crystal may be less than 1 mm. However, experiments have shown that even in this case some barrier effects are noted.¹

Since it appears to be extremely difficult to completely eliminate barrier effects with single crystals, we have tried a somewhat different approach, that of deliberately introducing a known insulating barrier. A thin insulating film of Mylar with a semitransparent coating of aluminum on one side was cemented to each flat surface of a CdS crystal with the aluminum coating on the outside. With ac impedance measurements, the

intrinsic conductivity under various types of excitation and ac fields was determined.

PROCEDURE

The CdS crystals were grown from the vapor phase at 900°C according to the method of Frerichs and Warminsky^{2,3} and copper activated with CuCl by the Hupp Corporation. These crystals were flat platelets whose approximate dimensions were 1 cm×1 cm×0.3 mm. The Mylar (0.001 cm thick) was applied to both surfaces, and leads attached to the aluminum coating with silver paste.

A General Radio 650-A impedance bridge was used for most measurements; the capacitance, C_0 , and dissipation factor, D_0 , of the crystal-Mylar combination could be obtained by correcting for the capacitance and dissipation factor of the leads. The crystal-Mylar combination could be considered to be two capacitors in series (both Mylar sheets are equivalent to one capacitor), with the capacitor that represents the crystal shunted by a light-sensitive resistance.

C_x and R_x are the equivalent parallel capacitance and resistance which describe the ac behavior of the crystal. C_x need not be constant; its behavior will be determined from the experiments. C_{My} is the capacitance of the Mylar.

C_x and R_x can be obtained from C_0 and D_0 through the relations

$$C_x = \frac{C_0(1+D_0^2)D_x}{D_0(1+D_x^2)}, \quad (1)$$

$$D_x = \frac{C_{My}D_0}{(C_{My}-C_0)(1+D_0^2)}, \quad (2)$$

$$R_x = 1/(\omega D_x C_x), \quad (3)$$

if C_{My} is known. The capacitance of the Mylar was obtained by two independent methods. In one method the intensity of excitation was increased until

* This investigation was supported by the Hupp Corporation, Cleveland, Ohio, from July, 1954 to July, 1957.

† Also with Physics Department, Hunter College, Bronx, New York.

¹ Work done by S. Jaffe in this laboratory.

² R. Frerichs, *Naturwissenschaften* **33**, 281 (1946).

³ R. Warminsky, Ph.D. thesis, Technical University of Berlin, 1948 (unpublished).

C_0 reached a saturation value. In this range the crystal is shorted out by the small R_x and $C_0=C_{My}$. The second method involved making a capacitor by cementing two Mylar sheets together; the C_{My} obtained by this method was within 10% of that obtained by the first method.

In order to ascertain how critically C_x and R_x depend upon the value selected for C_{My} , an interation procedure was applied using Eqs. (1) and (2) and the values of C_0 and D_0 obtained at different intensities. This procedure showed that C_x and D_x are not critically dependent upon C_{My} , so that a small error in the value of C_{My} does not affect C_x and D_x to any great extent.

EXPERIMENTAL RESULTS

The crystals were contained in a light-tight box, which also held the source of illumination, a 7½-watt incandescent lamp. The light was collimated and reached the crystal from below. Filters could be

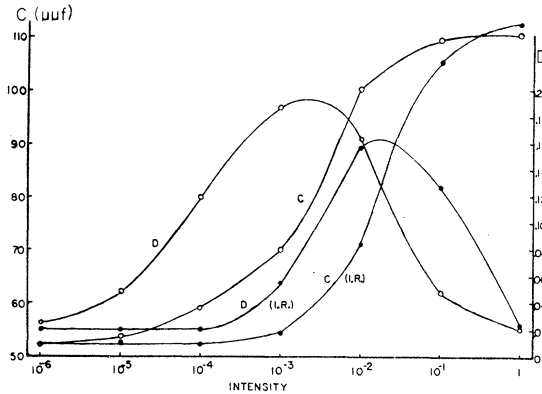


FIG. 1. Measured values of the capacitance C and dissipation factor D of crystal-Mylar combination No. 1 as a function of intensity with and without simultaneous infrared irradiation. The ac potential is 1.9 volts rms at a frequency of 1000 cps.

inserted between the crystal and the source. Infrared radiation could be applied to the crystal from above through a shutter at an angle of about 45° with the vertical. The intensity of visible radiation (through a Corning 1-56 filter) incident on the crystal (after having passed through the coated Mylar) was about 5 microwatts/cm².

(a) Crystal 1

An ac potential of 1.9 volts rms at a frequency of 1000 cps was applied across the combination; this corresponds to ~1.6 volts across the crystal in the unexcited state, and, of course, a much lower voltage in the illuminated state. With excitation containing visible wavelengths on both sides of the absorption edge so that the crystal was nonuniformly excited, the results given in Table I were obtained. The measured values are given in Fig. 1. The figures in the table show that C_x does not remain constant, but increases with

TABLE I. Capacitance, dissipation factor, and resistance for crystal 1, for different intensities of nonuniform excitation, with an ac potential of 1.9 volts rms and a frequency of 1000 cps. C_0 and D_0 are the capacitance and dissipation factor of the crystal-Mylar combination; C_x , D_x , and R_x the parallel capacitance, dissipation factor and resistance of the crystal alone; and C_s the series capacitance of the crystal alone. ND refers to a neutral density filter, the number following it denoting the logarithm of the ratio of the incident to the transmitted light.

Filters	$C_0(\mu\mu f)$	D_0	$C_x(\mu\mu f)$	D_x	$R_x(\text{ohms})$	$C_s(\mu\mu f)$
1-56	68.4	0.0277	6×10^4	...
1-56 and ND1	67.7	0.0708	158	5.98	2×10^5	5850
1-56 and ND2	56.0	0.275	80.6	2.29	1×10^6	506
1-56 and ND3	25.6	0.471	32.9	0.87	5×10^6	59.2
1-56 and ND4	16.3	0.393	20.1	0.54	1.6×10^7	26.2
1-56 and ND2 and ND3	11.7	0.173	14.2	0.21	5×10^7	14.8
1-56 and ND2 and ND4	10.6	0.0737	12.6	0.087	1.6×10^8	12.7
no illumination	10.4	0.0199	12.3	0.027	5×10^8	12.3

increasing excitation. R_x decreases approximately as the square of the intensity.

Crystal 1 was also investigated at a frequency of 200 cps with all other conditions the same as above. The results are given in Table II. These results show that again the capacitance of the crystal increases with increasing intensity. The resistance values are slightly higher than with 1000 cps. Results at 200 cps with 9 volts were no different from those obtained at 1.9 volts.

Uniform excitation of the crystal was effected by a Corning 3-66 filter used in conjunction with the 1-56 filter. This filter combination transmits only those wavelengths between 5700 and 6800 Å and thus reduces the intensity to roughly one-half that transmitted by the 1-56 filter alone. Between 1% and 10% of this light is probably absorbed by the crystal. With an ac potential of 2 volts and a frequency of 200 cps, the results were those shown in Table III.

These results are similar to those in Table II where the excitation was not uniform, the difference being attributable to the decrease in intensity which accompanied the use of the 3-66 filter. Since the R_x values are only slightly higher than those in Table II for the same neutral density filter, one is inclined to

TABLE II. Capacitance, dissipation factor, and resistance of crystal 1 for different intensities of nonuniform excitation, with an ac potential of 1.9 volts rms and a frequency of 200 cps.

Filters	$C_0(\mu\mu f)$	D_0	$C_x(\mu\mu f)$	D_x	$R_x(\text{ohms})$	$C_s(\mu\mu f)$
1-56	66.3	0.0059	7.5×10^4	...
1-56 and ND1	66.3	0.0153	1.9×10^5	...
1-56 and ND2	64.2	0.0961	242	2.36	1.5×10^6	1600
1-56 and ND3	45.7	0.399	66.4	0.985	1.0×10^7	131
1-56 and ND4	22.7	0.412	28.0	0.584	5.0×10^7	37.5
1-56 and ND2 and ND3	16.0	0.317	20.2	0.431	1.0×10^8	24.0
1-56 and ND2 and ND4	12.8	0.221	15.6	0.276	2.0×10^8	16.6
1-56 and ND3 and ND4	12.3	0.186	14.9	0.230	2.5×10^8	15.7

TABLE III. Capacitance, dissipation factor, and resistance of crystal 1 for different intensities of uniform excitation with an ac potential of 2 volts rms and a frequency of 200 cps.

Filters	C_0 (μf)	D_0	C_x (μf)	D_x	R_x (ohms)	C_s (μf)
1-56 and 3-66	67.0	0.0107	1.3×10^5	...
1-56 and 3-66 and ND1	66.1	0.0422	408	3.57	5.5×10^5	5060
1-56 and 3-66 and ND2	57.5	0.240	92.1	2.32	3.7×10^6	590
1-56 and 3-66 and ND3	30.9	0.485	39.1	1.13	1.8×10^7	89.0
1-56 and 3-66 and ND4	19.0	0.356	24.8	0.526	6.1×10^7	31.6
1-56 and 3-66 and ND2 and ND3	16.0	0.348	19.9	0.475	8.4×10^7	24.4
1-56 and 3-66 and ND2 and ND4	16.0	0.332	20.1	0.452	8.7×10^7	24.2

conclude that the strongly absorbed light did not contribute in great measure to the conductivity.

An increase in voltage to 9 volts for the two points of highest intensity did not give rise to any pronounced change in R_x .

The effect of applying infrared radiation simultaneously with visible light was also investigated. The infrared radiation was that transmitted through the Corning 7-56 and 4-97 filters, i.e., wavelengths greater than 1.25 microns. Wavelengths shorter than this were found to excite the crystal rather than quench it. The applied potential was 1.9 volts and the frequency 1000 cps. The results are given in Table IV and Fig. 1 and should be compared with those of Table I.

It can be seen from the figure that the infrared radiation has a definite quenching effect, which is much stronger at medium intensities than at high intensities. This is in agreement with measurements on powdered materials⁴ where the quenching effect of infrared decreases with increasing excitation. The table shows that R_x is linear with intensity, a situation which did not exist at 1000 cps when the infrared radiation was absent. This may be coincidence arising from the fact that infrared radiation has a greater effect at lower intensities than at higher ones, thus making the nonlinear lower intensity region linear while leaving the higher intensity region unaffected.

In addition to the measurements with constant

TABLE IV. Capacitance, dissipation factor, and resistance of crystal 1 for different intensities of nonuniform excitation applied simultaneously with infrared radiation ($\lambda > 1.25\mu$) with an ac potential of 1.9 volts rms and a frequency of 1000 cps.

Filters	C_0 (μf)	D_0	C_x (μf)	D_x	R_x (ohms)	C_s (μf)
1-56	70.2	0.0294	6.7×10^4	...
1-56 and ND1	63.4	0.204	75.1	4.08	5.2×10^5	1340
1-56 and ND2	29.2	0.364	42.5	0.690	5.5×10^6	62.6
1-56 and ND3	12.2	0.201	14.8	0.246	4.4×10^7	15.7
1-56 and ND4	10.4	0.054	12.3	0.0635	2.0×10^8	12.3

⁴ Kallmann, Kramer, and Perlmutter, Phys. Rev. **89**, 700 (1953).

illumination described above, the effect of infrared radiation on a decay curve was investigated. This is shown in Fig. 2 where the curves for C and D were plotted from the values of the capacitance and dissipation factor as given by the bridge not corrected for the effect of leads. The quenching effect of the infrared radiation is pronounced, as can be seen from a comparison with the regular decay curve in the figure. The first point on each curve is that taken just before the light was turned off.

The R_x values obtained from these measurements (see Tables I to III) show a decrease with increasing intensity (as I^n where n is between 1 and $\frac{1}{2}$). In Table I (1000 cps) the decrease in intensity goes from 1 to 10^{-6} ; in the range of 10^{-1} to 10^{-5} an increase of 10^4 in intensity produces an increase of 2.5×10^2 in conductivity. At 200 cps, however, (Table II) the change in conductivity is more proportional to intensity; an increase in intensity by a factor of 1000 produces an increase in conductivity by a factor of 250. The reason

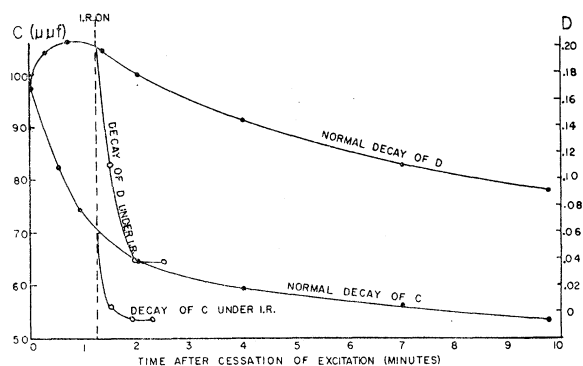


FIG. 2. Normal decay of the capacitance C and dissipation factor D of crystal-Mylar combination No. 1 as a function of time, and the decay under infrared irradiation.

for this difference between 1000 and 200 cps is not clear, but may be due to the fact that at 1000 cps the electrons cannot fully follow the field. A comparison of the values of R_x for 1000 cps and 200 cps when C_0 has just reached saturation shows that R_x at 200 cps is several times higher than R_x at 1000 cps, which is to be expected. (Compare the third value in Table II with the second in Table I.)

(b) Crystal 2

The equilibrium capacitance of crystal 2 was investigated as a function of intensity in the same manner as crystal 1 in order to ascertain whether the change in C_x with intensity was peculiar to crystal 1. No conclusions regarding the C_x of crystal 2 could be drawn with a frequency of 1000 cps, because a reliable saturation value of the measured capacitance and dissipation factor of the crystal-Mylar combination could not be obtained. This is most likely due to the lower sensitivity of this crystal. The maximum light intensity used for crystal 1

was not sufficient to produce a conductivity in crystal 2 which would insure saturation.

Measurements were taken at a frequency of 10 cps in order to get a better saturation value. The lower frequency has the effect of making the capacitance *versus* intensity curve rise more steeply, that is, the capacitance will be higher for the same intensity than with a frequency of 1000 cps, and will thus reach a saturation value earlier. Then, as was the case with crystal 1, C_x was found to increase with increasing intensity.

The effect of different voltages on the measured values C and D for this crystal are shown in Fig. 3.⁵ There is a decided voltage quenching, the higher voltage causing the capacitance to approach saturation more slowly for a given intensity of illumination, with the D curve correspondingly displaced in the direction of higher intensity.

OTHER CRYSTALS

Two other crystals were also investigated and similar results were obtained, C_x increased with intensity, R_x increased by factors of 4 or 5 as the intensity decreased by factors of 10, and there was no difference between the effects of uniform and non-uniform excitation. The voltage characteristics of these crystals were not investigated.

CONCLUSIONS

The results reported above are in general agreement with those obtained from powder measurements.⁴ As was the case there, the capacitance of the sample increases with increasing intensity of excitation, and the D value goes through a maximum. One can readily account for the shape of the curves for the capacitance and dissipation factor with the model given above. As the light intensity is increased R_x goes from an essentially infinite value to a low value, shorting out C_x . Thus the capacitance of the crystal-Mylar combination goes from a low value when the two capacitors are in series to a high value, the value of the Mylar alone, when the crystal capacitance is shorted out. The dissipation factor is low at low intensities where there is little conductivity (R_0 is large and $D_0 = 1/(R_0\omega C_0)$). At high intensities R_x is small, C_x is shorted out, and what remains is C_{M_y} in series with R_x .

In the case of powders, the barrier layers or layers near the electrodes serve as insulators and play the role of the Mylar in the present experiments. The fact that with powders the measured capacitance increases by a factor of 2 while for crystals it increases by a factor of 5 with the intensities employed is due to the increased ratio of conductive to nonconductive thickness for the crystal-Mylar combination.

⁵ These measurements were done by J. Shain in this laboratory. The authors wish to express their gratitude for this and other information he contributed.

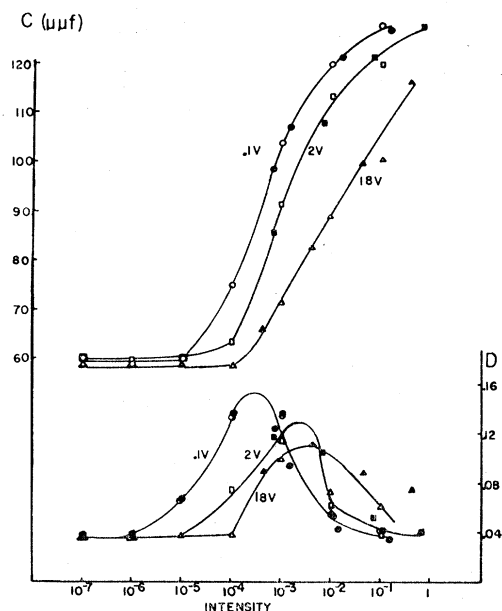


FIG. 3. Capacitance C and dissipation factor D of crystal-Mylar combination No. 2 as a function of intensity for different voltages at 10 cps.

It would be meaningless to interpret the results of these experiments as due to a change in the dielectric constant of the crystal with excitation. The order of magnitude of the number of trapped electrons in the crystal is known. A change in the dielectric constant due to these electrons which would essentially short out the capacitance of the crystal would involve these electrons being displaced through the entire crystal, which, in effect, would amount to bulk conductivity.

The fact that the effective parallel capacitance of the crystal, C_x , increases with increasing intensity is particularly interesting and requires some discussion. We have described the crystal as a capacitor in parallel with a resistor which shorts it out at high intensities. This picture is only valid, however, when there are ohmic contacts and current can flow into and out of the crystal. In the present case, with Mylar sheets between the electrodes and the crystal, no current enters or leaves the crystal. The charges produced by the excitation pile up at either side of the crystal depending upon the instantaneous polarity of the field, and are prevented from leaving by the Mylar. Therefore, at the crystal surface a finite field exists which is determined by the condition that the displacement vector be continuous across the boundary between the Mylar and the crystal. This means that whatever displacement exists in the Mylar must also exist at least near the surface of the crystal, which is contrary to the assumption that the capacitance is shorted out by a parallel resistance. At high excitation intensities, there is a strong field in the crystal close to the electrodes while the center of the crystal remains essentially field-free. That is, instead of the resistance shorting out the

entire crystal, the situation may be such that only the center of the crystal is shorted out, and instead of a capacitor shunted by a resistance, we have a capacitor in series with a resistance. Thus instead of R_x and C_x we might use a model containing C_s and R_s in series. The capacitance of the crystal is then due to the thin charged layers near the electrodes. This capacitance C_s can be quite high, as is shown in Tables I through IV in the column headed C_s , but it will be masked by the much lower capacitance of the Mylar with which it is in series. The series resistance, R_s , will not differ appreciably at high intensities from the parallel resistance, R_x , since R_s is related to R_x through the relation $R_s = R_x / (1/D_x^2 + 1)$ and in this region D_x is high.

The thickness of a layer which could be responsible for the value of C_s at a high intensity is about 10^{-4} cm, which is not too different from the Debye length calculated from the density of conduction electrons inside the crystal⁶ under the assumption that the time variation of the electric field is not sufficiently slow for equilibrium between conduction electrons, trapped electrons, and ionized activators to always exist. At lower frequencies this equilibrium condition may hold and not only the free electrons but the trapped electrons as well may be able to follow the field. This would reduce the Debye length and thus increase C_s . The investigation of the dependence of the capacitance C_s on the frequency, therefore, may provide an independent source of knowledge of the rapidity with which equilibrium is established.

The rapidity with which equilibrium is established can also be obtained from frequency measurements in the following way. As can be seen from Eqs. (1) and (2), when one eliminates D_0 , C_0 depends only upon C_x , D_x , and C_{My} , but not on the angular frequency ω directly. If one starts at a frequency low enough for equilibrium between conduction electrons, trapped electrons, and ionized activators to exist at all times, then for a fixed intensity R_x and C_x are constant and C_0 depends upon ω through its dependence on D_x , where $D_x = 1/(R_x C_x \omega)$. As the frequency is increased a point will be reached where equilibrium no longer exists. At that frequency C_x will change and C_0 will no longer be the same function of frequency as it had been up to that frequency. This "critical" frequency, then, is a measure of the time required for equilibrium to be established.

A brief theoretical discussion of the crystal capacitance at constant potential is given in the Appendix. This might be considered to be the limiting case of the slowly varying ac field.

Regarding the decrease in capacitance with increase in potential which is shown in Fig. 3, this may be

similar to the voltage quenching effect which was noted in experiments with luminescent powders.⁷ The increase in potential causes an increase in the concentration of charge, which in turn produces a greater rate of recombination. The increase in potential thus acts, in effect, like a decrease in excitation.

APPENDIX

Consider the simple situation of a condenser in series with a battery V_0 . Between the condenser plates we have two dielectrics, the crystal with capacitance C_x , and the sheets of Mylar which flank it, with capacitance C_{My} . When light is incident on this condenser electrons are released. There are n_1 electrons per unit volume at the face of the crystal closest to the light, and n_2 per unit volume at the second face. The expression for the current density, j , in the crystal is

$$j = Ene\mu + Ddn/dx = 0, \quad (1a)$$

where E is the field, n the number of charges per unit volume, e the electronic charge, μ the mobility, and D the diffusion coefficient. j is equal to zero in this case because the insulating layers of Mylar prevent the flow of dc current.

Integrating from one side of the crystal to the other and substituting $D = \mu kT$ where k is Boltzmann's constant, one gets for the voltage across the crystal

$$V = (kT/e) \ln(n_1/n_2). \quad (2a)$$

If one assumes that the field is constant in the Mylar and equal to E_0 , one has for the total voltage V_0

$$V_0 = E_0 d + V, \quad (3a)$$

where d is the thickness of the Mylar.

The capacitance of the entire system C can be expressed as $C = \epsilon E_0 A / V_0$, and if we now substitute for E_0 from Eqs. (3a) and (2a) we get

$$C = \frac{\epsilon A}{d} \left(1 - \frac{kT}{eV_0} \ln \frac{n_1}{n_2} \right). \quad (4a)$$

If we consider the total capacitance C to consist of C_{My} and C_x in series then we get

$$C_x = \frac{CC_{My}}{C_{My} - C} = \frac{\epsilon A}{d} \left(\frac{eV_0}{kT \ln(n_1/n_2)} - 1 \right). \quad (5a)$$

From this expression for C_x one can see that at high intensities, where $n_1 \approx n_2$, C_x becomes very large, which is what was found experimentally. At low intensities the ratio n_1/n_2 is very large and is essentially meaningless, because at this low concentration of charge the ratio would imply a fraction of an electron at one side of the crystal.

⁶ B. Jaffe, Ph.D. thesis, New York University, 1959 (unpublished).

⁷ H. Kallmann and P. Mark, Phys. Rev. **105**, 1445 (1957); Kallmann, Kramer, and Mark, Phys. Rev. **109**, 721 (1958).