Microwave photodielectric effect in AgCl

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A microwave photodielectric effect was observed in pure AgCl powders on a fast time scale (~ 1 μsec) at both 90 and 295 K. It appears that this effect was caused by shallow trapping at a density of $\sim 10^{17}$ centers/cm^3, a number not inconsistent with other estimates of shallow trap densities in silver halides. This effect caused changes in the resonant frequency of a microwave cavity, which led to errors as large as 25% in the observed "fixed-frequency" microwave photoconductivity. A kinetic study of the photodielectric shift at 90 K indicates that the photodielectric effect is caused by shallowly trapped electrons in equilibrium with the conduction band for times ≥ 10 μsec after exposure. This suggests that the concept of "drift mobility" in AgCl is meaningful for these and longer times. For times ≤ 7 μsec after exposure, a rapidly decaying photodielectric signal was observed, the origin of which is as yet unknown.

I. INTRODUCTION

It is well known that the illumination of many photoconductors and semiconductors can result in a change of dielectric constant; such "photodielectric effects" have been reported in various materials ranging from CdS (Ref. 1) to organic photoconductors. Dielectric changes are often caused by the trapping of carriers at shallow (≤ 0.1 eV) sites, so that the measurement of photodielectric changes presents an ideal method for studying shallow-trapping processes in photoconductors. Shallow trapping is important in silver halides, where it reduces carrier mobilities from their microscopic values to "drift" values, smaller by several orders of magnitude.[2]

Several workers[3,4] have recently reported photodielectric changes in silver halides. One approach[3] involves the use of microwave methods quite similar to those employed in the popular microwave photoconductivity technique, so that all the advantages inherent in microwave methods are retained. In fact, conduction-band (photoconductive) and shallow-trap (photodielectric) phenomena have been measured simultaneously on a slow (~ 100 msec) time scale. It has been pointed out[3] that photodielectric changes detune a resonant microwave cavity and so may introduce an error into microwave photoconductivity measurements. This error was observed for exposures of ~ 1 sec, but instrumentation limitations prevented observations in a faster time domain. Thus, it was uncertain whether photodielectric changes were affecting microwave photoconductivity measurements on shorter time scales (typical times being ~ 1 μsec).

Photodielectric measurements also have the potential to resolve several important experimental questions involving silver halides. A study of "photodielectric kinetics" may indicate the time required for equilibrium to be established between conduction-band and shallowly trapped carriers; this in turn will indicate when microwave photoconductivity may provide a measure of the photoelectron drift mobility, an important parameter in photographic models. In addition, it is possible that photodielectric changes may be caused by shallowly trapped holes as well as electrons, so that the technique may provide a means to directly observe photoholes in silver halides.

The present work represents an effort to observe microwave photodielectric effects in silver chloride powders on a fast time scale (~ 1 μsec) and to determine their magnitude and the optimal experimental conditions for their observation. Photodielectric kinetics at high exposure levels were also studied in an effort to explore their origin.

II. THEORY OF THE MICROWAVE PHOTODIELECTRIC EFFECT

A. Change of dielectric constant

At microwave frequencies, both ionic (lattice) and electronic polarization contribute to the dielectric constant. The lattice term appears because the·

microwave frequency $\omega << \omega_{TO}$, where ω_{TO} is the frequency of a TO phonon ($\sim 10^{13}$ sec^{-1} in silver halides).[5] Dipolar effects, such as those caused by lattice defects (vacancies and interstitials), are not expected to contribute because their response time is very long compared to one period of microwave oscillation.[6]

Photoinjection of carriers into the lattice changes the dielectric constant. The magnitude of the changes caused by carriers in various states may be evaluated by simple models. From the Lorentz model for free carriers,[7] the polaron mass,[8] and deducing a relaxation time from the Hall mobility,[9] it can be shown that the polarizability of free electrons in AgCl is about 6×10^4 Å^3 at 10 GHz. For shallowly trapped carriers in hydrogen-like states, the polarizability is estimated from the second-order Stark effect; such calculations suggest a polarizability of $\sim 2 \times 10^5$ Å^3. This type of estimate has been experimentally validated in silver halides by trap depth[10] and polarizability[11] measurements. Because of the highly localized state of carriers in deep traps, the polarizability for these centers is of the order of atomic polarizabilities (1−10 Å^3).[12] From the above estimates, it is expected that photodielectric shifts at 10 GHz will result only from free or shallowly trapped carriers.[1,3,4]

Dielectric constants generally do not vary linearly with the number of polarizable sites because of local-field effects which result in Clausius−Mosotti-type behavior.[7] This nonlinearity does not occur for free carriers[13−15] but may arise for shallowly bound carriers.[16,17] Nonlinear effects are negligible when $4\pi \sum_j N_j \alpha'_j / 3\epsilon' << 1$, where ϵ' is the lattice dielectric constant, α'_j the polarizability, and N_j the density of centers j.[16,17] Using the α' estimated with the hydrogenic model, one may predict that linear behavior is expected for $N << 2 \times 10^{18}$/cm^3. This condition is satisfied by the relatively low levels of light intensity used in these experiments.

Changes in the resonant frequency (ω) and quality factor (Q) of a microwave cavity may be related to changes in the complex dielectric constant ($\epsilon^* = \epsilon' + j\epsilon''$) of a sample within the cavity by perturbation theory.[18] Powdered samples are assumed to be a collection of spherical grains which do not interact with each other via depolarization fields; these assumptions are not strictly valid, but the model will still predict the qualitative features of the experiment. For large cavity Q and the sample positioned at an electric field maximum, it can be shown from the results of Ref. 18 that the

photoinduced change in cavity parameters is

$$\frac{\delta\omega_0}{\omega_0} + j\left[\frac{1}{2Q}\right] = -\frac{1}{2G}\left[\frac{V_s}{V_c}\right]\left[\frac{3}{\epsilon_2^* + 2}\right]\left[\frac{3}{\epsilon_1^* + 2}\right]$$

$$\times (\epsilon_2^* - \epsilon_1^*) , \tag{1}$$

where V_s and V_c are the sample and cavity volumes, ϵ_1^* and ϵ_2^* are the dielectric constants before and after illumination, and G is a "filling factor" dependent on the experimental geometry. For small changes in dielectric constant $|\delta\epsilon^*/\epsilon^*| << 1$, one may approximate

$$\frac{\delta\omega_0}{\omega_0} + j\left[\frac{1}{2Q}\right] \approx -\frac{1}{2G}\left[\frac{V_s}{V_c}\right]\left[\frac{3}{\epsilon' + 2}\right]^2$$

$$\times \left[\left[\delta\epsilon' + \frac{(\delta\epsilon'')^2}{\epsilon' + 2}\right] + j\delta\epsilon''\right] ,$$

$$\tag{2}$$

where $\epsilon' \equiv \epsilon_1^* = \epsilon_1'$ for AgCl in the dark.

To first order, the effects of the real and imaginary parts of $\delta\epsilon^*$ are separable: $\delta\omega_0$ depends only on $\delta\epsilon'$ and $\delta(1/2Q)$ depends only on $\delta\epsilon''$ $\propto \delta\sigma$. These changes represent the photodielectric and photoconductive effects, respectively.

The assumption $\delta\epsilon^*/\epsilon^* << 1$ is readily tested. The largest exposures used in these experiments were $\sim 10^{16}$ photons/cm^2, which are expected to lead to volume-averaged maximum carrier densities of $\sim 10^{17}$/cm^3. If all these carriers were trapped at sites of $\alpha' \approx 10^6$ Å^3 (a large α'), then the maximum $\delta\epsilon'/(\epsilon' + 2) \approx 0.01$. If all carriers were in the conduction band, then $\delta\epsilon''/(\epsilon' + 2) \approx 0.3$ at 90 K. It is very unlikely that most of the carriers remain in the conduction band because of shallow trapping, so that the latter estimate is probably highly overestimated. Therefore, the expansion (2) is justified, but the photodielectric shift term

$$\frac{\delta\omega_0}{\omega_0} \propto \delta\epsilon' + (\delta\epsilon'')^2/(\epsilon' + 2) \tag{3}$$

may be dominated by "photoconductive crosstalk," i.e., by the $(\delta\epsilon'')^2$ term. Determination of whether this occurs is not possible a priori, because it requires a knowledge of $\delta\epsilon''$ relative to $\delta\epsilon'$. There are, however, experimental means of identifying this behavior. Under crosstalk conditions, $\delta\omega_0 \propto (\delta\epsilon'')^2 \propto [\delta(1/2Q)]^2$; this behavior would be evident from the dependence of $\delta\omega_0$ and $\delta(1/2Q)$ on exposure intensity. Under conditions where $\delta\omega_0 \propto \delta\epsilon'$, the sign of $\delta\omega_0$ will indicate whether free carriers ($\alpha' < 0$, $\delta\omega_0 > 0$) or trapped carriers ($\alpha' > 0$,

$\delta\omega_0 < 0$) are dominating $\delta\epsilon'$.

It has been shown that, in appropriate limits, $\delta\omega_0$ and $\delta(1/2Q)$ depend only on $\delta\epsilon'$ and $\delta\epsilon''$, respectively. There are circumstances, however, when the technique used to measure $\delta(1/2Q)$ can depend on $\delta\omega_0$. In particular, measuring sample photoconductivity by monitoring the cavity power absorption at a fixed frequency can be subject to errors caused by photodielectric effects. These errors arise because photodielectric shifts change the cavity resonance frequency, which in turn detunes the cavity relative to the applied microwave frequency. The observed change in absorbed power is due to cavity detuning as well as photoconduction. The resulting "photodielectric error" is depicted graphically in Fig. 1. Such errors were originally reported on a slow ($\sim$100-msec) time scale using $Pb^{2+}/AgCl$,[3] and the question of their existence on a faster time scale is an important experimental concern. One must also be aware that the conventional automatic frequency control (AFC) circuits used to "lock" the microwave frequency to the cavity resonance[3] generally have response times which are far too slow ($\sim$1 msec) to compensate for fast photodielectric changes.

III. EXPERIMENTAL

Photodielectric and photoconductive changes in AgCl were observed by using the X-band microwave photoconductivity apparatus shown in Fig. 2. The microwave source was a 35-mW, 10.25-GHz Gunn diode oscillator tunable over 50 MHz. The microwave cavity was a rectangular TE_{103} cavity;
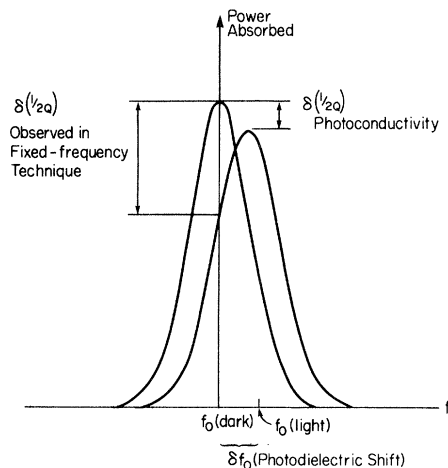
the loaded Q was variable from 300 to $\sim$2000 by means of a coupling iris (impedance match or mismatch). Microwave power was detected with an HP X424a diode with output directly connected to a preamp. The preamp output was monitored on an oscilloscope triggered by the light pulses used in the experiment.

Frequency shifts of the microwave cavity are much easier to observe when the cavity resonance profile is sharper, that is, when the cavity Q is high. A conflicting experimental concern was that the cavity response be fast compared with the photoconductivity decay time. The cavity time constant is equal to Q/ω_0; these experiments were performed at $Q = 500$, which corresponds to a time constant of 50 nsec. Typical conductivity decay times were ≥ 500 nsec, so that the cavity response was not expected to interfere with the measurements.

The apparatus could be operated in two different modes. In a straight detection mode, switch S (cf. Fig. 2) was open and the oscilloscope trace plotted photoconductivity versus time as in the usual fixed-frequency photoconductivity technique.[19] By closing switch S, the system could be operated in the resonance profile mode. In this mode, the photodiode triggered a TTL time delay, which in turn triggered a signal generator. The delayed output ramp from the signal generator caused the microwave frequency to sweep through the cavity resonance. In this manner the cavity power reflection as a function of frequency could be observed at any fixed time after the light pulse. The time required to sweep through resonance was $\sim$100 nsec,

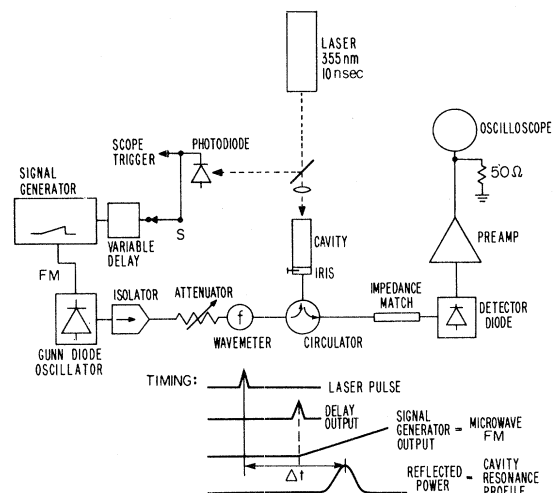FIG. 1. Relation of photoconductive and photodielectric effects to changes in the cavity resonance profile.

FIG. 2. Experimental apparatus and timing sequence.

which was "instantaneous" compared to decay times at low temperatures (> 40 μsec at 90 K).

By varying the time delay between the light pulse and the generator sweep, it was possible to monitor the resonance profile as a function of time. The smallest obtainable interval between exposure and display was 500 nsec; the interval was accurate to ± 50 nsec, owing to the change in the resonance position caused by the photodielectric effect.

The light source used for these experiments was the third harmonic of a 1.06-μm pulsed laser (Quanta Ray DCR-1A) at 355 nm. The fundamental Nd:YAG (yttrium-aluminum-garnet) and second harmonic outputs were removed from the beam by means of a Pellin-Broca prism and an aperture. The pulse width was measured to be 10 nsec [full width at half maximum (FWHM)] with a fast silicon photodiode. A fused-silica lens was used to defocus the beam so that it covered a spot ~ 5 m in diameter on a sample inside the microwave cavity; this was observed from the silver printout of a silver halide sample placed in the cavity. The maximum light power used in these experiments was 3 mJ/pulse $\approx 5 \times 10^{15}$ photons/pulse, which corresponds to 2×10^{16} photons/cm^2 pulse.

The material used for this investigation was a pure (< 1 ppm metal impurity) AgCl binderless precipitated powder. The material was prepared from 6N silver shot, distilled HNO$_3$, and distilled HCl. The AgCl was exposed to only red light (by means of Kodak Wratten gelatin filters No. 1A) prior to use so that pre-exposure would not affect its properties. The temperature of the sample was controlled with a gas-flow cryosystem, stable to ± 0.2 K. Experiments were conducted at 90 K and room temperature.

The effect of multiple exposures was investigated at both high and low temperatures by displaying each individual trace on a storage oscilloscope (Tektronix R7912/605 Transient Digitizer). At 90 K the photoconductivity peak height and kinetics remained unchanged over many exposures (10 pulses/sec for ~ 10 min); the peak height variation was $\sim 10\%$ which corresponds roughly to the jitter in laser pulse energy. At room temperature, the photoresponse appeared constant for ~ 2 min at 10 pulses/sec, but prolonged exposure resulted in a faster decay time. Samples used in the experiment were visually examined for silver (photographic) printout; none was observed except in the case of prolonged exposure at room temperature. Since

the photoconductivity decay time was always much smaller than 0.1 sec, photodecay always reached completion before the next exposure. Given these results, it was considered sufficient to use multiple pulses to obtain the data; this method made it easier to optimize the signal-to-noise ratio for each individual sample by fine tuning the cavity resonance. It also made it possible to avoid the problem of sample-to-sample variations when doing certain experiments.

IV. RESULTS AND DISCUSSION

The photodielectric effect was readily observable in AgCl at 90 K by using 355-nm pulses of $\sim 10^{14} - 10^{16}$ photons/cm^2. Typical experimental results are presented in Fig. 3. One picture of the peak of the cavity resonance profile was taken before exposure and another at some known time interval Δt (cf. Fig. 2) after the light pulse. Both curves were photographed on the same film to aid in comparison. The change in the vertical height of the resonance peak corresponds to an increase in power absorption due to sample photoconductivity and the change in the horizontal position of the peak corresponds to a change in the cavity resonance frequency, i.e., the photodielectric shift.
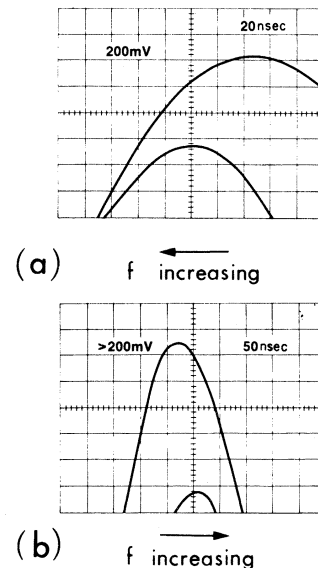

FIG. 3. Experimental resonance profiles showing photodielectric shifts. Bottom curves are before exposure, top curves are after exposure. Horizontal scale is ~ 0.24 MHz $= 20$ nsec. (a) 90 K, 2×10^{15} photons/cm^2 pulse, $\Delta t = 2.5$ μsec, 355 nm. (b) 295 K, 1×10^{16} photons/cm^2 pulse, $\Delta t = 500$ nsec, 355 nm.

The shift $\delta\omega_0$ was negative for all light-pulse intensities studied for time intervals Δt from 500 nsec to ≥ 30 μsec after exposure. The sign of the shift is consistent with either shallow trapping $(\alpha' > 0)$ or $(\delta\epsilon'')^2$ "crosstalk" terms dominating Eq. (2) for $\delta\omega_0$. To determine which of the two effects caused the frequency shift, we simultaneously measured the intensity dependences of both $\delta\omega_0$ and $\delta(1/2Q)$. The results (Fig. 4) show that the photoconductive and photodielectric changes at 90 K both vary in the same manner with light exposure intensity. This indicates that the $\delta\omega_0$ signal is not the result of photoconductive crosstalk $(\delta\epsilon'')^2$ terms because, in that case, the photoconductivity $\delta(1/2Q) \propto \delta\epsilon''$ would vary as $\sqrt{\delta\omega_0}$. The sign and intensity dependence of $\delta\omega_0$, therefore, suggest that the observed photodielectric effect in AgCl at 90 K is caused by a change $\delta\epsilon'$ in the real part of the sample dielectric constant due to shallow trapping.

The intensity dependence of $\delta\omega_0$ and $\delta(1/2Q)$ also show that these signals vary linearly with light intensity I at low I and vary with $\sqrt{I}$ at higher intensities. This behavior is consistent with a kinetic model in which the photosignal is limited by first-order (trapping) processes or exposure time at low carrier densities and second-order (recombinative) processes at higher densities. The fact that $\delta\omega_0$ and $\delta(1/2Q)$ both vary similarly with intensity and the magnitude of the experimental light pulses suggest that the observed photodielectric shift may be accounted for by the simple expres-

sion $\delta\epsilon' = 4\pi\sum_j \alpha_j \delta N_j$ rather than by the more complex Clausius-Mosotti relation.

The largest photodielectric shift observed for the AgCl powder was $\delta f_0 = -1.8$ MHz, which occurred for conditions $\Delta t = 500$ nsec, 90 K, and 2×10^{16} photons/cm^2. This shift is of the same magnitude as those observed in long-time-scale experiments with a comparable total number of photons incident on the sample.[3] From Eq. (2) (which is not strictly valid because it fails to account for depolarizing interactions between the powder grains), and assuming that the photodielectric shift arises from only $Z = 1$ effective-mass electron traps $(\alpha' = 2 \times 10^{-19}$ cm$^3)$, the 1.8-MHz shift corresponds to a total number of (filled) shallow traps, $NV_s \approx 1 \times 10^{16}$. The exposed sample volume was $V_s \approx 0.1$ cm^3, implying a volume-averaged shallow-trap density of $\sim 10^{17}$/cm^3. This is a reasonable order of magnitude, considering the photon flux and the known values of drift and Hall mobilities in AgCl. More quantitative evaluations of the shallowly trapped carrier population would require a more exact knowledge of the trap polarizabilities, energy distribution, etc.

The half width at half maximum of a cavity resonance at $f_0 = 10$ GHz, $Q = 1000$ is 5 MHz. Therefore, the observed photodielectric shifts of ~ 2 MHz can result in substantial errors in microwave photoconductivity observations, as outlined in Sec. II. For example, the 90-K photoresponse at $\Delta t = 2.5$ μsec (Fig. 3) can be analyzed for photodielectric error as in Fig. 1, indicating an error in the fixed frequency measurement of $\sim 26\%$. These data were obtained at $Q = 500$; at higher Q, larger errors are expected. Therefore, it is clear that photodielectric effects can cause significant errors in fixed-frequency photoconductivity measurements.

Photodielectric shifts were also observed in AgCl at room temperature. Care was taken to ensure that data were taken before multiple exposures altered the sample photoresponse; "first flash" data were often used. Room-temperature effects were not characterized in detail, because much of the photodecay occurred before the resonance profile was displayed; the fixed-frequency photoconductivity half-life was ~ 500 nsec, which was the shortest Δt available experimentally. The measured photodielectric shift at room temperature, $\Delta t = 500$ nsec, and 10^{16} photons/cm^2 pulse was $-\delta f_0 = 0.4 - 0.5$ MHz. This value is substantially smaller than the shifts observed at 90 K, but the change may be due to the decay occurring before
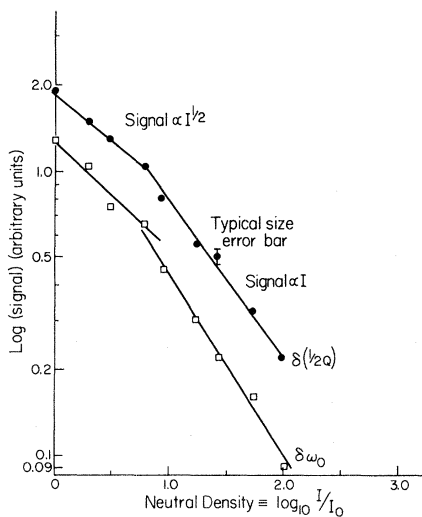

FIG. 4. Intensity dependence of $\delta\omega_0$, $\delta(1/2Q)$ at 90 K for a pure AgCl powder; $\Delta t = 1$ μsec. $I_0 = 9 \times 10^{15}$ photons/cm^2 pulse and $\lambda = 355$ nm.

the measurement. These measurements demonstrate that much faster instrumentation may be required to observe photodielectric effects at room temperature.

The evolution of photodielectric and "true" photoconductive changes as a function of time at 90 K was also observed. The measurements were made by varying Δt and recording the data from pictures such as those in Fig. 4. A resonance profile in the dark was always observed as well as one after exposure to ensure that the measurement did not include extraneous changes in the dark resonant profile. A single sample was used for a range of values of Δt so that sample-to-sample variations were avoided. As stated in Sec. III, multiple-exposure effects did not appear to change the sample photoresponse. The observed kinetic behavior was reproducible over many samples and was qualitatively similar for exposure intensities from 2×10^{16} to $\sim 5 \times 10^{14}$ photons/cm^2 pulse.

Typical kinetic results are presented in Fig. 5. The kinetics show that for times $\Delta t \gtrsim 10$ μsec after exposure, the photodielectric and photoconductive responses both decay exponentially with roughly

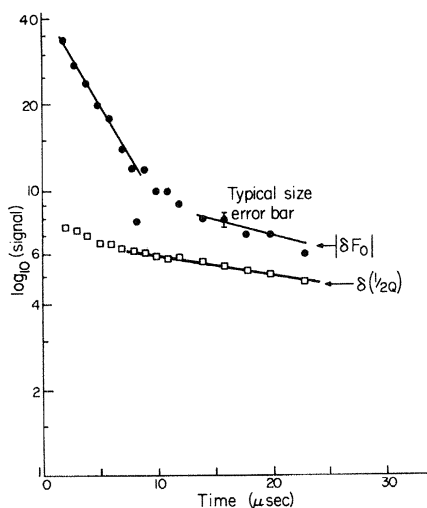the same time constant. It is generally assumed that the photoconductivity of silver halides is due only to photoelectrons and not to photoholes.[19] When the shallowly trapped carrier population ($\delta\omega_0$) decays in the same manner as the conduction-electron population $\delta(1/2Q)$, it suggests that the $\delta\omega_0$ signal is caused by shallowly trapped electrons in equilibrium with the conduction band. Therefore, for $\Delta t \gtrsim 10$ μsec, the photodielectric effect can be attributed to electrons in shallow traps which are in equilibrium with the conduction band; at these times, the observed photoconductivity is proportional to the drift mobility.

For the time interval 500 nsec to ~ 7 μsec after the exposure, the photodielectric shift decays much more rapidly than the photoconductivity. The photoconductivity decay is also faster during this time but does not decay as rapidly as the photodielectric shift. The explanation of this behavior is not obvious, but several possibilities can be explored. If one believes that shallow-trap—conduction-band equilibration occurs for times ≤ 7 μsec after exposure, then the anomalously rapid segment of the photodielectric decay may be due to photoholes. Alternatively, such an equilibration may not be in effect, in which case the decay represents a redistribution of the relative populations of conduction-band and shallowly trapped electrons. Yet another possibility may be the introduction of plasma effects to the dielectric response of the powder at high densities of carriers in the conduction band.[20] Such effects are possible when the plasma frequency $\omega_p \gg \sqrt{\omega/\tau}$, suggesting that plasma effects are important only for conduction-band carrier densities of $n > 10^{15}$ cm^{-3}.

V. CONCLUSIONS

Photodielectric shifts of microwave cavity resonance frequencies do occur in AgCl at both room temperature and 90 K. These shifts can cause significant errors in fixed-frequency microwave photoconductivity measurements utilizing microwave cavities.

The photodielectric effect in AgCl at 90 K appears to be caused by shallowly trapped carriers and appears to be linear in carrier density. Photoconductive crosstalk and Clausius-Mosotti behavior do not appear to be important for the experimental light intensities used. For times $\gtrsim 10$ μsec after exposure, the photodielectric shift is attributable to shallowly trapped photoelectrons "in equilibrium"

FIG. 5. Photosignal kinetics (semilog plot). δf_0 is photodielectric shift ("10" corresponds to ~ 0.55 MHz) and $\delta(1/2Q)$ is photoconductivity (arbitrary units). Accuracy of data points in relative scale units is ± 0.8 (photodiel), ± 0.3 (photocond). The data were taken at 90 K using an intensity of 5×10^{15} photons/cm^2 pulse, $\lambda = 355$ nm.

with the conduction band. For times $\lesssim 10\,\mu$sec after exposure, the photodielectric effect may be due to "unequilibrated" photoelectrons, photoholes, or plasma effects. Further work in this area is already in progress.

ACKNOWLEDGMENTS

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