

new type: engineer physicists, by his long and brilliant pedagogical and scientific activity. Abram Fedorovich is the teacher of several generations of Soviet physicists. He succeeded in instilling in his students a love for science and a desire to apply the results of their studies for the good of their country, that is, those features which are characteristic of all of his activity.

Now, in the days of his seventy-fifth anniversary Abram Fedorovich Ioffe is full of creative powers,

full of ideas for new work and plans for wide practical applications of semiconductors.

All the physicists of the Soviet Union warmly congratulate Abram Fedorovich on his seventyfifth birthday and wish him great success in his future activity and many years of fruitful work.

Translated by E. Rabkin
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Photoelectric Quantum Yield in Silver Bromide Crystals

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The quantum yield of the photoelectric effect in silver bromide was determined. It was shown that as one increases the concentration of electron emitting centers, one decreases the magnitude of the quantum yield.

A GREAT deal of work has been devoted to the study of the photoelectric effect in silver halides.¹ Only Lehfeld² and Hecht³, however, actually measured the quantum yield of the reaction. The difficulty of determining this quantity, even in terms of the energy absorbed, is due to the fact that it depends on the quantum yield as well as on the "displacement" of the electrons. For this reason Lehfeld performed his experiments under saturation conditions when all electrons freed by the light quanta reach the anode. Measurements at such great field strengths (3000 v/cm) are hard to perform at room temperature, because of the presence of large and unsteady background (dark room) currents. For this reason Lehfeld and Hecht performed their experiments at liquid air temperatures. They found the quantum yield to be between 0.1 and 0.6 and the electron dis-

placement per unit field strength was of the order of 4×10^{-4} cm / (volt/cm).

The literature contains no data on the above quantities at room temperature. It was this lack that inspired the present work.

EXPERIMENTAL METHOD

Silver bromide crystals were prepared by allowing the fused salt to flow between two glass discs, as was previously described by one of the authors.⁴

In order to measure the photoelectric current we built a special ac amplifier that was calibrated by means of an audio oscillator with a vacuum tube voltmeter as well as with a 50 cycle alternating current. In the latter case a known voltage was attenuated by means of a voltage divider. The silver bromide crystals were placed in a metal box in which the electrodes rested on insulated discs. The box was connected to the amplifier by means of a coaxial cable. The inner conductor applied the voltage from one of the electrodes

¹ E. A. Kirillov and A. S. Fomenko, Trudy Odessa Inst. 3, Odessa, 1951, p. 7.

² W. Lehfeldt, Nachr. Akad. Wiss. Göttingen Math.-physik. Kl I, 171 (1933).

³ K. Hecht, Z. Physik 77, 235 (1932).

⁴ P. V. Meikliar, J. Exper. Theoret. Phys. USSR 21, 42 (1951).

to the input grid of the amplifier through a coupling condenser. The input impedance was 47.5 megohms. The second electrode and the metal box were grounded. The photoelectric current was amplified, rectified with a diode and then measured on a moving pointer type galvanometer. When relaxation times were to be observed, the electrodes were connected directly to an oscillograph of type EO-4. Windows in front and back of the metallic box allowed light to shine through the crystal. This permitted us to measure both the photoeffect and the absorption without disturbing the position of the crystal. An oven was mounted in such a way that when needed it could be lowered so that the crystal was inside it. The oven was equipped with windows that allowed the crystal to be illuminated. It was thus possible to measure the photoeffect and the absorption at higher temperatures. The crystal was illuminated by means of a monochromator of type UM-2. The monochromator lamp was fed from a stabilized 12 volt, 30 watt source. The light was modulated by means of a slotted disc driven by a constant current motor. The needed current for a given speed of rotation was predetermined by means of a stroboscope and kept constant throughout the experiment. The angular rotation of the disc was such as to modulate the light at 50 cycles per second. The coefficient of absorption was measured with the help of a selenium photocell attached to a high sensitivity mirror galvanometer. A special apparatus was used to measure the coefficient of reflection. Monochromatic light was made to pass through a half mirrored surface, reflected from the crystal and again made to fall on the semitransparent surface, 45° to the path of the beam, from which it was reflected to the photocell. One compared the galvanometer deflection in this case with the deflection when the crystal was replaced by a mirror of known coefficient of reflection (close to unity). The energy distribution in the monochromator was determined by means of a thermocouple previously calibrated against a standard light of known color temperature and known intensity.

In the region of wavelength between 400 and 450 $m\mu$ the galvanometer deflection was very small. In this region we made use of a photomultiplier, a specially designed tube that gave a galvanometer deflection of 45 mm when the output slit of the monochromator was set at 1.0 mm.

The low temperature measurements were made in a cylindrical container with the crystal placed in it in a horizontal position. The container was in a wooden box packed with solid carbon dioxide. Light from the monochromator was deflected down on the crystal by means of a mirror. After passing through

the crystal the light fell on the selenium cell underneath the crystal. This allowed the determination of the photoelectric current and the coefficient of absorption at low temperatures. The temperature in all cases was measured with a thermocouple.

In some of our experiments the crystal was illuminated with light of wavelength 365 $m\mu$. This was obtained from a mercury lamp of type SVDSH-250 passed through a type FS-2 filter. In this case the light was modulated by the alternating current through the mercury lamp.

RESULTS OF THE EXPERIMENT

Figure 1 shows the conductivity of silver bromide

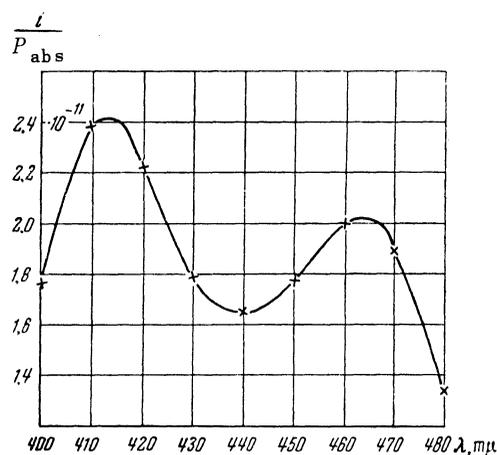


FIG. 1. Photoelectric current in AgBr expressed per unit of energy absorbed.

as a function of wavelength expressed in coulombs per erg, i.e., per unit energy absorbed at room temperature. Figure 2 shows a similar curve for silver

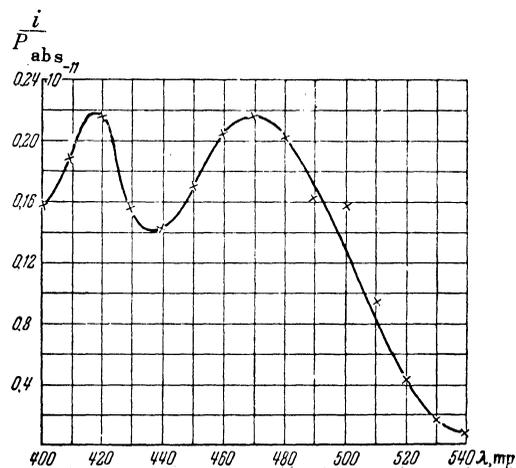


FIG. 2. Photoelectric current in AgBr with 10 percent of AgI (per unit energy absorbed.)

bromide crystals that contain 10 mole per cent silver iodide as an impurity. We see that in the blue portion of the spectrum the curve has two maxima, one at $\lambda = 410$ to $420 \text{ m}\mu$ and one at $\lambda = 460 \text{ m}\mu$. This agrees with the results of Kirilov and Fomenko¹ and those obtained by Zaidman⁵.

Changes in the temperature of the crystal greatly effect the magnitude of the photoelectric effect. Figure 3 shows graphs of the photoelectric sensi-

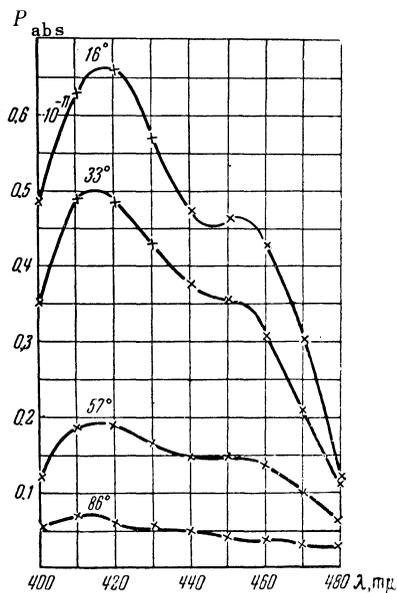


FIG. 3. Curves of photoelectric current in AgBr at different temperatures.

tivity at various temperatures. It is seen that as the temperature goes up there is a drastic change in the photoelectric sensitivity. This agrees with the qualitative observations of Putseiko and Meiklier⁶. One could suspect that the decrease in the photoelectric sensitivity with increase in temperature was due to a higher relaxation time. We therefore performed special measurements of the relaxation time at temperatures that were used in our experiments. These showed that always during the time that the crystals were illuminated, the relaxation curves showed saturation.

In order to clarify the reason for the decrease in photoelectric sensitivity with increase in temperature, we determined the quantum yield of the photoeffect as well as the electron displacement, both per unit field strength. For uniform illumination

of the entire crystal one may use Hecht's equation⁷

$$\psi = \frac{w}{l} \left[1 - \frac{w}{l} (1 - e^{-l/w}) \right],$$

where ψ is the ratio of the total charge Ne released by the light to the charge $Ne(\bar{x}/l)$, which passes through the measuring apparatus. Here e is the charge on the electron, l is the distance between electrodes, \bar{x} the mean free path of the electrons and w is the electron "displacement", i.e., the distance in which the number of free electrons released by the light and traveling towards the anode is diminished by e .

Hecht and Lehfield found that the electron displacement w is proportional to the field strength E . One may therefore introduce the constant $c = w/E$. Furthermore $N = P_{\text{abs}} \eta / h\nu$ where P_{abs} is the amount of monochromatic energy absorbed by the crystal, $h\nu$ the energy of the quantum, and η the quantum yield of the photoeffect. One can therefore rewrite Hecht's equation in the form

$$i = \frac{P_{\text{abs}}}{h\nu} e \eta \frac{cE}{l} \left[1 - \frac{cE}{l} (1 - e^{-l/cE}) \right]$$

The above equation expresses the photoelectric current i as a function of field strength E . Figure 4 shows the experimental curve of $i = f(E)$. The

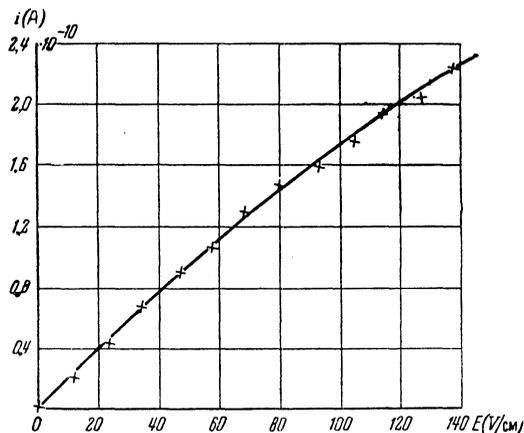


FIG. 4. Photoelectric current as a function of field strength.

independent determination of η and c was performed as follows: We determined the value of $\tan \alpha = (di/dE)_{E=0}$. Letting $l/cE = a$ we obtained

$$\left(1 - \frac{1}{\tan \alpha} \frac{i}{E} \right) a = 1 - e^{-a}.$$

⁵ H. M. Zaidman, Zh. Fiz. Khim 26, 1791 (1952).

⁶ E. K. Putseiko and P. B. Meiklier, J. Exper. Theoret. Phys. USSR 21, 341 (1951).

⁷ R. Gerni and N. Mott, *Electronic Processes in Ionic Crystals*, p145.

From this we obtain a graphically as the abscissa of the point of intersection of the curves

$$y = \left(1 - \frac{1}{\tan \alpha} \frac{i}{E}\right) a, \quad y = 1 - e^{-a}.$$

The magnitude of E was varied from 0 to 100 volts at each wavelength; η and c were measured for a variety of values of E and i ; l was measured independently. In addition, the resistance of the crystal was always measured for each trial. This was necessary because the applied voltage was divided between the crystal and the input resistance of the amplifier. η and c were both fairly constant with different values of E . This gives experimental justification to Hecht's equation.

In addition to the above method η and c were also determined by considering two points on the $i = f(E)$ curve, i.e., by using two pairs of values of i and E . Both methods gave approximately the same results.

Figures 5 and 6 show the dependence of the

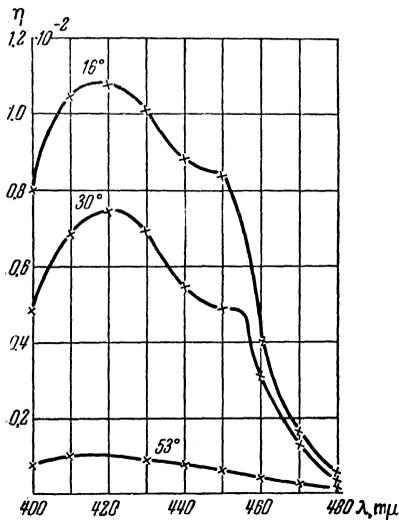


FIG. 5. Graphs showing the dependence of the quantum yield upon wavelength at different temperatures.

quantum yield η on wavelength at various temperatures. Figure 7 shows η and c as a function of temperature at a fixed wavelength. These curves show that the quantum yield decreases as the temperature goes up.

Although changes in temperature have a very great effect on the quantum yield of a given crystal, one must realize that from crystal to crystal the yield may differ by as much as ten fold. In order to find out what it is that determines the quantum yield, we measured the concentration of

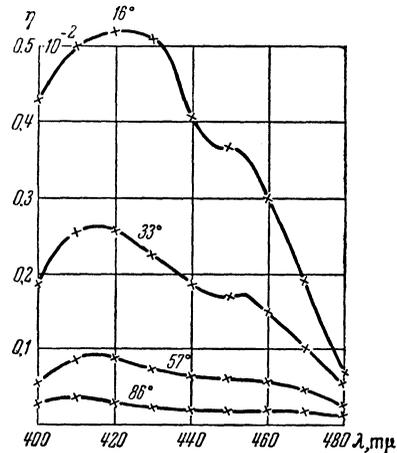


FIG. 6. Graphs showing the effect of wavelength upon the quantum yield at different temperatures.

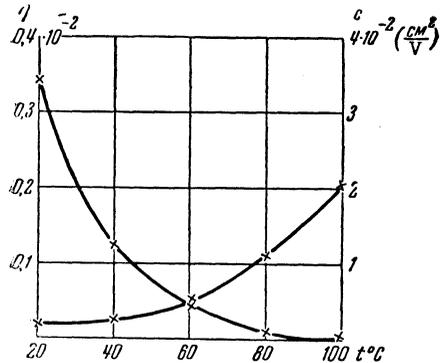


FIG. 7. Graphs showing η and c as a function of temperature.

the centers from which the electrons are freed in a silver bromide crystal. We consider those to be identical with the so called F -centers in the alkali halides. Our results, by the way, apply to any kind of photoelectrically active centers.

The concentration of F -centers was determined as follows: The optical density of the crystal was measured at a number of temperatures (see Fig. 8). From the area under the curve one determined the increase in the number of F -centers, ΔN_{F_8} , from room temperature to the given temperature⁸. Considering that

$$N_F = N_0 e^{-W/kT},$$

we can write $N_0 = \Delta N_F / (e^{-W/kT_1} - e^{-W/kT_2})$,

⁸ P. V. Meiklier and R. S. Shimanski, J. Exper. Theoret. Phys. USSR 27, 156 (1954).

Where w is the activation energy (0.15 ev), T_2 = room temperature and T_1 = the crystal temperature after it was heated. Having once established N_0 from known ΔN_F for several temperatures, it was possible to determine the concentration of F -centers at any temperature.

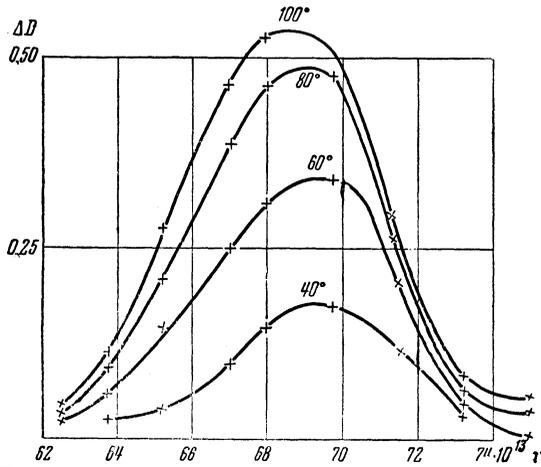


FIG. 8. Increase in the optical density of AgBr crystals as a function of frequency at different temperatures.

The concentration of F -centers was also varied by means other than temperature; such as by illumination of the crystals, cooling, and the addition of impurities. In each case the concentration of F -centers was measured.

It was determined that as the crystal was illuminated the concentration of F -centers went up while the quantum yield went down. Similar results were obtained when the crystals were quickly cooled from a temperature of 200 to 250°C. In each case, regardless of the method used to increase the concentration of F -centers, the quantum yield went down as the concentration of F -centers went up. The relation is shown in Fig. 9 (for $\lambda = 430 \text{ m}\mu$) where a linear relation

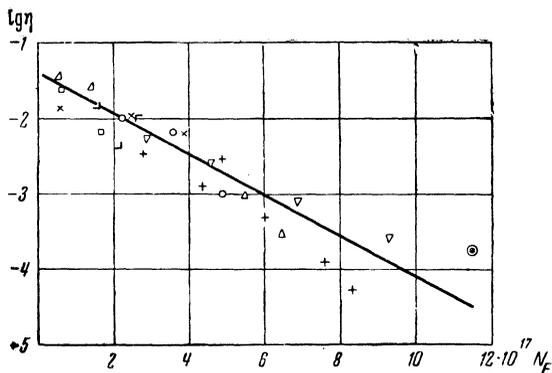


FIG. 9. Dependence of $\log \eta$ on the concentration of F -centers, N_F .

is seen to obtain between $\log \eta$ and N_F , that is a relation of the form $\eta = A \exp(-BN_F)$, (where $A = 0.04$ and $B = 0.65$). The table shows the complete data.

The decrease in photoelectric sensitivity with increase in temperature takes place also at $\lambda = 365 \text{ m}\mu$, that is in the region of absorption of crystalline silver bromide. The dependence of the quantum yield η on the temperature at $\lambda = 365 \text{ m}\mu$ is shown in Fig. 10. Figure 11 shows $\log \eta$ as a function of N_F , the concentration of F -centers.

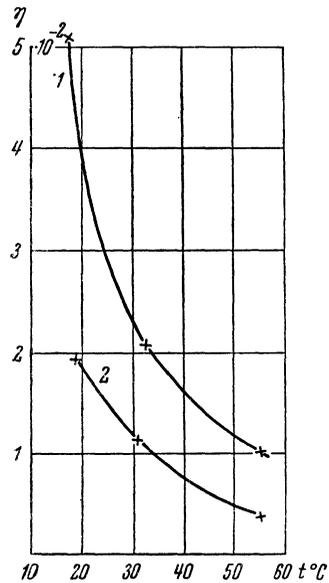


FIG. 10. η as a function of temperature for $\lambda = 365 \text{ m}\mu$; 1 - No. 18, 2 - No. 32.

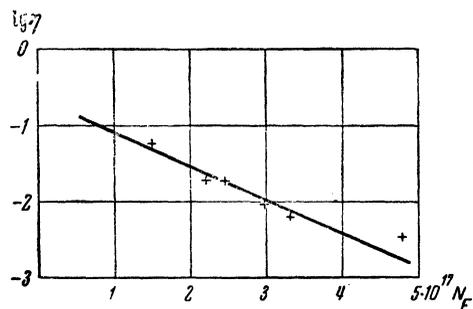


FIG. 11. $\log \eta$ as a function of F -centers for $\lambda = 365 \text{ m}\mu$.

DISCUSSION

It is hard to establish definitely the reason for the dependence of the quantum yield upon the concentration of F -centers. One might venture the following hypothesis: In the case of the lumines-

Test No.	3			12			22			34		38	25	28		21	
	Temperature in °C.	Concentration of F-centers $\times 10^{17}$	Quantum yield $\times 10$	100	30	16	30	30	53	20	20	20	20	20 before cooling	20 after cooling	20 before illumination	20 after illumination
	20	2.75	0.34	8.35	5.48	6.44	3.58	4.9	0.58	1.45	2.28	1.82	1.63	2.21	0.55	3.86	
	40	4.34	0.12	8.35	5.48	6.44	3.58	4.9	0.58	1.45	2.28	1.82	1.63	2.21	0.55	3.86	
	60	5.98	0.047	8.35	5.48	6.44	3.58	4.9	0.58	1.45	2.28	1.82	1.63	2.21	0.55	3.86	
	80	7.60	0.011	8.35	5.48	6.44	3.58	4.9	0.58	1.45	2.28	1.82	1.63	2.21	0.55	3.86	
	100	8.35	0.005	8.35	5.48	6.44	3.58	4.9	0.58	1.45	2.28	1.82	1.63	2.21	0.55	3.86	
	20	2.75	0.34	0.005	0.097	0.05	0.68	0.087	3.57	2.78	0.99	1.36	1.42	0.39	1.29	0.64	

cence of dyes one recognizes the phenomenon of concentration quenching. It consists of the fact that as the concentration of the luminescent dye goes up, the luminescent yield decreases. There is a transfer of energy absorbed by one molecule to another similar molecule, as a result of which there is an increase in the probability of energy degradation into heat or some photochemical reaction. Vavilov⁹ obtained the following equation for the probability of nontransfer of energy as a function of molecular concentration C : $q(C) = e^{-aC}$ where a is a linear function of time.

The presence of a dependence of photoconduction upon the concentration of F -centers gives reason to believe that we are dealing here with a concentration quenching of photoconductivity.

Experiments show that the concentration effects for dye solutions occur at concentrations of 10^{-3} mol per liter, where the mean distance between the molecules in solution is about 50 Å, although, according to the quantum theory, the phenomenon should begin to be apparent at mean molecular separation of about 200 Å. The phenomenon that is observed in silver bromide occurs when the concentration of F -centers is 10^{17} to 10^{18} cm^{-3} , i.e., when the distance between neighboring centers is about 100 Å.

The energy flowing through the crystal may be degraded into heat or it may bring about a photochemical reaction yielding sensitized silver bromide. Favoring the latter assumption is the fact that the lesser photoconductive crystals are usually more active photochemically. Similarly it is known that the photoelectric sensitivity of photographic emulsions is negligible. It is of course possible that production of photoactivated silver may be due to the migration of electrons as is suggested by the experiments of Haynes and Shockley¹⁰.

The intrinsic photoelectric activity of crystals also seems to be related to the concentration of F -centers. From this we might deduce the active nature of absorption in the region of self absorption and release of F -centers.

⁹ A. N. Terenin, *Problems in Physical Optics*, Papers presented in memory of S. I. Vavilov, GTTI, Moscow, 1951, p20

¹⁰ J. R. Haynes and W. Shockley, Report on Conference on Strength of Solids, London, 1948 p151.