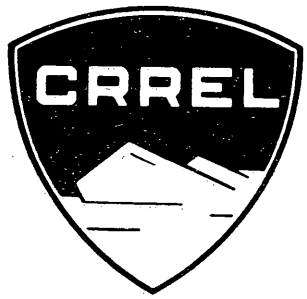

Research Report 175

CONDUCTIVITY CHANGES PRODUCED IN ICE BY OPTICAL IRRADIATION 0.8 to 2.7 μ

by

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and
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U.S. ARMY MATERIEL COMMAND
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PREFACE

This report was prepared by Dr. P. Camp, Physicist at Large, and SP D. L. Spears for the Research Division (Mr. J. A. Bender, Chief), USA CRREL.

USA CRREL is an Army Materiel Command laboratory.

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LIST OF SYMBOLS

c	velocity of light (cm sec^{-1}
E	activation energy (kcal/mole)
E_o	net energy to create a mole of defect pairs
E_g	activation energy for thermal generation
G	conductance (ohm^{-1})
g	rate of generation (cm^{-3} sec^{-1}) of defect pairs
g_t	thermal rate of generation (cm^{-3} sec^{-1}) of defect pairs
h	Planck's constant
I	intensity (photons cm^{-3} sec^{-1})
I_o	incident intensity
i	current (amperes)
n	concentration (cm^{-3})
n_b	number of bonds (cm^{-3})
n_d	number of defects (cm^{-3})
n_ℓ	number of defects produced by light (cm^{-3})
n_o	number of defects (cm^{-3}) in thermal equilibrium
N_o	Avogadro's number
R	gas constant
R_ℓ	load resistance
s	signal amplitude
T	absolute (Kelvin) temperature
V	voltage
x	distance
α	optical absorption coefficient (cm^{-1})
δ	thickness (cm)
ε	efficiency of photo production
ε_o	enthalpy of formation of a defect or ion pair
λ	wavelength, or decay constant
λ_B	wavelength for creation of orientational defects
λ_i	wavelength for creation of ion pairs
μ	micron
ν	frequency (sec^{-1})
ν_1, ν_2, ν_3	frequencies of the normal modes of vibration for the water molecule
σ	molecular cross section for pair production
τ	decay time (sec)
$\tau_{\frac{1}{2}}$	half life (sec)
ϕ	light flux (photons cm^{-2} sec^{-1})

SUMMARY

The existence of orientational (or Bjerrum) defects in the lattice is an important feature of present theories of electrical conduction and dielectric relaxation in ice. Ion states also are required in accounting for steady state conduction. If non-thermal equilibrium concentrations of these defects could be generated, it would be possible to study their characteristics and dynamics in a very direct way.

This report describes a series of experiments in which it was attempted to produce orientational defects and ions by optical injection. The basic experiment was one on transient photo-conduction produced by an intense light pulse. The effects of intensity and wavelength of the incident light, temperature of the sample and area of illumination of the sample were studied.

It was concluded that neither orientational defects nor ion pairs were produced in appreciable quantity by the light but that the apparent photo-conduction observed was the result of flash-heating of a thin surface region which had significantly different properties than had the bulk of the sample. Simple and somewhat speculative assumptions regarding the photo-generation process lead to the conclusion that the photo-efficiency, at least for ion pair production, must be very low indeed.

CONDUCTIVITY CHANGES PRODUCED IN ICE BY OPTICAL IRRADIATION 0.8 to 2.7 μ

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P. R. Camp and D. L. Spears

INTRODUCTION

An essential feature of the general theory of electrical properties of ice as developed by Granicher et al. (1957) is the existence of orientational defects and ions in the ice lattice. The orientational defects are point defects which may be thought of as resulting from the rotation of molecules in normal lattice sites as shown below in Figure 1. Figure 1a shows a normal lattice arrangement. In Figure 1b, the molecule at A has rotated so that a double bond D and a vacant bond L are created. This is a highly unstable situation and the probability is large that the structure will revert to that in Figure 1a. However, if, before this happens, molecule B rotates as in Figure 1c, the defects L and D become separated by a normal bond and cannot recombine without first diffusing to the same molecule. Thus at any temperature T°K there will be a steady state concentration of these defects in the lattice given by the law of mass action:

$$\frac{n^D n^L}{n_b^2} = A^2 e^{-E_0/RT}$$

where n^D = concentration of D defects (cm^{-3})

n^L = concentration of L defects (cm^{-3})

n_b = concentration of normal bonds (cm^{-3})

E_0 = energy in kcal/mole to create a mole of defects.

Since $n^D = n^L$

$$n^D = An_b e^{-E_0/2RT} = n^L.$$

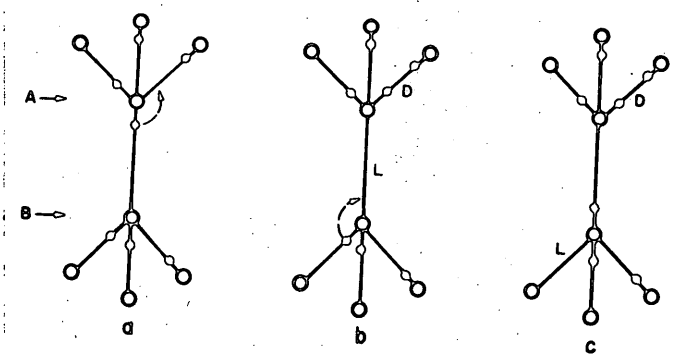


Figure 1. Formation of a Bjerrum defect pair. Open circles represent oxygen atoms, solid circles hydrogen atoms.

These kinds of point defects were first proposed by Bjerrum (1951) and they are often called Bjerrum defects. The precise structural model of these defects has been criticized by Dunitz (1963) on the very reasonable grounds that the D defect is energetically improbable as shown, a more likely situation being one in which the double bond becomes distorted so that one hydrogen atom assumes a somewhat interstitial position. However, the details of this structure do not appear explicitly in the theory of dielectric processes and so are unimportant to it. Of course, they do become important if one attempts to deduce the energy of formation from electrostatic interactions of the model.

According to Granicher et al. (1957), dipole (molecular) rotation can take place much more easily at a molecule adjoining an orientational defect than at a normal site. Thus when an electric field is applied to an ice crystal, only those dipoles adjacent to defects are able to rotate. Since the defects are constantly being created and destroyed, all lattice sites are eventually sampled and the crystal reaches an equilibrium state in the field. The long time required for dielectric relaxation is thus the result of there being relatively few such defects at any given time.

In the case of d-c conductivity, the model asserts that both rotation of molecules and translation of ions (protons) must take place, so to speak, in series. That is, the translation of a proton as in Figure 2 leaves the molecules in its path so oriented that before another proton can pass along the same route,

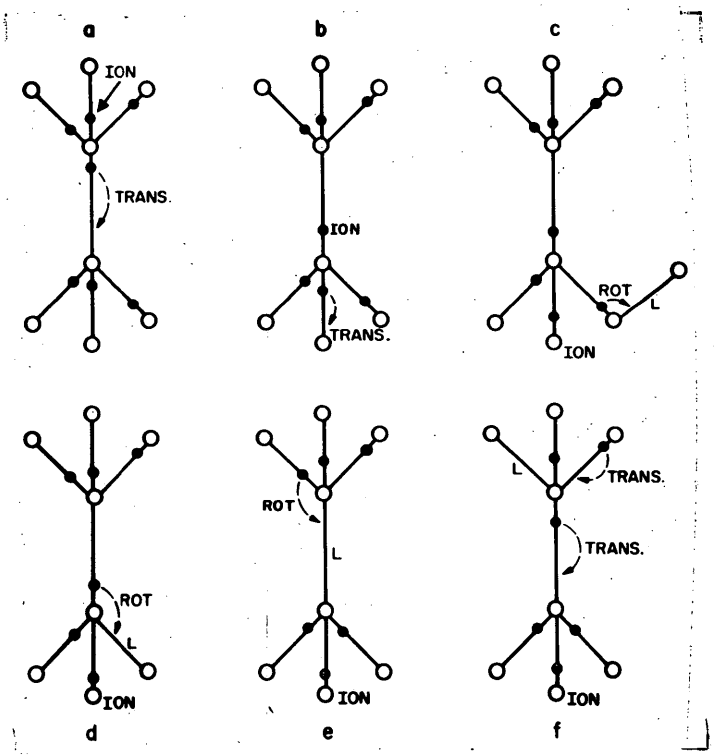


Figure 2. Conduction via both translation and rotation.
abc: Translation of a proton leaves molecules oriented to oppose further translation.
def: L defect passing up the chain permits conduction of a second proton.

they must be reoriented by rotation. Thus for conduction, orientational defects as well as ions are necessary. That d-c conductivity occurs by the migration of protons has been demonstrated by Decroly, Granicher and Jaccard (1957) who showed that hydrogen was liberated at the cathode.

In order to test for the existence of defects and to measure their properties, one must be able to vary their concentration and observe the consequences. One method of doing this is to replace some of the water molecules by others which will enter the lattice substitutionally providing less than or more than two hydrogen atoms per impurity molecule. For example, HF replacing H_2O would be deficient in one proton and lead to the formation of one L defect. It also dissociates according to the equation $HF + H_2O \rightleftharpoons H_3O^+ + F^-$, creating more H_3O^+ ions. HF will enter the ice lattice substitutionally and the consequences of this have been explored by Granicher et al. (1957). Unfortunately, no molecule of the form H_3X has been found which will enter the ice lattice substitutionally. Thus, the defect picture cannot be fully tested by measurement on impure samples. Moreover, this method of producing defects creates them in thermal equilibrium concentrations. Thus, one is unable to measure directly properties such as lifetime and cannot really show their independent existence.

It is most desirable, therefore, to produce these defects in non-equilibrium numbers. A possible method of doing this is by optical injection. The idea is to subject a crystal to a strong flux of radiation of wavelength such that the photon energy is sufficient to create a defect pair and then to measure the resulting change, if any, in electrical properties. Similarly, it should be possible to produce ion pairs as well by optical injection. If the energy required to create an ion pair in ice is sufficiently different from that required for the production of a Bjerrum defect, there is the intriguing possibility of creating at will either excess orientational defects or excess ion pairs by proper selection of the wavelength of the radiation. From a series of experiments of this kind (Camp, 1963) it was found that both the a-c and d-c conductivities were apparently increased when ice was strongly illuminated with light of certain wavelengths. However, the results of these experiments did not seem to lead to a clear interpretation either in terms of injection or of simple heating of the sample due to the absorbed energy.

The experiments reported here are an attempt to improve and extend that work in the hope of providing a better understanding of the phenomenon. We have studied the d-c conductivity as a function of wavelength and intensity of the incident light, the extent and region of the sample illuminated, the ambient temperature from -25C to -5C, the magnitude of the applied voltage, and the impedance of the load.

Photon interaction with the water molecule in such a way as to produce rotation in the ice lattice probably occurs as a resonance phenomenon. That is, the photon must have an energy large enough to form the defect pair but beyond this the efficiency of production will drop off. Thus, for a given photon flux, the maximum rate of defect production should occur at a vacuum wavelength λ_B such that

$$\lambda_B = \frac{hc}{\epsilon_0} \qquad N_0 \epsilon_0 \equiv E_0$$

where h is Planck's constant, c is the velocity of light in vacuum, N_0 is Avogadro's number, and E_0 is the energy required to create a mole of Bjerrum defect pairs. The production rate should drop very sharply toward zero as the

wavelength becomes longer and should fall off, but perhaps not so rapidly, as the wavelength becomes shorter. An entirely similar situation should hold for the production of ions yielding a similarly defined wavelength λ_i.

In Granicher et al. (1957), E_0 was given as lying between 22.3 and 26.8 kcal/mole ($0.96 < \overline{\epsilon_0} < 1.15$ ev)*. In later work Jaccard (1959) and Granicher (1963) both use

0.68 ± 0.04 ev for the energy to create an LD pair (15.8 kcal/mole),

1.2 ± 0.1 ev for the energy to create an ion pair (28 kcal/mole).

The respective concentrations at -10C are given (Granicher, 1963) as 7×10^{15} cm^{-3} for Bjerrum defects and 8×10^{10} cm^{-3} for ions in pure ice (from Eigen et al., 1958).

From the above energies, we conclude that the interesting wavelengths will be in the vicinity of

$$\lambda_B = 1.83\ \mu$$

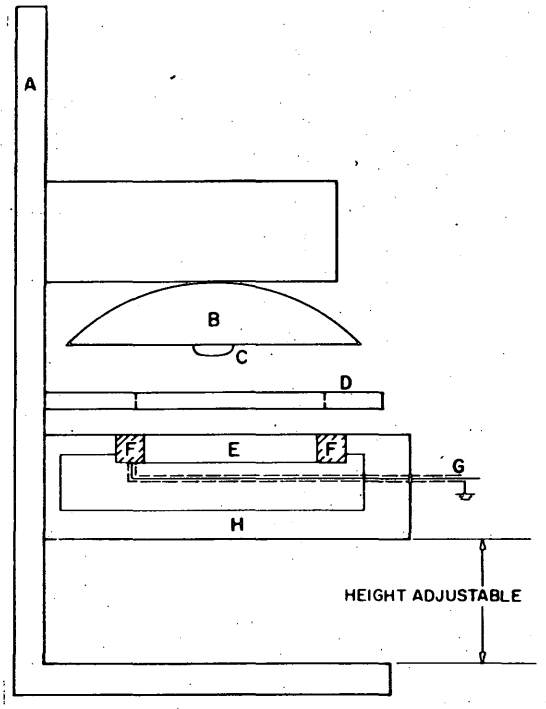
$$\lambda_i = 1.03\ \mu.$$

EXPERIMENTAL PROCEDURE

Since we do not know the cross sections for photogeneration of Bjerrum defects or ion pairs and since we can give only a crude estimate of their lifetimes, we are unable to predict the light flux necessary to cause a measurable change in the electrical properties of ice. However we do know experimentally (Camp, 1963) that very large light fluxes are required to produce an effect. Large light fluxes are most easily obtained in pulse form. Moreover since steady state illumination by high intensity light will cause sample heating and upset the measurements, a pulse technique is a logical choice. Thus we have used the same fundamental experimental procedure as is outlined in Camp (1963). Our sample was connected in series to a battery and a resistive load, the input resistance of a cathode ray oscilloscope. An appropriate pulse light source was mounted so as to illuminate the desired portion of the sample. The oscilloscope was balanced for the steady state dark condition and its trace was triggered just before the light pulse. The trace was photographed with a Land camera and in this way, the transient imbalance due to the light pulse was recorded. In some experiments, the output of a photomultiplier tube was recorded on a second trace (dual beam oscilloscope) in order to show the time relation between the light pulse and the signal.

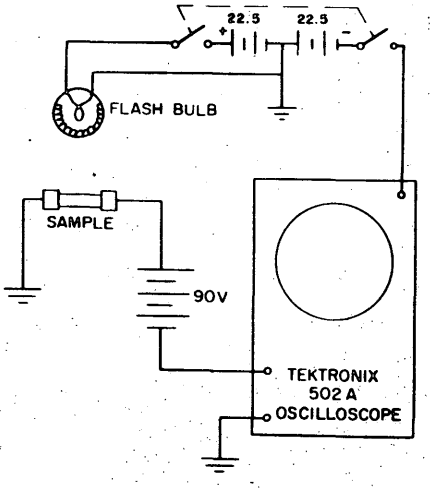
The details of the experimental arrangement are shown in Figures 3a and 3b. A General Electric M-2 flash bulb was used for each light flash because it has a color temperature of 3800K. That is, in the spectral region of interest it radiates approximately as a black body at 3800K. Thus it provides its peak intensity from about 0.4 to 1.7 μ. It has a pulse duration of the order of 2×10^{-2} sec and a light output in the peak region of the order of 7×10^{5} lumens as shown in Figure 4. If the bulb radiates as a black body at 3800K each square centimeter should radiate at an average rate of about 500 watts per micron wavelength interval in the region of interest. This corresponds to a flux of the order of 4×10^{21} photons per second per micron per square centimeter of radiating surface.

*1 ev per particle = 23.29 kcal/mole.



a. Arrangement.

A Aluminum stand
B Reflector
C M-2 flash bulb
D Filter holder
E Ice sample
F Platinum-foil-coated electrodes
G Shielded lead wires
H Bakelite frame



b. Circuit diagram.

Figure 3. Experimental apparatus.

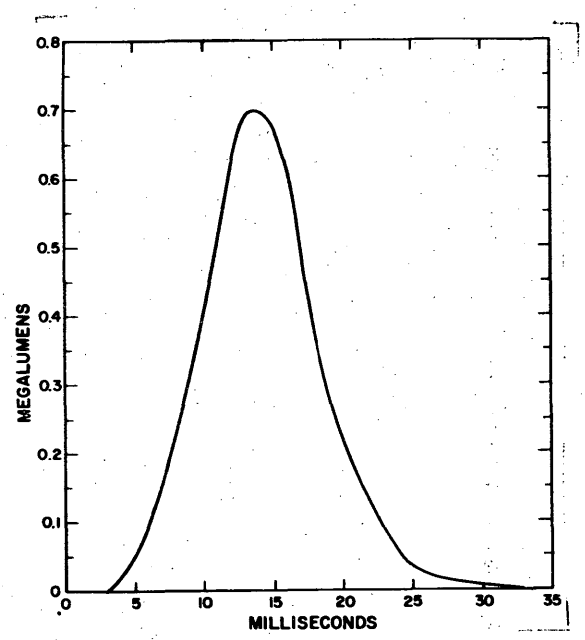


Figure 4. Visible light output vs time for M-2 flash bulb (manufacturer's data).

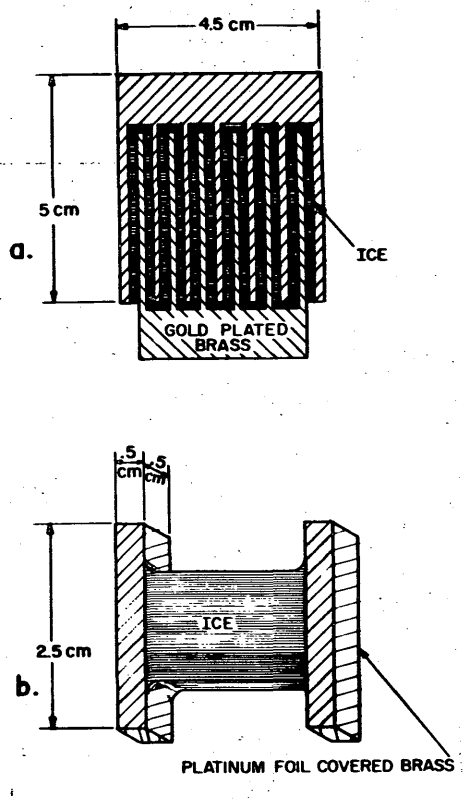


Figure 5. Sample holders. a. Comb type. b. Bar type.

Two different types of sample holders were used. The first (Fig. 5a) was the interlocking comb arrangement described in Camp (1963). It was made of gold plated brass and was designed to provide a low sample impedance (large cross section and small length). A second sample holder (Fig. 5b) was simply a pair of platinum-foil-covered brass bars supported and spaced as shown. This arrangement allowed us to study the effect of illuminating various regions of the crystal separately.

The flash bulb and sample holder were mounted on a stand so that the distance between them was adjustable. In normal use the distance from the flash bulb surface to the ice was about 1.5 cm. Between the bulb and the sample a black Bakelite plate with a 2 x 2 in. hole cut in its center was mounted as a filter holder. When a filter was not being used, a 2 x 2 x 1/8 in. plate of clear glass was put in its place to reduce contamination of the ice surface.

The oscilloscope used was a Tektronix model 502A dual beam instrument having a 1-megohm input resistance. The oscilloscope was triggered from a 22 1/2-v battery by a switch operated nearly in synchronism with the switch which actuated the flash.

At the lowest signal levels, considerable difficulty was encountered with noise and hum pickup. Much of the noise was found to be microphonic pickup by the 90-v battery which was in series with the sample. By shock-mounting this, carefully shielding everything (sample, battery, flash assembly, etc.), and using

double-shielded leads, it was possible to reduce the background noise to about 0.0002 v.

The light source and sample assembly were housed in a styrofoam box containing a heater, a fan and a thermistor probe. This in turn was placed in a freezer. The sample temperature was controlled by bucking the heater against the freezer in response to the signal obtained from the thermistor. The control unit was a Yellow Springs Instrument Company Model 63 controller with a stainless steel probe.

The samples were prepared from demineralized distilled water of about 2×10^6 ohm cm resistivity at 20C. Both single crystal and polycrystal samples were used and no differences were observed between them. Since all samples were mounted and measured in air, we believe that there was some contamination from dissolved gases and airborne impurities. Thus moderate fluctuations in the purity of the water would probably be masked by the impurities picked up after freezing. No striking differences were found between the results obtained for samples made from different batches of water.

Figure 6 shows a typical response to illumination. In this case the ambient temperature was -6C; 90 v was applied to the comb-type sample. The voltage developed across the 1-megohm input resistor of the oscilloscope before the light flash was 0.24 v. In discussing these results it will be convenient to describe the response in terms of two parts as was done in Camp (1963), the pulse and the step. As shown in Figure 6, the pulse is a transient of short peak duration (of the order of 10^{-1} sec) which appears superimposed on a transient of longer duration, the step (of the order of 10^2 sec). These two parts are separated by drawing the dashed line as shown in the figure. This procedure involves a certain amount of judgement since it is sometimes not clear that the pulse has really decayed to the step by the end of the oscilloscope trace.

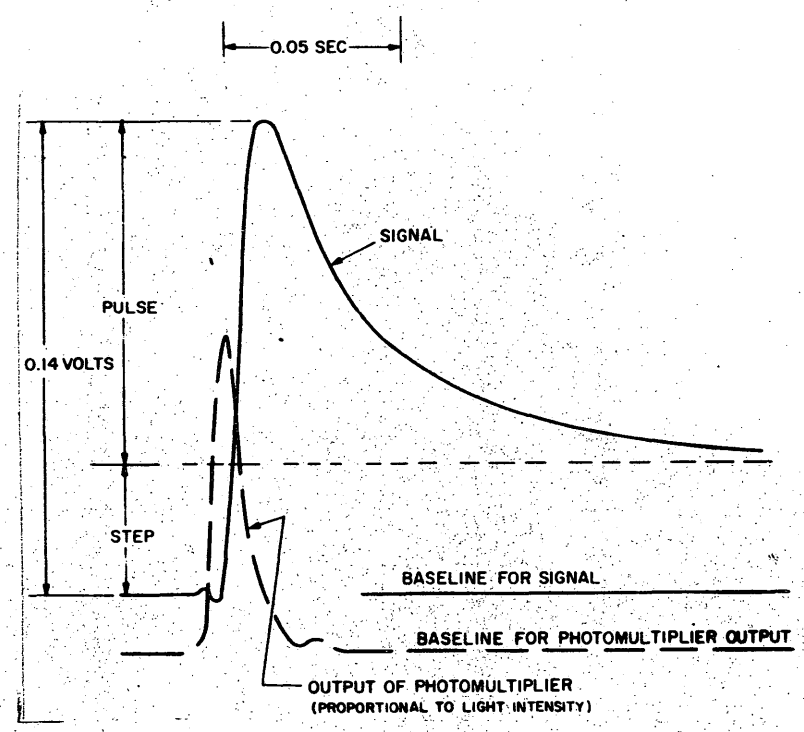


Figure 6. Typical photo response curve, no filter, -6C.

EXPERIMENTS

Dependence on wavelength of light

We have mentioned already that the values cited in Jaccard (1959) and Granicher (1963) for the creation of orientational defect and ion pairs would lead us to look for a photo response at wavelengths of the order of 1.8 and 1.0 μ respectively. Our previous wavelength measurements (Camp, 1963) were inconclusive because suitable filters were not available. Nonetheless, we were able to show that the photo effect was wavelength-dependent and was a maximum in the 1.5 to 2-μ vicinity. We found also that a sheet of ice only 1 mm thick would eliminate the pulse while only modestly attenuating the step. It is thus a matter of great interest to determine just how the response varies with wavelength.

To resolve this matter we performed a set of experiments in which the sample was illuminated with nearly monochromatic light at 0.1-μ intervals from 0.7 μ to 2.7 μ and the relative response was measured. The nearly monochromatic light was obtained by interposing an interference filter of the desired characteristic between the sample and the bulb. The filters used were the Optics Technology sets 12, 15 and 20. Each filter has a pass band of less than 0.1 μ. Some broadening of this band may have resulted from the fact that not all the light incident on the crystal passed normally through the filter. In order to obtain true relative response values, each measurement had to be corrected for the 3800K black body radiation curve (Fig. 7) and the transmission curve for the particular filter. These correction factors are listed in Table I.

The data for three different runs on two different samples of single crystal ice at -7C are shown in Table II. The average relative pulse height is plotted in Figure 8 as a function of wavelength. The vertical bars indicate the estimated uncertainties of our experimental points. The solid line shows the absorption coefficient for ice as a function of frequency as given by Ockman (1958). A similar plot for the step height as a function of wavelength is shown in Figure 9.

It can be seen from Figure 8 that the pulse height has the same general wavelength dependence as does the absorption coefficient over most of the range. A somewhat better agreement might be obtained if the response curve were shifted slightly toward shorter wavelengths. This difference may be due to the fact that not all the light passes through the filters at perpendicular incidence. Since the response characteristics of the interference filters shift toward shorter wavelengths as the angle of incidence increases, the net effect of an oblique component is to broaden the pass band on the short wavelength side.

Three significant peaks occur in the pulse height curve, one at about 2.5 μ, one at 2.0 μ and at 1.7 μ. The first two of these appear to coincide with absorption peaks and may be due to sample heating. More will be said on this subject in the section on temperature dependence. The peak at 1.7 μ is unique in that it occurs where the absorption is weak. Note also the absence of peaks at 1.5 μ and 1.25 μ where the absorption is again strong. (The actual magnitude of the absorption coefficient at 1.25 μ is uncertain because of ambiguity in the way the data are presented by Ockman.) These three peaks have been assigned by Ockman to combinations of the fundamental vibrational frequencies (ν_1 = 3143 c (sec^{-1}), ν_2 = 1640 c (sec^{-1}), ν_3 = 3252 c (sec^{-1}), where c = the velocity of light = 3×10^{10} cm sec^{-1}). He associated the peak at 2 μ with $\nu_2 + \nu_3$, that at 1.5 μ with $\nu_1 + \nu_2$ and that at 1.25 μ with $\nu_1 + \nu_2 + \nu_3$.

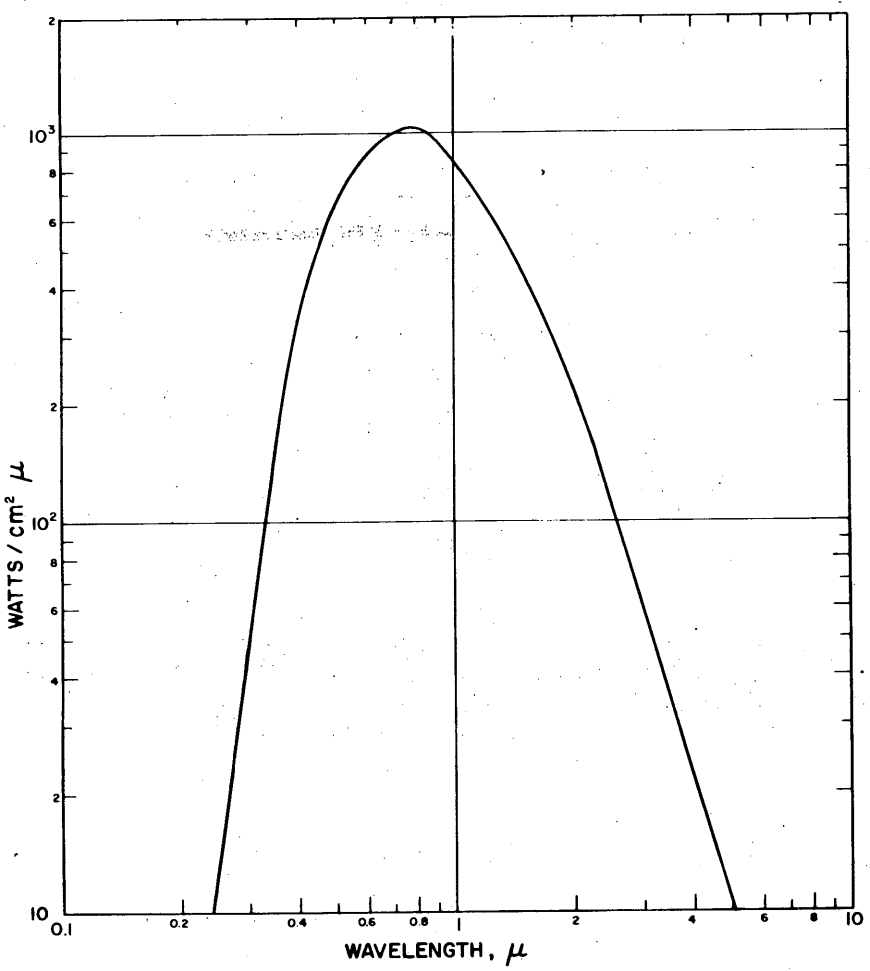


Figure 7. Black body radiation curve, 3800K.

Table I. Filter correction factors.

Wavelength of peak transmission of filter (μ)	a Relative transmission of filters (Arbitrary units)	b Intensity of black body radiation at 3800 K (10^3 W/cm²-μ)	c Correction factor $c = \frac{1}{ab}$
.7	3.2	.98	.32
.8	1.3	1.00	.76
.91	2.8	.91	.39
1.02	1.7	.80	.74
1.08	1.3	.74	1.04
1.18	1.8	.66	.84
1.28	2.8	.58	.62
1.39	1.8	.49	1.14
1.49	2.1	.44	1.09
1.58	3.1	.38	1.85
1.68	1.9	.34	1.54
1.81	2.0	.285	1.75
1.92	2.1	.25	1.92
1.99	2.6	.23	1.67
2.09	2.6	.195	1.96
2.18	3.0	.17	1.96
2.28	2.7	.15	2.50
2.40	3.1	.125	2.56
2.49	2.7	.11	3.33

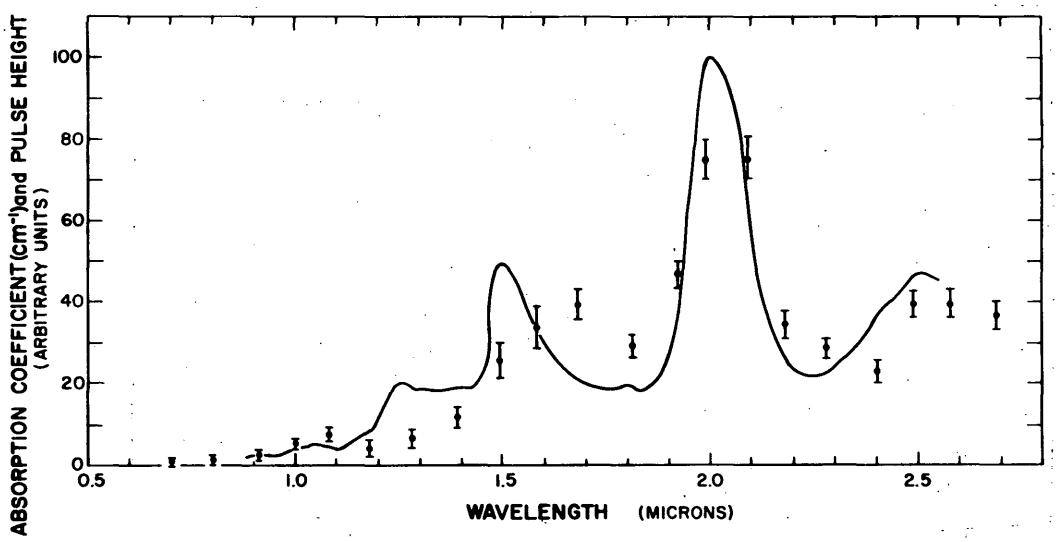


Figure 8. Corrected pulse height (points) vs wavelength of irradiation at a sample temperature of -7 C (average of three runs) compared to absorption coefficient (solid line) vs wavelength as given by Ockman (1958). Bar type capacitor.

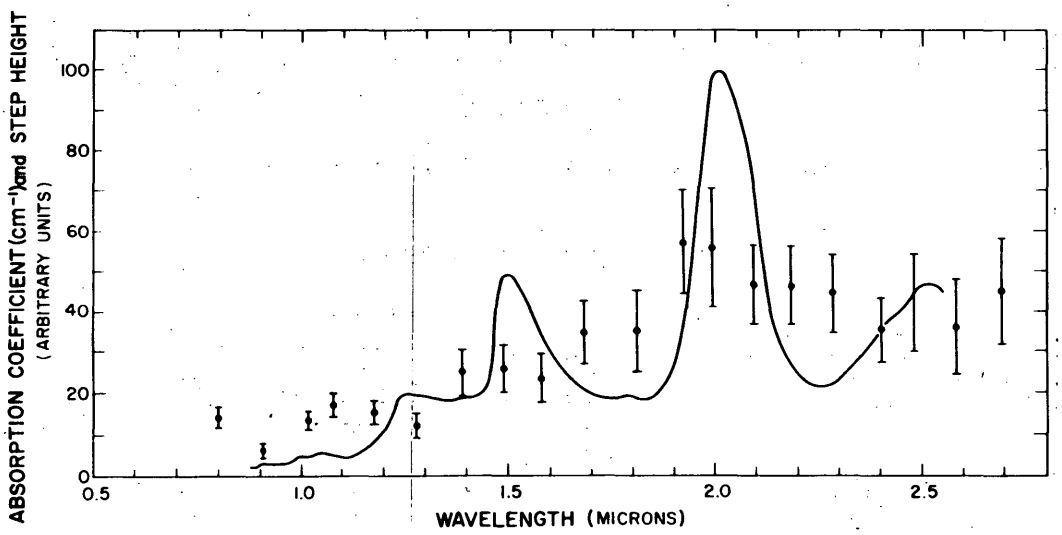


Figure 9. Corrected step height (points) vs wavelength of irradiation at sample temperature of -7 C (average of two runs) compared to absorption coefficient (solid line) vs wavelength as given by Ockman (1958). Data were obtained using a comb type sample in the range 0.8-1.7 μ and using a bar type sample for 1.8-2.7 μ.

Table II. Pulse and step height measurements (arbitrary units) corrected for black body curve and filter characteristics. Typical signals are .005 v for pulse and .001 v for step at 2 μ.

	Pulse height				Step height			
(microns)	8/27	8/29	8/29	Average	7/15	8/29	8/29	Average
0.7	0.8			0.8				
0.8	1.8			1.8	13.5			13.5
0.91	2.8			2.8	6			6
1.02	5.5			5.5	13			13
1.08	7.7			7.7	17			17
1.18	4.6			4.6	15			15
1.28	7.4	5.2	4.6	5.7	12			12
1.39	9.2	13.7		11.4	25			25
1.49	23.0	35.3	18.7	25.7	26			26
1.58	31.1	43.8	26.8	33.9	23.5			23.5
1.68	43.1	36.0	38.1	39.1	35			35
1.81	30.1	30.2	25.9	28.7		52.5	18.5	35.5
1.92	46.0	46.1	48.3	46.8		75	39.5	57.5
1.99	78.0	79.7	64.9	74.2		81	31	56
2.09	80.0	67.2	77.5	74.9		58.5	39	47.5
2.18	25.9	32.9	43.5	34.1		63.5	31.5	47.5
2.28	27.6	30.0	28.7	28.8		56	31.5	45
2.40	21.4	24.0		22.7		36		36
2.49	42.9	36.0		39.5		43		43
2.58	34.0	44.4		39.2		37		37
2.69	40.0	32.9		36.5		46		46

If the cross section for photogeneration of Bjerrum defects or ion pairs is comparable to that for the excitation of lattice vibrations, we would expect an absorption peak due to this process. If not and if the energy of creation were of the order of that of these vibrational states, the absorption due to defect creation would be masked by the vibrational absorption. However, the conductivity should not be affected by light which excites lattice vibrations except insofar as its absorption results in heating the crystal. It should be affected by photoproduction of defects. Thus the peak in photoconductivity at 1.7 μ coupled with the absence of absorption peaks in this region suggests a photoconductive rather than a thermal response. Of course, as pointed out above, the peak of 2.0 μ and 2.5 μ may be photoconductive too. Other factors which bear on the interpretation of these absorptions will be discussed in later sections.

It was shown (Camp, 1963) that a thin sheet of ice interposed between the source and the sample almost completely destroyed the pulse while leaving most of the step. This implies that the radiation causing the pulse is almost all absorbed in a thin layer of ice while that causing the step is not. It also shows that they are two separate processes. The step does not result from the dissipation of surface heat into the bulk of the crystal. These are important consequences and so we have attempted to make them more quantitative.

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A series of experiments was performed with the comb capacitor in which an ice sample was mounted so that most of it was between the source and the tynes of the comb (Fig. 10). (Only two tynes are shown.) If the pulse results from processes in a surface layer of thickness δ, it will have little effect on the current between the two tynes unless the region δ is close to them. Thus as the surface of the crystal is planed down, a big increase should appear in the pulse (or step) when the sample thickness, d, above the tynes is of the order of δ.

The results are plotted in Figure 11. The experimental scatter of the points is large and the data meager because it is difficult to prepare and measure accurately an ice sample of this cross section which has a thickness much less than 1 mm. For thicker samples, the signal is so small that it is difficult to measure.

It can be seen that both pulse and step are very strongly attenuated within the first 0.2 mm of ice, the pulse by a factor of about 45 and the step by a factor of about 3.3. Subsequently they are further attenuated but much more slowly, a factor of about 3.2 per centimeter of path for each. If the signal is proportional to the intensity of the light, I (see p. 18) then the light intensity falls off in a similar way with distance. Defining an attenuation coefficient, α (cm^{-1}), by

$$I = I_o e^{-\alpha x}$$

where I_o is the intensity of the incident light and x is the thickness of the ice layer we find in the first 0.2 mm an attenuation coefficient of at least 190 for the pulse and 59 for the step. Beyond about 0.2 mm, the coefficient becomes approximately 11 for for each. Because of the way in which these numbers were obtained, they must be regarded as indicative only of orders of magnitude. However, they do suggest that most of the pulse is produced by the absorption peak at 2 μ for which Ockman gives α of the order of 100 cm^{-1} and that most of the step is produced by the absorption peak at 1.5 μ for which α is of the order of 50 cm^{-1}. But if the latter is true, our peak at 1.7 μ must in reality be

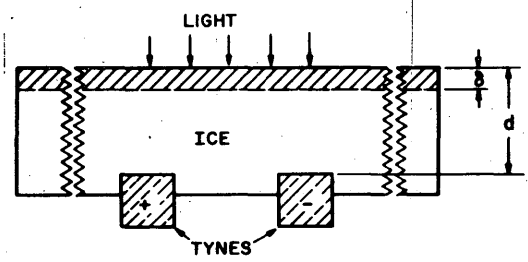

Figure 10. Sketch of the ice filter experiment. Effective thickness of surface layer = δ.

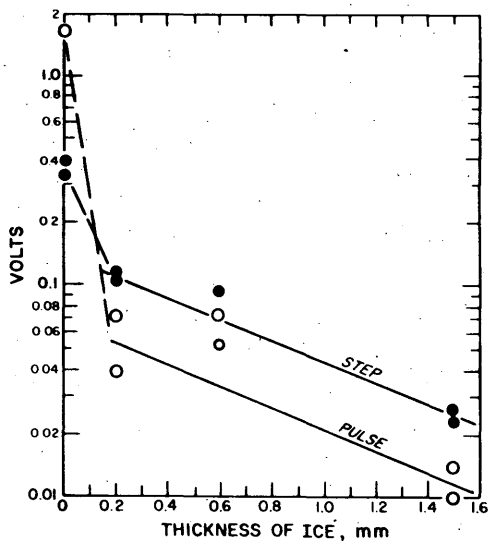

Figure 11. Ice filter thickness vs pulse height and step height.

Ockman's peak at 1.5 μ. The remainder is then due to other absorptions and the value $\alpha = 11$ is reasonable when one considers the spectrum of the incident light. The existence of this remainder suggests the need for experiments with shorter wavelength light and a thick (1 to 10 cm) sample.

Effects of ambient temperature

One factor which has an important bearing on the interpretation of the photo response is the way in which it varies with the temperature of the ice. In order to determine this, the sample was mounted in the same way as for the wavelength experiments except that a clear glass plate was substituted for the filter. The reason for omitting the filters is that at temperatures below about -10 C no signal at all is detected with a narrow band filter in place. (These filters reduce the total illumination by a factor of more than 100.) It is unfortunate that this is necessary because we lose thereby our ability to distinguish between peaks. Measurements were first made of the dark current through the sample by measuring the input voltage to the oscilloscope when a potential of 90 v was applied in series with the crystal. (One volt developed across the 1-megohm input resistance of the oscilloscope indicates a sample current of 1 microampere.) Then the bulb was flashed and the response photographed. As mentioned before, the step height was estimated from the later part of the trace after the pulse seemed to have died out. It was then extrapolated back to the start of the trace and the pulse height measured from it. This procedure for separating the pulse from the step is somewhat arbitrary and leads to rather large estimated errors in their values. Moreover, there is the possibility that this procedure introduces a systematic error which affects the ratio of pulse to step in an unknown way. However it was considered the least arbitrary scheme.

Several runs were made at temperatures between -4 C and -25 C. An example of the temperature dependence is shown in Figure 12. The vertical bars indicate estimated errors. If the temperature dependence is caused by a simple barrier type process, the slope of the appropriate line gives the activation energy.

The results of four such experiments are listed in Table III. Two additional temperature runs for the steady state condition are also listed.

An examination of Table III shows that the steady state activation energies for the bar and comb type samples are in the same range, the average for the bar being about 30 kcal/mole, that for the comb about 27 kcal/mole, and the average value for all 28.3 kcal/mole. The average value for activation energy of the step is 29 kcal/mole. This indicates that the step and the steady state result from the same basic process and that the step is merely the result of sample heating. It can be seen in Figure 12 that the amplitude of the step is about 22% that of the steady state voltage. In order to change the steady state by 22% it is only necessary to change the sample temperature by about 1 C. The fact that a sample temperature rise of about 1 C upon flashing the bulb was measured by a thermocouple imbedded in one of the electrodes supports the interpretation based on heating.

The activation energy for the pulse is much larger than that for the step. It seems to be more variable also. This indicates that, as proposed in Camp (1963) two different processes are involved-one for the step, probably sample heating, and one for the pulse, as yet undetermined.

Some further insight into the mechanism for the pulse can be gained by considering the way in which the signal should depend on temperature under conditions of optical injection or heating.

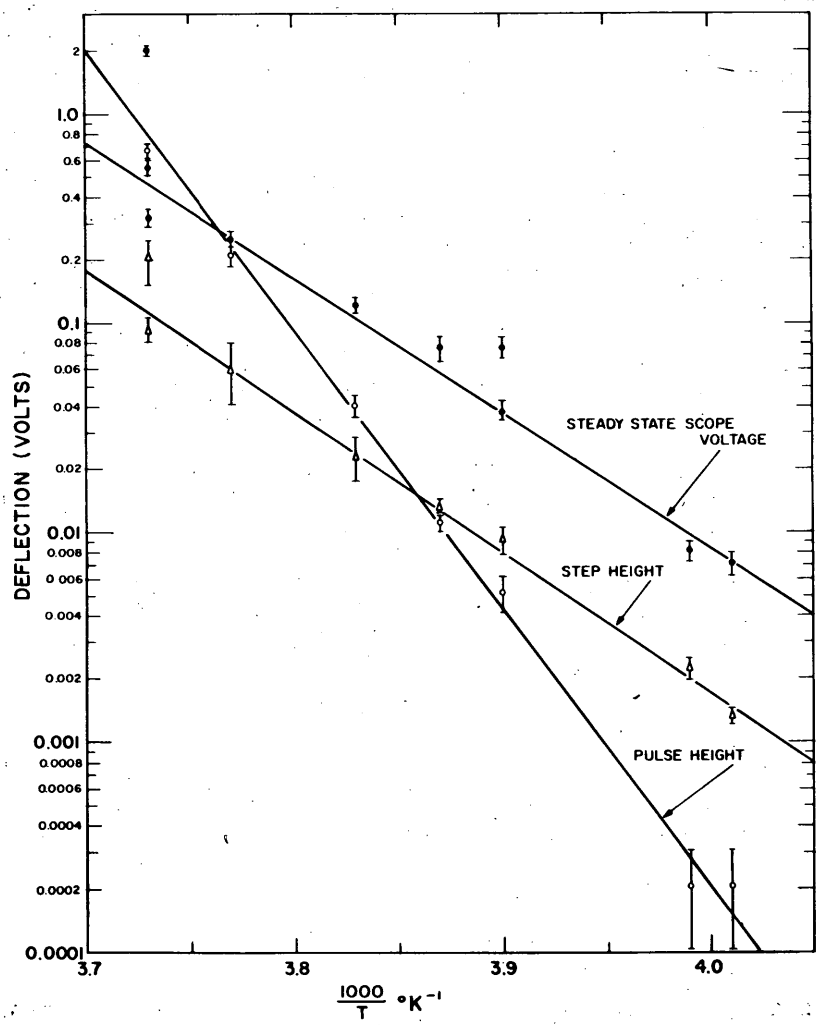

Figure 12. Pulse height, step height, and steady state scope voltage before flash versus 1000/T°K for comb type polycrystalline sample no. 5 (white light). Measurements were made beginning at low temperature.

Table III. Apparent activation energies.

Sample			Activation energy (kcal/mole)		
Number	Type	State	Steady state	Step	Pulse
2	Comb	Polyxtal	29.5 ± 5		
5	Comb	Polyxtal	29.5 ± 5	30 ± 5	60 ± 8
6	Comb	Polyxtal	23 ± 3	31 ± 5	54 ± 6
2A	Bar	Polyxtal	33 ± 4		
3A	Bar	Polyxtal	25 ± 5	25 ± 5	30 ± 5
5A	Bar	Single	31 ± 5	30 ± 10	40 ± 5

In a unit volume, let the rate of generation of photon-produced defects be g, proportional to the light flux ϕ (photons cm^{-2} sec^{-1}) with the constant of proportionality ε the efficiency of production. Let the rate of defect (or ion) pair production due to thermal vibrations be g_t. The rate of decay of defects, d, is assumed proportional to n^2 (a bimolecular reaction) where n is the concentration of defects of one kind (L or D) or of ions (+ or -) and λ is the constant of proportionality. Both ϕ and n are functions of time. Before the light is switched on, $g_t = \lambda n_0^2$ where n_0 indicates the value of n at t = 0.

Then during the flash

$$\frac{dn}{dt} = g + g_t - d = \varepsilon \phi + \lambda (n_0^2 - n^2).$$

When dn/dt = 0 (steady state) (light pulse long compared to relaxation time)

$$\frac{\varepsilon \phi}{\lambda} = -(n_0^2 - n^2) = (n - n_0)(n + n_0) = (n + n_0)\Delta n$$

where $\Delta n \equiv (n - n_0)$.

If $\Delta n << n_0$ we may write $\varepsilon \phi/\lambda = 2 n_0 \Delta n$

and $$\Delta n = \frac{\varepsilon \phi}{2\lambda n_0} = \frac{n_0 \varepsilon \phi}{2 g_t} = \frac{n_0}{2} \frac{g}{g_t}.$$

Thus $$\frac{\Delta n}{n_0} = \frac{g}{2g_t}.$$

We will assume that n_0 depends on temperature according to

$$n_0 = Ae^{-E_0/2RT}$$

where E_0 is the net energy necessary to create a mole of defect pairs and A is a constant. We have

$$\frac{\Delta n}{n_0} = \frac{g}{2\lambda n_0^2} \quad \text{or} \quad \Delta n = \frac{g}{2\lambda n_0}.$$

Case 1

Thus for an experiment in which the signal, s, is proportional to Δn, with b as the constant of proportionality

$$s = b\Delta n = \frac{bg}{2\lambda n_0}:$$

a. If g = const (optical injection):

$$s = \frac{bg}{2\lambda A} e^{E_0/2RT}$$

and the signal will decrease on rising temperature.

b. If g is due merely to a rise in temperature by an amount ΔT

$$\left(g = \frac{d(g_t)}{dt} \Delta T\right),$$

$$s = \frac{b\, g n_0}{2 g_t} = \frac{b\, n_0}{2 g_t} \frac{d(g_t)}{dt} \Delta T.$$

If the rate of thermal generation is exponential in T, that is, if

$$g_t = Be^{-E_g/RT},$$

where E_g is the activation energy for generation, B is a constant,

$$\frac{d\, g_t}{dt} = \frac{E_g}{RT^2} g_t$$

and

$$s = \frac{bn_0}{2} \frac{E_g}{RT^2} \Delta T.$$

Thus heating results in an increase of signal with rising temperature because n_0 increases exponentially with temperature.

Case 2

For an experiment in which s is proportional to $\frac{\Delta n}{n_0}$,

$$s = b' \frac{\Delta n}{n_0} = b' \frac{g}{2 g_t}.$$

a. Optical injection: g = constant

$$s = \frac{b'g}{2B} e^{E_g/RT}.$$

Signal decreases with rising temperature.

b. Heating:

$$s = \frac{b'}{2 g_t} \frac{dg_t}{dt} \Delta t = \frac{b'}{2} \frac{E_g}{RT^2} \Delta t.$$

Thus s decreases slowly with rising temperature. The results are summarized in Table IV.

The assumptions upon which these results are based are:

1. $n = Ae^{-E_g/2RT}$
2. Bimolecular law for recombination of defects
3. Small signal $\Delta n << n_0$

Table IV. Temperature dependence of signal for different hypotheses.

	Signal		Effect on signal of temp rise	
Exp. sensitive to	Δn	$\Delta n/n_0$	Δn	$\Delta n/n_0$
Injection	$\frac{bg}{2\lambda A} e^{E_0/2RT}$	$\frac{b'g}{2B} e^{E_g/RT}$	Decrease	Decrease
Heating	$\frac{b}{2} \frac{E_g}{RT^2} Ae^{-E_0/2RT} \Delta T$	$\frac{b' E_g}{2RT^2} \Delta T$	Rise	Slow decrease

4. $g_t = B e^{-E_g/RT}$

5. Relaxation time for generation equilibrium short compared to light pulse.

We interpret our d-c experiments as follows: The d-c conductance, G, of our sample is in series with a battery of voltage V, and a load resistance R_ℓ. A change in the current, i, through the circuit results from the photo-induced change in G, ΔG. If G results from the action of ions and defects in series, then ΔG is caused by a change in whichever is in the minority. Since our d-c experiments are really pulse experiments, the shape of the signal will depend on other factors such as the capacitance of the sample. Some of the consequences of this will be treated in a later section. We will assume for the calculations here that the pulse height is the same as, or at least proportional to, the signal which would be obtained in a true d-c experiment.

We have then

$$i = \frac{V}{R_\ell + \frac{1}{G}}, \quad \Delta i = \frac{-di}{dG} \Delta G = \frac{V \Delta G}{(R_\ell G + 1)^2}.$$

We observe the voltage across R_ℓ. Since the sample resistance is greater than the load resistance $R_\ell G < 1$, our signal voltage $= R_\ell \Delta i \cong -R_\ell V \Delta G$.

Since we have assumed ΔG proportional to Δn, the signal is proportional to $-\Delta n$ (a drop in voltage across R_ℓ). Thus we are forced to conclude that, subject to the assumptions of the above argument, the pulse is due also to sample heating. However, by this same argument, the activation energy for the pulse should be the same as that for the steady state, which is contrary to experiment.

A possible explanation of the temperature behavior of the pulse is the following: We know from the spectral response curves and from the thin ice filter experiments that most of the pulse-causing radiation is absorbed in a very thin surface layer of the ice (1/10 mm or less). We also have evidence from other experiments conducted in this laboratory (Camp, et al., in prep.) that the conducting properties of the thin surface layer of ice are quite different from those of the bulk, particularly if the surface is exposed to the air. Apparently the thickness of this region of anomalous conductivity is temperature dependent. Thus, when the temperature is changed, both the properties and thickness of this region change. This can give rise to a very high apparent activation energy. It follows that, in a case where

much of the energy is being absorbed in the surface, we would have a temperature dependence different from that caused by bulk heating.

Surface melting is an extreme case of this kind. However the heat of fusion is so much larger than the specific heat that the thickness of a pulse-melted layer cannot be very dependent on the ambient temperature. Thus surface melting seems an improbable solution. A simple calculation shows that 10 w/ cm^2 for 10^{-2} sec would only melt a layer about 2.5 μ thick. This is much thinner than the region over which the energy is believed to be absorbed. We are led to believe that the pulse from white light occurs mostly as the result of heating of a surface layer whose properties and thickness both vary with ambient temperature. We have been unable to test the temperature behavior of the response to nearly monochromatic light of $\lambda = 1.7\mu$ because the signal is too small at temperatures below -10 C.

Variation with intensity

A set of experiments was also performed to determine whether or not the response varies linearly with the intensity of incident light. The same general setup was used except that the filter was omitted and an aperture 1.5 in. in diameter was placed in front of the reflector. This aperture represented a realistic compromise between having a point source of light and having sufficient intensity to produce a signal. The distance from the source to the sample was then varied in order to change the intensity of the light in a known way without disturbing the spectral distribution. A bar type sample 1.5 x .7 x .6 cm was used with platinum electrodes. Two sets of data were taken, one at -5 C and one at -12C for both pulse height and step height as a function of distance. The results are plotted in Figure 13. Experimental errors are large as can be seen from the scatter of the data.

Since the source is not a point, the light flux does not vary strictly as the inverse square of the distance, x, from sample to source. Moreover, the source does have some collimation and so does not strictly obey Lambert's law. If it did we would expect the illuminance, E, on the axis to vary with x as

$$E = \frac{\pi B a^2}{a^2 + x^2}$$

where a is the radius of the source and B is a constant (Sears, 1949). Thus for $x >> a$, the illuminance will vary as x^{-2}. But for $x << a$ it will approach independence of x. Under the conditions of the present experiment, we would expect a dependence on $1/x$ to a power somewhat less than two. Thus it appears that the signal is roughly proportional to light intensity. This strengthens the argument for the small signal approximation which is used throughout this paper.

Dependence on illuminated area

To determine if the response was confined to a particular region of the sample, two selective illumination experiments were performed. In both, the illumination of a bar type sample 4.5 cm long having platinum foil electrodes was restricted to a band 1.5 cm wide across the sample. In the first, successive portions of the sample were illuminated by moving the mask and a measurement was made at each position. These showed a peak for the central part of the sample which was subsequently traced to an uneven illumination field

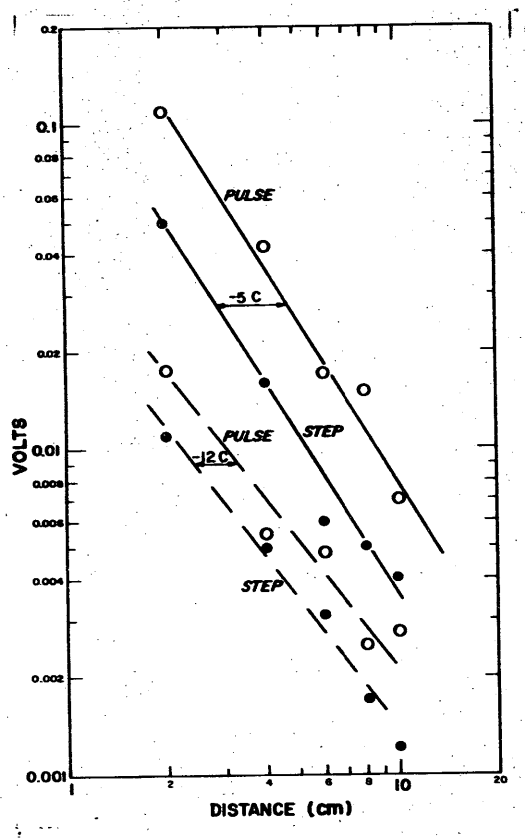

Figure 13. Pulse and step heights as a function of the separation of the source and the sample for a bar type sample at -5C and -12C.

resulting from the geometry of the experiment. In the second experiment, the mask and the light source were held fixed and the sample was moved, thus insuring the same light flux in each case. The results are shown in Figure 14. There is a modest change in step and pulse heights as different portions of the sample are irradiated. Slight variations in the impurity concentration in the sample might well be responsible for such behavior. It is clear that the whole sample, or at least the whole illuminated surface, takes part in the process and that it is not primarily an electrode effect. The pulse shape and decay constant appeared relatively unchanged during these experiments.

Variation with applied voltage

A series of runs was made to determine whether or not the photo response was linear with applied voltage. The sample used was polycrystalline 1.48 cm long x 0.72 cm x 0.6 cm mounted lengthwise between platinum foil electrodes. Pulse and step height were measured as a function of applied voltage at -7 C and at -15 C. No filter or stop was used. In both cases, the pulse and step were found to be linear functions of the applied voltage from 1 to 90 v dc. The pulse shape also remained unchanged over this range.

Effect of load resistance

Further information about the processes involved can be deduced from the shape of the response curve. However, in order to do this we must know how this shape depends on the electrical circuit external to the sample, namely, the load resistance. By studying the decay characteristic of the signal as a function of the value of the load resistance we can, in effect, obtain an equivalent circuit for the sample. Therefore a series of experiments was conducted at constant temperature, -5 C, and with no filter, using different load resistors. Polycrystalline ice and the comb type sample holder were used. This sample holder provides an effective sample length of 1.0 mm and cross section of 10 cm^2 .

Photographs were taken with load resistances from .01 to 89 megohms and the decay constants were measured from them. As can be seen from representative photographs of Figure 15, this is difficult to do precisely and therefore the errors involved are large. However it can be seen that the decay

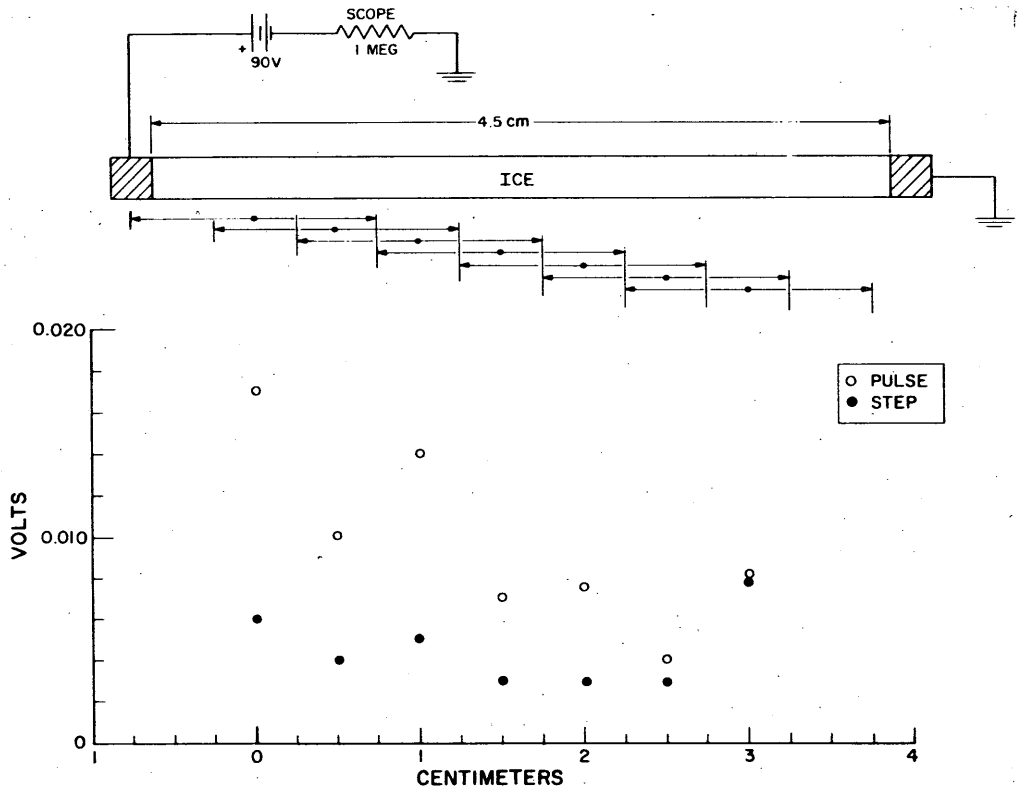

Figure 14. Dependence of pulse height, o, and step height, ●, on the region illuminated. Arrows indicate the portion of sample illuminated for each point.

time increases very markedly in the range of load resistance 1 to 89 megohms. Decay times measured in this way are plotted in Figure 16 as a function of load resistance. In evaluating these decay times we have assumed that the decay is exponential as appropriate to a simple RC network. That is

$$i = i_o e^{-t/\tau}$$

in which τ is the decay time in seconds.

The simplest equivalent circuit for the sample which we have been able to fit to this data (for -5C) and which allows d-c conduction is also shown in Figure 16. It comprises a capacitance $C = 4.8 \times 10^3$ picofarad (p.f.) in series with a resistance $R_1 = 3.2 \times 10^6$ ohm and a second resistance $R_2 = 1/G_{dc} = 2.8 \times 10^8$ ohm in parallel with this series circuit. From the geometry of the sample, this requires a d-c conductivity of 3×10^{-9} ohm cm and an apparent dielectric constant of about 560. This indicates a fairly large low frequency polarization (which is found in the steady state experiments). As nearly as could be determined, the rise time of the pulse varied only slightly with the load resistance.

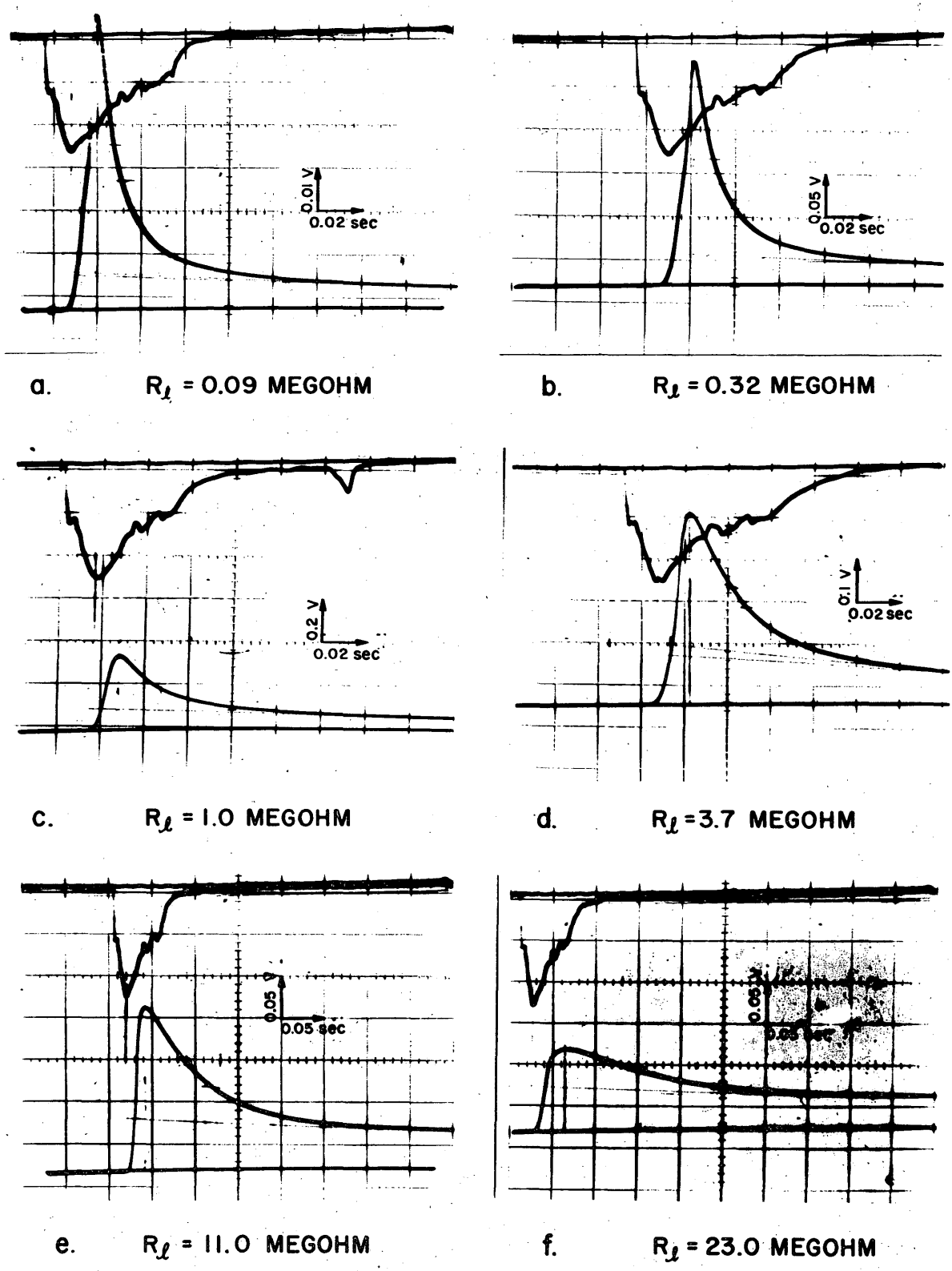

Figure 15. Photographs of oscilloscope trace for different values of load resistance R_l (-5C). The bottom trace shows the change in current through the sample due to the light pulse. The top trace, showing the output of a photomultiplier tube which also detects the light flash, serves only as a marker for the peak intensity of the light flash. It is jagged because of saturation and overloading. (The deflection is down.)

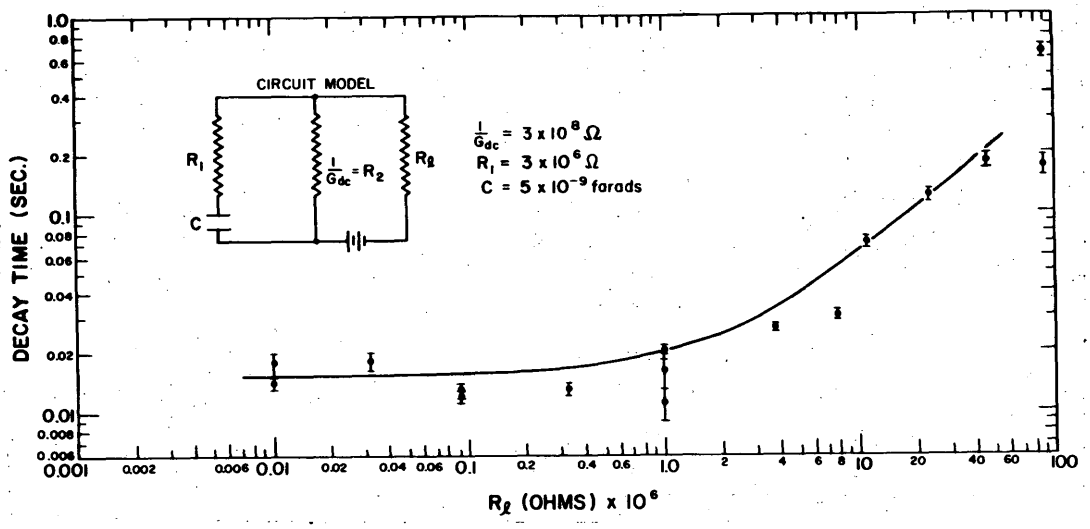

Figure 16. Decay time of pulse as a function of load resistance. The solid line shows the calculated response of the circuit shown.

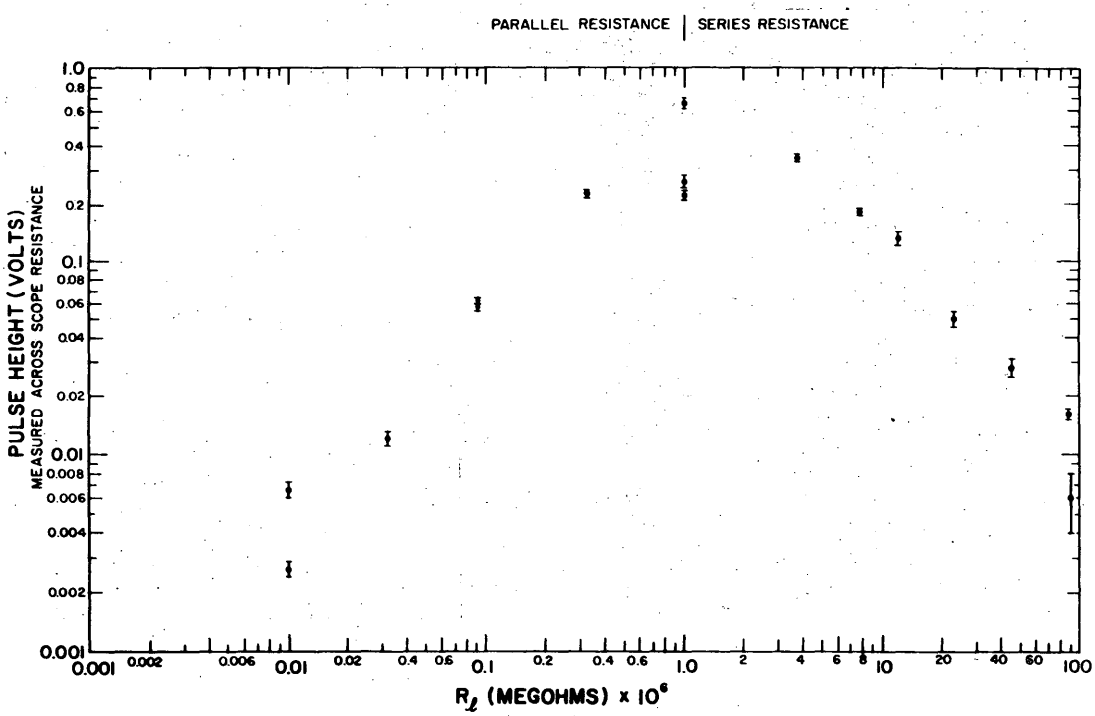

Figure 17. Pulse height as a function of load resistance. Load resistances of less than 10^6 ohms were obtained by shunting the input resistance of the oscilloscope. For higher resistance series resistors were used.

In terms of the electrical analogue the sequence of events is as follows: in steady state, the current is determined by R_ℓ and R_2 in series. When a light is turned on R_2 decreases lowering the voltage across the series $R_1 C$. The capacitor C must then discharge through R_1 in series with R_ℓ and R_2 in parallel. This discharge and the form of the leading edge of the light pulse govern the rise time of the response. For a step rise in light intensity, the rise time would be τ_r where

$$\tau_r = \left(R_1 + \frac{R_\ell R_2}{R_\ell + R_2}\right)C.$$

The decay time would be given by the same equation.

In our experiment, we do not have a step of light but rather a pulse. Thus the rise time of the response cannot be shorter than the rise time of the light nor can it be longer than the pulse itself. We find that the rise time of the response is comparable to that of the light pulse (5 ms) for load resistances of less than 1 megohm. Above 1 megohm there is a gradual increase to the order of 20 ms, the duration of the light pulse.

When the light is turned off, the signal will decay with a time constant given by the above equation, C charging through the same circuit. The solid curve of Figure 16 is a plot of τ_r as a function of R_ℓ for the values of R_1, R_2 and C given above. Figure 17 shows how the pulse height varies with load resistance. To achieve loads below 1 megohm this resistance was shunted by suitable resistances. Above 1 megohm, resistances were inserted in series with the load. Since the voltage measured is that developed across the 1 megohm input resistance of the scope, this accounts for the maximum value at 1 megohm.

In addition to providing an electrical analogue for our sample, an important consequence of this experiment is that the lifetime of the disturbance we are measuring cannot be larger than the shortest decay constant we have measured, about 15 ms.

DISCUSSION

We wish to find out what our negative result means in terms of limits on such parameters as pair half life, $\tau_{\frac{1}{2}}$, efficiency of pair production, ϵ, molecular cross section for pair production, σ, and partial absorption coefficient due to photo-production of defect pairs, α_p. To do so, we must estimate somehow the concentration of pairs resulting from illumination of the sample, n_ℓ, and compare this with a realistic estimate of the concentration which would produce a detectable signal.

The criterion for detectability is that the number of defect pairs produced optically must be large enough to be distinguishable from the noise and from any signal produced by sample heating. Since we do observe a signal which we have attributed to heating, it is the latter number which we must use.

If, as discussed above, enough heat is absorbed by the sample to raise its temperature 1 C, there will be a thermal signal resulting from the thermal generation of Δn_t defects per unit volume of the sample. Thus since

$$n_0 = Ae^{-E_0/2RT}, \quad \Delta n_t = \frac{E_0}{2RT^2}\, n_0 \Delta T.$$

For $\Delta T = 1$ K and $T = 263$ K, E_0 (Bjerrum) = 15.8 kcal/mole and E_0 (ion) = 28 kcal/mole

$$\Delta n_t \text{ (Bjerrum)} = 0.057\ n_0$$

$$\Delta n_t \text{ (ion)} = 0.10\ n_0 .$$

These numbers represent (spatial) average concentrations and thus it is the average concentration of optically injected defects to which they must be compared. Because of the large optical absorption coefficient, the optically injected defects will be concentrated near the surface of the sample and all of the useful light flux may be considered to be absorbed. Thus the average concentration of optically injected defects $\bar{n}_\ell$ is given by

$$\bar{n}_\ell = \varepsilon \phi_0 \tau_{\frac{1}{2}}/d$$

where d is the sample thickness. For a typical sample thickness d = 0.5 cm the criterion for detectability becomes

$$\bar{n}_\ell = 2 \varepsilon \phi_0 \tau_{\frac{1}{2}} \geq 0.05\ n_0 \text{ for Bjerrum defects}$$

$$\geq 0.1\ n_0 \text{ for ion pairs.}$$

Using n_0 (Bjerrum) = 7×10^{15} cm^{-3} and n_0 (ion) = 8×10^{10} cm^{-3} and ϕ_0 of the order of 10^{21} photons per cm^2 per second we find that a null result requires $\varepsilon \tau_{\frac{1}{2}} \leq 2 \times 10^{-7}$ for orientational defects or $\varepsilon \tau_{\frac{1}{2}} \leq 4 \times 10^{-12}$ for ion pairs.

One may make a very crude estimate of $\tau_{\frac{1}{2}}$ as follows: The rate of thermal generation, g_t, is given by $g_t = \lambda n_0^2$ (p. 15). For a bimolecular reaction it may be shown* that $\tau_{\frac{1}{2}} = 0.35/(\lambda n_0)$. Thus $g_t = 0.35\, n_0/\tau_{\frac{1}{2}}$. We assume that

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*Assuming, as we have, a bimolecular reaction for the recombination of defect or ion pairs, the decay constant λ may be used to define a pair half life $\tau_{\frac{1}{2}}$ as follows:

At t = 0, let there be a thermal equilibrium concentration of defects n_0 and let an additional number Δn per cm^3 be created suddenly. We define $\tau_{\frac{1}{2}}$ as the time it takes for half of these defects to recombine. We then have

$$dn/dt = \lambda (n_0^2 - n^2)$$

where n is the instantaneous concentration of defects. Then

$$\int_{n_0 + \Delta n}^{n} \frac{dn}{n_0^2 - n^2} = \int_0^t \lambda\, dt .$$

Integrating we obtain

$$\lambda t = \frac{1}{2n_0} \log_e \frac{(n_0 + n)\,\Delta n}{(n - n_0)(2n_0 + \Delta n)} .$$

(cont'd page 25)

$g_t = n_b \nu e^{-E_g/RT}$ where n_b is the concentration of normal bonds (or molecules), ν is a lattice frequency appropriate to the formation of defect or ion pairs and E_g is the activation energy for the formation of an ion pair and is greater than or equal to E_0 the enthalpy of formation of such a pair. Then

$$\tau_{\frac{1}{2}} = (0.35\, n_0/n_b\, \nu)\, e^{E_g/RT} \geq (0.35\, n_0/n_b\, \nu)\, e^{E_0/RT}.$$

At T = 263 K

For orientational defects	For ion pairs
E_0 = 15.8 kcal/mole	E_0 = 28 kcal/mole
$\nu = 1.6 \times 10^{14}$ sec^{-1}	$\nu = 2.9 \times 10^{14}$ sec^{-1}
$n_b = 6.7 \times 10^{22}$ cm^{-3}	$n_b = 3.3 \times 10^{22}$ cm^{-3}
$E_0/RT = 30$	$E_0/RT = 53$
$n_0 = 7 \times 10^{15}$ cm^{-3}	$n_0 = 8 \times 10^{10}$ cm^{-3}

Therefore

$$\tau_{\frac{1}{2}}\,(\text{Bjerrum}) \geq 2.4 \times 10^{-9} \text{ sec}$$

$$\tau_{\frac{1}{2}}\,(\text{ion}) \geq 3 \times 10^{-4} \text{ sec}.$$

Thus ε (Bjerrum) must be less than one hundred, which is fair enough since by definition it is less than one. This means that, if the assumptions on which the foregoing analysis is based are correct, the thermal signal would mask the injection signal by at least two orders of magnitude.

For ion pairs, we are led to a value for ε of less than 10^{-8}. This is very small indeed. In terms of partial absorption coefficient, α_p, where $\alpha_p = \varepsilon \alpha$, we have (since α is of the order of 100 cm^{-1}) $\alpha_p < 10^{-6}$ cm^{-1}. The molecular cross section is $\sigma = \alpha_p M/N_0$ where M is the molecular weight and N_0 is Avogadro's number. Thus σ (ion) $< 3 \times 10^{-29}$ cm^2.

From the work of Granicher et al. (1957) and Jaccard (1959) which indicate that d-c conduction in pure ice is ion-limited, it would appear that a d-c experiment such as this would be sensitive to ion generation. Thus within the framework of the assumptions stipulated, we conclude that the cross section for photogeneration of ion pairs is exceedingly small. However, we have shown also that the pulse apparently results from processes occurring in a very thin (100 μ thick) surface layer. The properties of this region may differ significantly from those of the bulk both because of the disordering effect of the surface and because contamination from the air will affect only the surface. Thus without more detailed knowledge of the surface, we must admit the possibility that the surface current is orientational-defect-limited.

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*(cont'd from page 24)
For $\Delta n \ll n_0$ this reduces to

$$\lambda t = \frac{1}{2n_0} \log_e \frac{\Delta n}{n - n_0}.$$

Inserting $n = n_0 + \Delta n/2$ at $t = \tau_{\frac{1}{2}}$ we have

$$\tau_{\frac{1}{2}} = 0.35/n_0 \lambda.$$

CONCLUSIONS

The results of these experiments may be summarized as follows:

1. Irradiation of an ice sample by high intensity light in the wavelength range 0.8 to 2.7 μ causes a detectable increase in the conductivity of the ice.

2. The signal varies linearly with the applied voltage (which means that the change in conductivity is independent of applied voltage).

3. The amplitude is roughly proportional to the light intensity.

4. The conductivity increase results from processes occurring in all of the illuminated area, not, for example, just that near the electrodes.

5. The response can be described in terms of a step which is due to sample heating and a pulse whose origin is not completely identified (see Fig. 6).

6. The spectral response of the pulse is approximately proportional to the optical absorption coefficient as given by Ockman except in the region 1.6μ to 1.9 μ. Here the response goes up when the absorption coefficient goes down which suggests a non-thermal phenomenon.

7. The response to white light increases as sample temperature increases. This is not necessarily true for all spectral components (for example 1.6 to 1.9 μ). The temperature dependence of the response is not the same as that for bulk conductivity.

8. The weight of the evidence indicates that for white light the pulse results from the heating of a surface layer whose effective thickness is itself a function of temperature and whose properties are different from those of bulk ice. This is consistent with a model for the surface structure of ice which has been proposed on the basis of widely different experiments. This subject has been reviewed recently by Fletcher (1962). Limits on signal to noise ratio prevented our studying this for narrow band illumination. Thus defect generation processes in one wavelength region may be masked by heating due to absorption in another.

9. The seemingly negative result of these experiments in regard to the photoproduction of defects indicates either an extremely small cross section for photoproduction of ions or an ion pair lifetime orders of magnitude smaller than that given by rough calculations. (This assumes that the surface current is ion-limited. If it is Bjerrum-defect-limited a null result is acceptable.)

10. Some of the problems we have encountered in this experiment suggest the possibility of studying the optical absorption of ice by using the conductivity of the sample to measure the energy absorbed when the sample is illuminated with light of different wavelengths.

11. There are several avenues which further work might take. The regions 1.6 to 1.9 μ should be studied under conditions of better signal to noise ratio. One possibility for doing this is to use a modulated light source of relatively low intensity and a phase sensitive detection system. Perhaps the surface contamination problem can be eliminated by preparing and using the samples in suitable glass or quartz cells. A similar set of experiments using high frequency alternating current ($\geq$ 10 kc) and, hopefully, increased sensitivity should be conducted. These would favor the detection of orientational defect pairs.

Experiments might be useful also in the wavelength region $\lambda > 2.8\ \mu$ where the absorption coefficient of ice is very large. Since this is a region of low photon energy, we may be quite sure that defect injection plays no part. We have thus the opportunity of studying the electrical (and other) properties of very thin surface layers by virtue of the local heating of these surface layers. The localization of the light absorption provides a means of separating surface and bulk phenomena. One matter we have not considered in this paper is the possibility of ion traps. Since these would involve energies small compared to those for ion pair formation, trapping might give rise to anomalous photo response at long wavelength.

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13. ABSTRACT

A series of experiments attempt to produce orientational defects and ions by optical injection. The basic experiment was one on transient photo-conduction produced by an intense light pulse. The effects of intensity and wavelength of the incident light, temperature of the sample and area of illumination of the sample were studied. It was concluded that neither orientational defects nor ion pairs were produced in appreciable quantity by the light but that the apparent photo-conduction observed was the result of flash-heating of a thin surface region which had significantly different properties than had the bulk of the sample. Simple and somewhat speculative assumptions regarding the photo-generation process lead to the conclusion that the photo-efficiency, at least for ion pair production, must be very low.

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