Dember Effect in Silver Chloride*

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The Dember effect has been investigated in silver chloride using a chopped light-ac amplification system of measurement. The effect has been resolved into a self-sustaining component which reaches a steady state (for a particular wavelength and intensity of incident light) and a nonself-sustaining component which decays with time. The steady-state self-sustaining effect has been found to be of only one polarity (normal polarity) when the illuminated face of the sample is coated with silver, but of both polarities when the illuminated face is not coated. The normal or positive polarity self-sustaining effect shows up at a shorter wavelength and the inverse self-sustaining effect at longer wavelengths, both in the vicinity of the optical absorption edge. A possible explanation for this behavior based on the existence of surface states is suggested. In the coated sample, the normal polarity effect was found to exhibit a peak at a wavelength of about 0.383 μ at $T=88°K$.

INTRODUCTION

THE appearance of a potential difference between two faces of a crystal when radiation is incident on only one face of the crystal is known as the Dember effect or crystalline photoeffect. Dember[1,2] attributed this voltage to the diffusion of optically excited electrons when the light was absorbed nonuniformly throughout the sample. Based on this postulated mechanism, the potential of the illuminated face should be positive with respect to that of the dark face. When this occurs, the effect is said to be positive or normal. If the potential is reversed, the effect is said to be negative or inverse.

A more extensive theory for the effect, taking into account the motion of both electrons and holes, was first developed by Frenkel.[3,4] He pointed out the basic equations describing the effect and obtained solutions to these equations for two special cases in an intrinsic semiconductor. One solution assumed intense illumination or low temperature so that the carrier concentration during illumination was large compared to its thermal equilibrium value. The other solution assumed very weak illumination or high temperature.

More recently, solutions for an n-type semiconductor have been obtained by Moss *et al.*[5] for the same two limiting cases treated by Frenkel. The only essentially new feature in this work was the inclusion of surface recombination.

These solutions have certain features in common. They both predict no variation of Dember potential with light intensity at high light levels and a linear variation at low levels. Both assume a very large optical absorption coefficient so that all generation of hole-electron pairs occurs in a very thin layer adjacent to the illuminated surface. As a result, the solutions exhibit no dependence of the potential on the wavelength of the incident radiation. In addition, even though all generation is assumed to occur adjacent to the surface, the possible existence of a space charge layer near the the surface is not considered.

In the course of this work a solution was obtained using approximations more appropriate to an insulator like AgCl. This solution does exhibit a wavelength dependence, but one which differs appreciably from the observed dependence. A more refined solution is now being attempted, but the utility of such a solution if it can be obtained, may be questionable.[6]

Experimentally, the Dember effect in AgCl has been investigated both in single crystals[7–9] and in polycrystalline samples.[10] The results of the most recent work, that of Kotliarevsky,[9] are somewhat puzzling.

According to Kotliarevsky, the peak of the effect, which occurs near the wavelength region where AgCl becomes intrinsically absorbing, is of positive polarity and moves toward longer wavelengths with decreasing temperature, at least down to $T=203°K$. On the other hand, if one varies the light wavelength in order to maintain a constant optical density as the temperature changes, it is found[11] that the wavelength has to decrease with decreasing temperature. Since the Dember effect and optical absorption are closely related, one might expect that their wavelength dependence would change similarly, or at least shift in the same direction, with a change in temperature. Kotliarevsky could not follow

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[1] H. Dember, Physik. Z. **32**, 554, 856 (1931).
[2] H. Dember, Physik. Z. **33**, 207 (1932).
[3] J. Frenkel, Nature **132**, 312 (1933).
[4] J. Frenkel, Physik. Z. Sowjetunion **8**, 185 (1935).
[5] T. S. Moss, L. Pincherle, and A. M. Woodward, Proc. Phys. Soc. (London) **66**, 743 (1953).
[6] For a discussion of this point of view see A. Rose, in *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley & Sons, New York, 1956).
[7] E. Kirillov, M. Kitaigorodski, and A. Molchanov, Acta Physicochim. (U. R. S. S.) **3**, 2 (1935).
[8] M. Kitaigorodski, Proc. Odessa State Univ. **2** (1940).
[9] A. B. Kotliarevsky, J. Exptl. Theoret. Phys. (U. S. S. R.) **17**, 516 (1947).
[10] A. P. Molchanov, J. Exptl. Theoret. Phys. (U. S. S. R.) **9**, 2 (1939).
[11] M. A. Gilleo, Phys. Rev. **91**, 534 (1953).

the peak of the effect at temperatures below 203°K because of what he termed an "unstable polarization."

In addition to the positive effect, Kotliarevsky also found the inverse effect at longer wavelengths at temperatures of 255°K and 203°K. He could not obtain a spectral distribution of the effect below 203°K, but he noted that at 100°K the effect was negative over the entire spectrum. This would indicate that if the observed photoeffect were truly a photodiffusion effect, the mobile carriers were principally holes. The findings of most investigators[12–14] indicate that in AgCl, holes are much less mobile than electrons if they are mobile at all.

The object of the present investigation was to make a more thorough study of the effect in AgCl preliminary to using it as a tool for further studies on the electronic properties of the silver halides.

EXPERIMENTAL TECHNIQUE

A chopped light-ac amplification system was used for all the measurements. The radiation from a tungsten filament source with a quartz envelope was square wave modulated at 13 cps before entering a monochromator with a quartz prism. For a monochromator slit width of 200 μ, the incident photon current on the sample varied from 10^{11} photons/sec at 0.35 μ to 5×10^{11} photons/sec at 0.4 μ. The electrical signal from the sample was amplified by a preamp followed by a 13-cps amplifier, and then was rectified by a mechanical rectifier operating in synchronism with the light chopper. To permit compensation for the phase characteristics of the sample, the rectifier was connected to the light chopper through a differential. The output of the rectifier was recorded after passing through a low pass filter.

All measurements, unless otherwise noted, were made at liquid nitrogen temperature.

Four samples were cut from a crystal grown at Eastman Kodak Research Laboratories.[15] Details of the growth, treatment, and analysis of the crystal are given elsewhere.[16] Spectrochemical analyses indicated just detectable concentrations of Al, Mg, and Si, in this particular sample. After being cut from the main boule, the samples were treated by a method similar to that described by Haynes.[17] Following this treatment a grid of semitransparent silver lines 3 mils wide separated by 3-mil spaces was evaporated on to one face of samples 1 and 2, while the other face of each sample was coated with Aquadag. The dimensions of the final specimen were approximately $1.5\times0.8\times0.3$ cm, with the smallest dimension in the direction of the incident light.

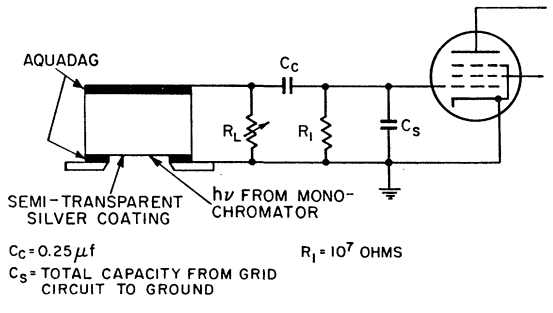

FIG. 1. High impedance preamplifier.

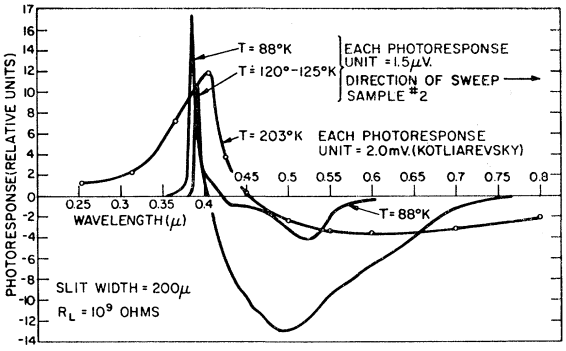

FIG. 2. Wavelength dependence of photoresponse for AgCl with a silver electrode on the illuminated face. Kotliarevsky's data at 203°K are included for comparison.

EXPERIMENTAL RESULTS AND DISCUSSION

Photoresponse of Sample 2 in the Region 0.35 to 1.0 μ

The significant electrical circuit is shown in Fig. 1. If the branch containing R_L is open circuited, the effective value for R_L is greater than 10^9 ohms. All experimental data are given in terms of the voltage at the grid of the input tube in Fig. 1.

With $R_L > 10^9$ ohms, the spectrum was scanned from the long wavelength end toward the short wavelength end. No electrical signal was detected during this first scan. However, upon sweeping through the spectrum in the opposite direction, a small peak of positive polarity was found near 0.38 μ and a much smaller and broader response of opposite polarity was found at somewhat longer wavelengths. Subsequent scans produced similar results, although the nature of the response during any scan depended quite strongly upon the previous illumination. A typical response is shown in Fig. 2. In the same figure, a response curve for a somewhat higher temperature (120–125°K) and Kotliarevsky's[9] dc measurements at 203°K are shown for comparison.

It should be noted that the peak of the positive response shifts toward shorter wavelengths with decrease in temperature from Kotliarevsky's measurements at

[12] W. Lehfeldt, Nachr. Ges. Wiss. Göttingen Fachgruppe **2**, 171 (1935).
[13] L. P. Smith, in *Semiconducting Materials*, edited by H. K. Henisch (Butterworth Scientific Publications, Ltd., London, 1951), p. 114.
[14] F. C. Brown, Phys. Rev. **97**, 355 (1955).
[15] The authors are indebted to Dr. Franz Urbach for supplying the crystal and the details of its characteristics, treatment, and spectrochemical analysis.
[16] N. R. Nail, F. Moser, P. E. Goddard, and F. Urbach, Rev. Sci. Instr. **28**, 275 (1957).
[17] J. R. Haynes, Rev. Sci. Instr. **19**, 51 (1948).

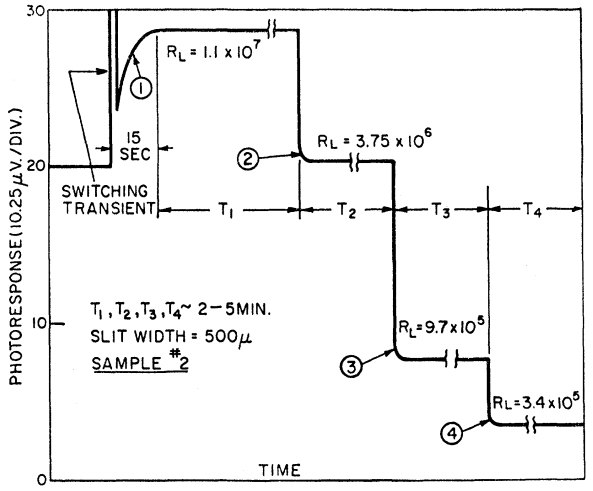

FIG. 3. Variation of photoresponse with time for different load resistances. Silver electrode on illuminated face.

203°K, through our measurements at 125°K, and to our measurements at 88°K. Because of the construction of our Dewar, we could not follow the wavelength shift of the peak above 125°K or below 88°K.

These two peaks behaved quite differently as functions of time. If the output of the monochromator was set for 0.38 μ, the photoresponse increased with time, reached a maximum, then decreased approaching a nonzero constant value asymptotically.[18] On the other hand, if the monochromator output was set at the middle of the broad longer wavelength peak, the response decreased with time and approached zero asymptotically. In fact, for any monochromatic radiation of wavelength longer than about 0.4 μ, the response appeared only if the sample had been given a prior exposure to radiation shorter than about 0.4 μ; and, after its appearance, the response always decayed to zero with time. We shall refer to the shorter wavelength response as "self-sustaining" (SS) and to the longer wavelength response as "nonself-sustaining" (NSS).

This time dependence suggests that the SS response arises from the intrinsic generation and subsequent motion of hole-electron pairs, but that the NSS response arises from the optical excitation, and subsequent motion, of electrons from traps. The polarity of the SS response is a consequence of the larger electron mobility as compared to the hole mobility. The inverse polarity of the NSS response indicates that the electrons released from traps move primarily by drift in the space charge or polarization field resulting from the nonuniform trapping of carriers during the SS response. The decay of the NSS response to zero with time results either from the depletion of traps, or a redistribution of charge in traps to destroy the internal field, or both.

The absence of any response during the first scan from longer toward shorter wavelengths even through the SS peak suggests that no response can appear until traps are filled.[19] The unfilled traps act as sinks for the first group of optically generated carriers preventing these carriers from diffusing through the sample to establish a photodiffusion potential across the sample.

Although this is probably an overly simplified interpretation, other observations to be discussed later tend to indicate that this interpretation is at least qualitatively correct.

The magnitude of the steady-state SS response varies with the magnitude of R_L as shown in Fig. 3, where $R_L > 10^9$ ohms before the switching transient. Time constants 2, 3, and 4 are characteristic of the amplifier and recorder, but time constant 1 is longer than any in the amplifier or recorder and must be characteristic of the sample itself.

The initial increase in response when R_L is decreased from $>10^9$ ohms to 10^7 ohms we attribute to a decrease in the space charge field against which the electrons

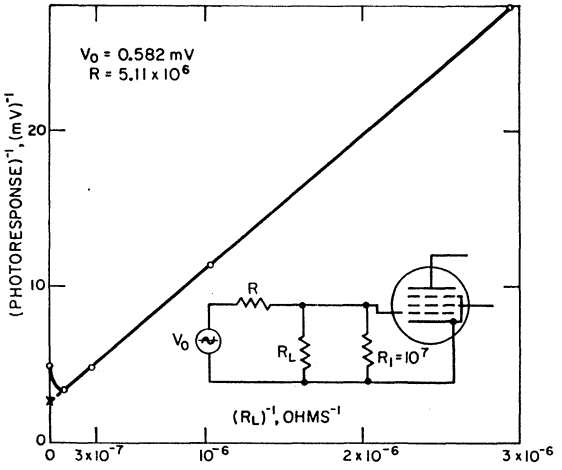

FIG. 4. Steady-state photoresponse of SS peak vs load resistance. The equivalent circuit for the illuminated crystal is given in the inset.

diffuse during the light-on portion of the chopping cycle. The decrease in response with further decrease in R_L is strictly a circuit effect.

If the illuminated crystal is replaced by a voltage generator with output voltage V_0 and series resistance R, because of the relative impedances at 13 cps of the various circuit elements the actual circuit of Fig. 1 may be replaced by the equivalent circuit shown in Fig. 4. The grid voltage in this circuit is

$$V^{-1} = (10^{-7}R + 1)V_0^{-1} + RV_0^{-1}R_L^{-1}.$$

A plot of V^{-1} vs R_L^{-1} from the data in Fig. 3 is shown in Fig. 4. The fact that the observed points lie on a straight line justifies the equivalent circuit assumed for the illuminated crystal. In addition, from this curve

[18] This response is referred to later as having an initial overshoot.

[19] For a discussion of the meaning of "trap filling" see A. Rose, Phys. Rev. **97**, 322 (1955).

we find $V_0=0.58$ mv and $R=5.1\times10^6$ ohms when the photon current incident on the crystal is approximately 10^{12} photons/sec.

It follows, then, that if R_L is increased from 10^7 ohms to $>10^9$ ohms, the photoresponse should increase immediately to the point x on the straight line of Fig. 4, after which it should decrease as the space charge field against which the carriers diffuse during the light-on portion of the chopping cycle increases. This behavior is observed experimentally as is shown in Fig. 5.

If one starts with an unpolarized crystal, the SS response increases with time shown in Fig. 6. For R_L equal to 10^7 ohms or less, there is no initial overshoot in the response. During the buildup time, the electronic population of traps is increasing and a steady-state response is achieved only after the trap population reaches a steady-state value appropriate to the incident light intensity and the temperature of the sample.

Further evidence for the influence of traps on the response is furnished by the phase difference between

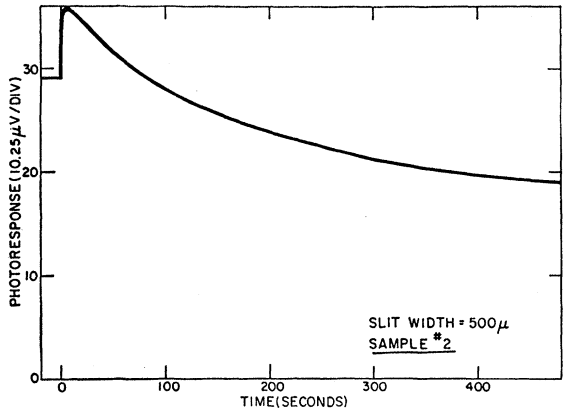

FIG. 5. Time dependence of photoresponse after load resistance is switched from 10^7 ohms to 10^9 ohms.

the photoresponse and the incident light. The differential setting for maximum response at the SS peak was about 48° lagging for $R_L\leq10^7$ ohms. That is, the synchronous rectifier lagged behind the chopper. In the neighborhood of the SS peak the optimum differential setting was practically independent of wavelength.

During the light-off portion of the chopping cycle the trap population decays as electrons are released thermally from shallow traps. After the light is turned on, the trap population must build up again to its steady-state value under illumination before the maximum response is achieved.

The variation of the steady-state SS response with light intensity is shown in Fig. 7. For these measurements, the monochromator slit width was constant and the attenuation was obtained with a Kodak photographic step tablet calibrated at the same wavelength at which the photoresponse was measured. At "high" light levels the response varies approximately as the

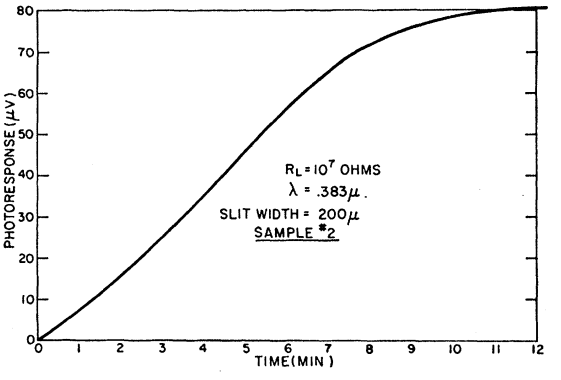

FIG. 6. Buildup of self-sustaining response at 0.383μ in unpolarized AgCl. Silver electrode on illuminated face.

0.7 power of the intensity, but at low levels the response is superlinear, varying even more rapidly than the square of the intensity.

This behavior points out the inability of the existing theories to describe the Dember effect in insulators, and indicates that the trap distribution must be fairly complex.[19] Because of this complex trap structure, a complete solution to the basic equations, if such were obtainable, would result in rather unwieldy expressions whose practical utility might be questionable.[6]

The wavelength dependence of the SS response was determined by sweeping through the spectrum first in one direction and then in the other. Typical results are shown in Fig. 8. As is evident from these results, the response depends upon the scanning direction. The time taken for one scan was about 1.5 minutes. A point by point measurement of the wavelength dependence was also carried out and these results are included in Fig. 8. At any wavelength, the response was time dependent. When the wavelength was changed, the response underwent an immediate change followed by a slow change

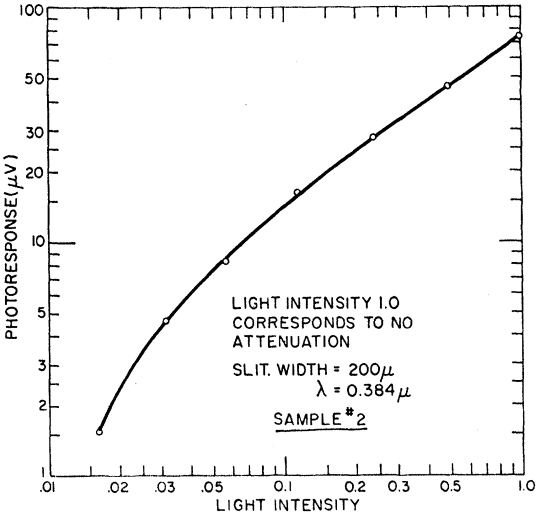

FIG. 7. Variation of steady-state self-sustaining response with light intensity. Silver electrode on illuminated face.

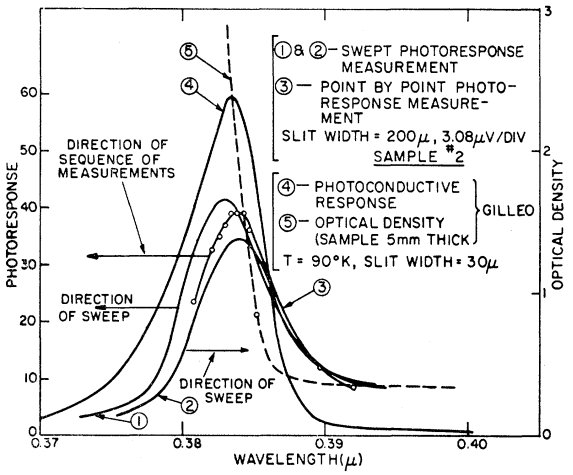

FIG. 8. Wavelength dependence of self-sustaining response. Silver electrode on illuminated face. The photoconductivity and optical density measurements of Gilleo are included for comparison.

over several minutes. In making the point by point measurements, a period of about 5 minutes was allowed for the response to reach a steady-state value after each wavelength change. For purposes of comparison, Gilleo's photoconductive response and optical density vs wavelength curves[11] are also included in Fig. 8.

Photoresponse of Samples 3 and 4 in the Region 0.35 to 0.45 μ

All the measurements described so far have been for sample 2. After these measurements had been made, it was observed that the grid of silver lines which had been evaporated on sample 1 had dissappeared. The grid of lines on sample 2 was still clearly visible, although some of the silver may have disappeared. Samples 1 and 2 were coated at the same time but had subsequently existed in different environments. Sample 1 had been kept in complete darkness at room temperature and atmospheric pressure awaiting use. Sample 2 had been at a pressure of 10^{-5} mm of Hg most of the time and at liquid nitrogen temperature part of the time during all the measurements which we have just described.

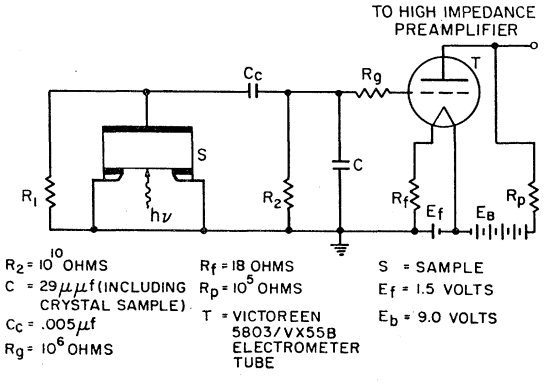

FIG. 9. Electrometer circuit.

The period during which the lines disappeared was 3 months or less. The reason for the disappearance was not investigated, but from the work of Wiegand[20] it seems reasonable to assume that the silver diffused into the AgCl.

Because of this observation we repeated the measurements on two more samples, samples 3 and 4, whose front surfaces were uncoated. For these measurements the electrometer circuit shown in Fig. 9 preceded the preamplifier of Fig. 1.

The photoresponse of sample 3 near the optical absorption edge differs considerably from that in sample 2, although there are features common to both. There is a buildup of response with time in both samples, but the differential setting for maximum signal is quite different between the two crystals. For crystal 2, the optimum differential angle at the 0.38 μ peak was 48° lagging, and in the neighborhood of the peak it was practically independent of wavelength. For crystal 3 the optimum phase angle was strongly dependent upon the wavelength of the incident light. In fact, for a given differential setting, either polarity of SS response could be observed depending upon the wavelength of the incident light.

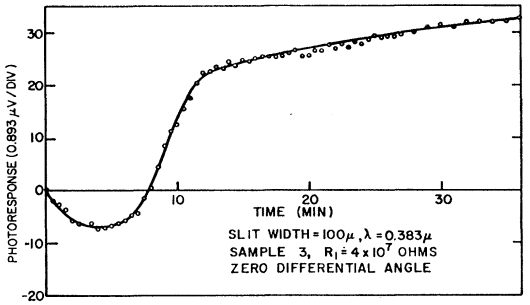

FIG. 10. Buildup of self-sustaining response at 0.383 μ in unpolarized AgCl. No electrode on illuminated face.

The buildup with time of the SS response at 0.383 μ for a differential angle of zero is shown in Fig. 10. The initial response is in the inverse direction but then it changes with time to the normal direction. The circuit parameters during these measurements were such that the nature of the inverse response can not be due only to a shift in the phase of the photoresponse signal with a change in the sample resistance.

The variation of SS response with wavelength for a differential angle of zero is shown in Fig. 11. Each point is the steady state value of the response at that wavelength, measured 5 minutes after the wavelength was changed. Instead of making point by point measurements as was done for the data in Fig. 11, one can sweep through the spectrum and obtain the type of results shown in Fig. 12. For these measurements the time for one complete sweep was 1.5 minutes. In these sweeping

[20] D. Wiegand (private communication).

measurements steady-state conditions are not realized, and the results depend on the speed, duration, and direction of the sweep, as well as on the previous state of the crystal. In Fig. 12 four consecutive sweeps are shown. Several preliminary scans were made before taking the data shown in order to obtain fairly reproduceable results.

If the sweep is extended in the longer wavelength direction, on the return sweep the negative peak decreases in magnitude but the positive peak increases. By extending the sweep far enough in the long wavelength direction, the negative peak may be eliminated completely on the reverse sweep. Conversely if the sweep is extended sufficiently far in the short wavelength direction, the positive peak may be eliminated on the subsequent sweep.

To determine whether shallow traps played a significant role in these results the sample was kept in darkness for 30 minutes at 88°K after sweep number 4 of Fig. 12.

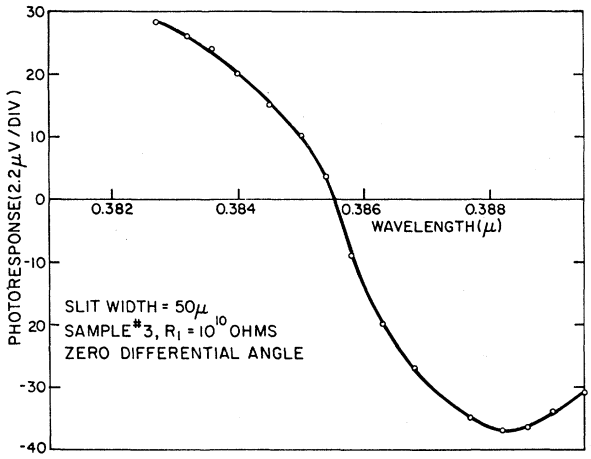

FIG. 11. Wavelength dependence of steady-state self-sustaining response. No electrode on illuminated face.

If all trap levels had activation energies of 0.3 ev or greater, the electronic state of the crystal should not change during this 30 minute standing time. The time constant for thermal emptying of traps of this energy (assuming a vibration frequency factor of 10^8 sec^{-1}) is of the order of 10^9 sec or longer. Thus only about 1 in 10^5 traps should empty during this 30 minutes standing time. Consequently the next sweep should produce a response much like that of curve 3 in Fig. 12.

The actual response after the standing time is shown in Fig. 13. The fact that this response is completely different from curve 3 in Fig. 12 indicates that shallow traps are playing a significant role in the photoresponse process.[21] Furthermore, the actual response curve may be synthesized by a superposition of the two dashed curves, suggesting that two competing processes, which

[21] Some preliminary work on thermally induced conductivity which we have done also indicates that shallow traps are present in our samples. See also reference 14.

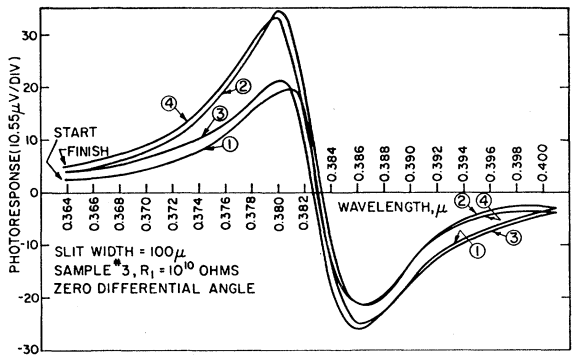

FIG. 12. Wavelength dependence of self-sustaining response with repetitive scans of the spectrum. No electrode on illuminated face. Each scan takes 1.5 minutes.

produce photoresponses of opposite polarity, may be operative.

Similar measurements were taken on sample 4 with the same qualitative results.

We propose the following explanation for the observed behavior of samples 3 and 4. If there is an electric field within the crystal, optically generated carriers may move by a combination of diffusion and drift. If this field is in the appropriate direction, these two mechanism tend to produce motion in opposite directions for the predominant carriers. We assume the normal Dember effect results when diffusion is the dominant process with the light on, whereas the inverse Dember effect results when drift is the dominant process.

Since there are no external fields applied to our sample, we postulate that an electric field exists just inside the free surface. Bardeen[22] has shown that such a field may exist under the proper conditions. Let us assume the energy band diagram of Fig. 14 for the free surface in equilibrium. In this diagram C and V are the edges of the conduction and valence bands, respectively, and μ is the Fermi energy of the crystal. The assumed distribution of surface states is such that there is a net positive charge on the surface which is compensated by a negative space charge layer extending a distance λ

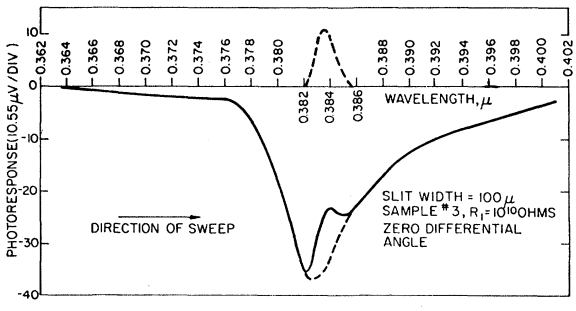

FIG. 13. Wavelength dependence of self-sustaining response after crystal has been kept in the dark at 88°K for 30 minutes following a scan from longer toward shorter wavelengths.

[22] J. Bardeen, Phys. Rev. 71, 717 (1947).

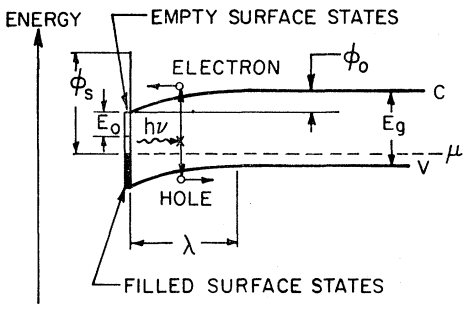

FIG. 14. Postulated energy diagram at free surface of AgCl at low temperatures. The Fermi level is indicated by μ. E_0 is the energy below the conduction band to which surface states must be filled for charge neutrality at the surface.

into the bulk of the sample. Thus there is an electric field over the range λ.

Free carriers generated in this space charge region would tend to drift as shown in Fig. 14 and to produce an inverse Dember effect. However, if the light is absorbed nonuniformly in this layer, both carriers would tend to diffuse away from the free surface and to produce a normal Dember effect. Thus there are two competing processes for the motion of the principal carriers in this assumed energy diagram.

We would expect drift to predominate when the concentration gradient in the space charge region is small, and diffusion to predominate when the concentration gradient is large. Thus we would expect to observe the inverse Dember effect at long wavelengths where the absorption coefficient for the light is small, but to observe normal Dember effects at shorter wavelengths where the absorption coeffcient is sufficiently high to produce a large concentration gradient. This is just what is observed in samples 3 and 4.

Additional evidence in support of this proposed model is furnished by the time variation of the response shown in Fig. 10, and by the phase characteristics of the signal for this sample.

Because of the nonuniform spatial generation of free pairs in the sample, traps should fill most rapidly at the illuminated surface and progressively less rapidly toward the dark surface. Thus drift in the space charge region should be the initial dominant process, leading to the initial inverse response. As traps fill throughout the rest of the sample, diffusion throughout the whole sample should become progressively more important and eventually should become the dominant process, leading to the final normal response.

The optimum phase of the signal for this sample varied considerably with the wavelength of the incident light. Such a phase characteristic would be expected if the electrical signal were actually the superposition of two signals with different phases (not 180° apart) and with amplitudes which varied differently with the wavelength of the incident light.

It should be pointed out, however, that even though the experimental evidence suggests the model we have proposed, we do not have independent evidence for the energy band diagram we have assumed, nor do we have an estimate of the order of magnitude of the extent λ of the space charge region.

FURTHER COMMENTS

The essential difference between samples 2 and 3 is that the front face of sample 2 was coated with silver while that of sample 3 was not. There are three ways in which the surface coating could affect the sample: (1) by changing the surface properties, i.e., the surface state distribution, (2) by producing a double layer of charge at the silver-silver chlorine interface, and (3) by diffusing into the AgCl and changing its bulk properties, i.e., the trap distribution. [It may not be possible physically to differentiate between (1) and (2).] Any one of these effects could explain the absence of a self-sustaining, inverse photoresponse on the coated sample. Not enough evidence has been obtained as yet to speculate further in this direction.

Since the results depend so strongly on the surface condition of the samples, it would appear that the Dember effect is not as useful in studying the bulk properties of insulators as are some other techniques, e.g., photoconductivity with uniform illumination on the sample. It may be a good tool for the study of interface layers between materials, but much more work must be done before this can be established.

SUMMARY

The Dember effect in AgCl has been resolved into a self-sustaining component which reaches a steady-state value (for a particular wavelength and incident light intensity), and a nonself-sustaining component which decays with time. The nonself-sustaining component occurs only after prior illumination with intrinsically absorbed light. The steady-state self-sustaining effect has been found to be of only one polarity when the illuminated face of the sample is coated with silver. However, both polarities are present when the illuminated face is not coated. The normal or positive effect shows up at a shorter wavelength and the inverse effect at a longer wavelength. A possible explanation for this behavior has been suggested.