Laser-Induced Electron Emission from Solids: Many-Photon Photoelectric Effects and Thermionic Emission*†

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A systematic study of the laser-induced electron emission from solids was attempted by studying both metals and insulators in the form of evaporated films and single crystals, using three different radiations (10 600, 6943, and 3472 Å) from a Q-switched laser, and measuring not only the intensity dependence of the electron emission, but also the energy distribution of the emitted electrons. The electron emission from Au, stainless steel, CsI, KI, and KCl can be explained in terms of (1) thermionic emission and (2) many-photon photoelectric effects. Two- and three-photon effects were observed, and their quantum yields were measured. The theory of two- and three-photon photoelectric effects is briefly developed by a perturbation calculation of the term $-(e/m)\,\mathbf{A}\cdot\mathbf{p}$ of the interaction Hamiltonian, and the formal expressions are evaluated for a simple three-band model of a solid and for a model that treats the properties of a solid in an average way. The degree of agreement between theory and experiment is discussed. Using a laser and a conventional light source, two-photon photoelectric spectroscopy was performed in CsI, and the spectrum obtained is interpreted in terms of parity-forbidden and -allowed transitions.

I. INTRODUCTION

AMONG the first experimental studies with lasers was that of the electron emission from solids under the influence of laser radiation. Honig and Woolston,[1] Lichtman and Ready,[2] Verber and Adelman,[3] and Giori *et al.*[4] reported at about the same time on the use of a focused (non-Q-switched) laser beam in effecting electron emission from solids, which was interpreted merely as thermionic emission. More experiments with non-Q-switched lasers were reported in 1964 and 1965,[5] the results of which were similarly interpreted in terms of thermal effects. In all these experiments, the fact that the laser pulses consisted of many irregular short spikes complicated attempts to arrive at accurate quantitative conclusions.

Ready[5] was the first to study electron emission from some metals using a Q-switched ruby laser. Using the consequent single-pulse irradiation, he was able to consider details of the electron-emission process. He concluded that for intensities up to 25 MW/cm^2 the electron emission was entirely thermionic. Using the Richardson equation, he determined the peak-temperature rise of his W surface as a function of the laser intensity and found good agreement with theoretical predictions obtained by solving the heat-transfer equation. Other experiments reported, however, do not agree with Ready's results. Knecht,[6] for example, using a Q-switched ruby laser found an additional electron emission from W corresponding to a temperature of 29 500°K. This, plus other experimental facts, cannot be interpreted as thermionic emission.

Recently, Ready[7] published a very detailed and comprehensive work on ion and electron emission from solids; the latter is interpreted as being entirely thermionic.

With lasers, two-photon absorption in solids has become a common effect in the last few years,[8] and significant information has been obtained in several cases. In analogy to one-photon photoelectric effects it is likely that two-photon photoelectric studies may supply additional information in the electronic structure of solids. However, from the large number of experiments on laser-induced electron emission from solids, only two had been interpreted as two-photon photoelectric effects. Sonnenberg *et al.*[9] observed an electron emission from Cs_3Sb (photocathode of an RCA 1P28 photomultiplier) which followed a square dependence on the light intensity of a Nd-doped glass laser. Teich *et al.*[10] in studying the electron emission from Na using an Ne-gas laser obtained a photocurrent versus intensity curve that was a mixture of one- and two-photon processes. There have, more recently, been other reports of similar results.[11]

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[1] R. E. Honig and J. R. Woolston, Appl. Phys. Letters **2**, 138 (1963).

[2] D. Lichtman and J. F. Ready, Phys. Rev. Letters **10**, 342 (1963).

[3] C. M. Verber and A. H. Adelman, Appl. Phys. Letters **2**, 220 (1963).

[4] F. Giori, L. A. McKenzie, and E. J. McKinney, Appl. Phys. Letters **3**, 25 (1963).

[5] J. F. Ready, Phys. Rev. **137**, A620 (1965); J. Appl. Phys. **36**, 462 (1965), and references therein.

[6] W. L. Knecht, Appl. Phys. Letters **6**, 99 (1965).

[7] J. F. Ready, E. Bernal, and L. T. Shepherd, Final Report to Ballistic Lab. No. 18-001-AMC-1040(x) (unpublished).

[8] J. J. Hopfield and J. M. Worlock, Phys. Rev. **137**, A1455 (1965); D. Fröhlich, B. Staginnus, and E. Schönher, Phys. Rev. Letters **19**, 1032 (1967), and references therein.

[9] H. Sonnenberg, H. Heffner, and W. Spicer, Appl. Phys. Letters **5**, 95 (1964).

[10] M. C. Teich, J. M. Schroeer, and G. J. Wolga, Phys. Rev. Letters **13**, 611 (1964).

[11] Very recently more two-photon photoelectric effects have been reported: S. Imamura, F. Shiga, K. Kinoshita, and T. Suzuki, Phys. Rev. **166**, 322 (1968); M. C. Teich and G. J. Wolga, *ibid.* **171**, 809 (1968).

The authors of the present study were interested in the photoelectric properties of the alkali halides and were attempting a study of many-photon photoelectric effects in them. In view of the several contradictions and disagreements between various experiments in the past it was felt, however, that understanding could not be achieved without first making some systematic study of laser induced electron emission from solids.[12,13] This was undertaken by: (i) studying both metals and insulators, (ii) carrying out studies on materials in the form of both thin evaporated films and single crystals, (iii) using several different laser radiations, and (iv) measuring not only the intensity dependence of the electron emission but also the energy distribution of the emitted electrons.

II. APPARATUS

The strong light intensities required for the experiments were obtained with a Q-switched laser (TRG Model No. 104). With a ruby rod in the laser cavity, the laser generated light pulses of about 40-nsec duration and 1-J energy at 6943 Å (1.786 eV). In combination with a KDP crystal, second harmonic (3471.5 Å or 3.57 eV) generated light pulses were also produced with about 27-nsec duration and 0.05-J energy. With an Nd-doped glass rod in the cavity light pulses of about 30-nsec duration and 1-J energy at 10 600 Å (1.17 eV) were generated.

Figure 1 is a block diagram of the experimental setup. A 90° quartz prism directs the laser beam through a window into the evacuated photoelectric cell. The light on its way to the cell passes through two irises used to control the beam dimensions and through a series of filters used to eliminate the laser flashlamp light and to change the intensity of the laser light. The laser beam is incident on the photocathode (of the material under study) at a 60° angle and is specularly reflected out of the cell through another window. The photoelectrons

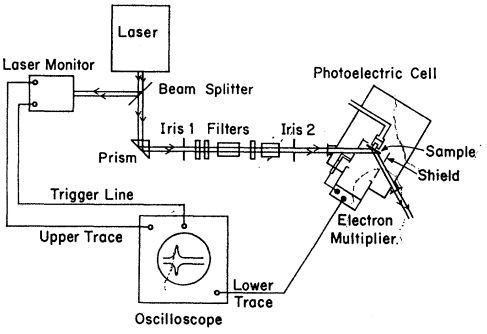

FIG. 1. Block diagram of the experimental setup.

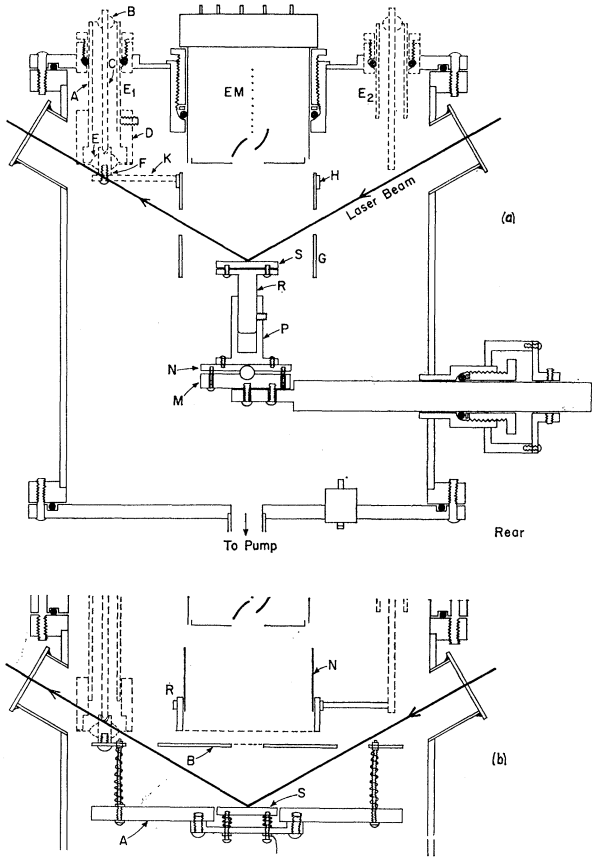

FIG. 2. (a) Top view of the photoelectric cell; (b) the planar electron-energy analyzer.

are directed into an electron multiplier, and the voltage signal generated across a 51-Ω load resistance is displayed on a Tektronix 547 oscilloscope. A beam splitter placed in front of the laser directs a portion of the laser light to two RCA 922 photodiodes. One diode serves to monitor the laser intensity, while the other supplies the signal to trigger the oscilloscope sweep.

The photoelectric cell is shown in Fig. 2. It consists of a brass cylinder with four 1-in. cylindrical openings, distributed symmetrically around its circumference, having their axes at a 60° angle with the cell axis. Three of them are sealed with quartz windows and one with plain glass. One pair of windows is used for the passage of the laser beam, while the other pair is used in an experiment in two-photon spectroscopy where a second light beam is needed. The laser beam is perpendicular to the windows so that the portion of the beam reflected from the windows follows the path of the main beam.

The cathode is a 1 in. stainless steel mirror disc S, on which the samples are evaporated or placed. It is mounted inside the photoelectric cell on a side shaft as shown in Fig. 2(a). External rotation of this shaft by 90° brings the mirror into evaporation position facing the evaporator. The evaporator (not shown in Fig. 2)

[12] E. M. Logothetis and P. L. Hartman, Phys. Rev. Letters **18**, 581 (1967).

[13] E. M. Logothetis and P. L. Hartman, Bull. Am. Phys. Soc. **12**, 273 (1967); E. M. Logothetis, Ph.D. thesis, Cornell University, 1967 (unpublished).

is a nickel-mesh boat mounted on long leads vacuum sealed through a lucite window. Observation of evaporated layers through the window allowed estimation of film thickness from their interference fringes.

The electron multiplier is mounted on the front plate of the cell. It was constructed from an unsealed 10-stage CBS 7812 photomultiplier having Be-Cu dynodes. The original glass envelope was cut in the plane of the focusing electrode of the multiplier structure, and the tube was used in this form as the fast amplifier for the photoemissive currents. The gain of the electron multiplier as a function of cathode-anode voltage was measured in a vacuum monochromator using the 1215 Å Lyman α radiation on a Cu photocathode from which the electron emission was separately measurable. The gain of the multiplier was 4×10^4 at 3000 V.

The cell chamber was evacuated with a conventional pump system consisting of an oil diffusion pump with liquid-nitrogen cold traps backed by a mechanical forepump. The vacuum was of the order of 10^{-5}–10^{-6} Torr.

For the determination of the energy distribution of the electrons emitted from the targets under the influence of laser radiation, a conventional two-electrode energy analyzer could not be used, because of the high photocathode currents (peak densities of the order of 10^{-5} Å cm^{-2}) that were required for these measurements; for such current densities, apparent space-charge effects were observed in the considerable but requisite distance between photocathode and retarding electrode. In order to perform the measurements, an energy analyzer was constructed having a third (semitransparent) electrode between the photocathode and the retarding electrode. This electrode was kept at a high positive potential relative to the cathode; space-charge effects of the accelerated electrons in this region were thereby largely eliminated. Electrons passing through the semitransparent accelerating electrode were then energy analyzed with the retarding electrode; by keeping the spacing between retarding and accelerating electrodes to a few mm, current saturation was obtained at zero retarding voltage[14] (i.e., retarding electrode at cathode potential).

In part of the experiment it was desirable to measure the component of the electron energy normal to the emitting surface. For this reason a planar analyzer was constructed as shown in Fig. 2(b). The emission occurs in a large plane capacitor consisting of two 5-in. disks. Disk A has a central hole in which the stainless-steel mirror (photocathode) is mounted. The accelerator disk B has two openings for the passage of the laser beam and a central opening which is covered with a fine Ni mesh (60% transmission). The retarder R is another Ni mesh mounted over the end of a cylinder so constituting the cathode and electrostatic shield of the electron multiplier. The photocathode and the retarder were kept at near the same high negative potential while the accelerating electrode was less negative by several hundred V. The small potential difference between photocathode and retarder was varied and used to analyze the energy of the electrons.

For the rest of the experiment, the total energy of the electrons was of interest; for this a spherical analyzer was constructed along the same lines.

III. MEASUREMENTS AND RESULTS

A. Electron Emission

This part of the measurements was concerned essentially with the investigation of the dependence of the electron-emission current from solids on the incident-light intensity.

The intensity of the laser light was controlled by filters. For the 6943 and 10 600 Å radiations, combinations of Corning color filters were used. In some cases neutral-density filters were also used. Various tests showed that there was no contribution to the electron emission from possible luminescence of the color filters. For the 3472 Å radiation, liquid filters consisting of water solutions of $NiSO_4$ of various concentrations[15] and, in some cases, color filters were used. The transmission of all filters at the laser wavelengths was measured in a Cary 14 spectrophotometer and also with the laser light itself using a TRG-100 thermopile. Both measurements gave the same results.

The intensity of the unattenuated laser beam (I_0) was calculated from the total energy per laser pulse measured with the thermopile. The pulse shape and duration needed for this calculation was measured with a fast photodetector and the oscilloscope. Figures 3(a)–3(c) shows typically the three laser pulses. The intensity was obtained by dividing the laser power by

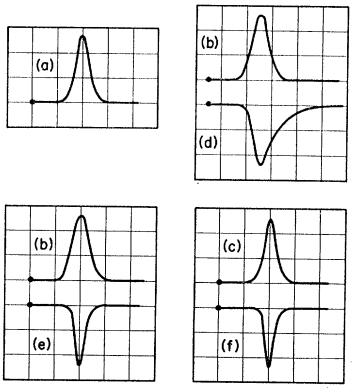

FIG. 3. Light and electron pulses. (a) 10 600 Å laser pulse, (b) 6943 Å pulse, (c) 3472 Å laser pulse, (d) electron pulse from stainless steel and Au resulting from the 6943 Å radiation, (e) electron pulse from the five solids resulting from the 3472 Å radiation, (f) electron pulse from Au resulting from the 6943 Å radiation at $I<0.7$ MW/cm². The sketches are exact reproductions of oscilloscope pictures, traced here for clarity. Time scale is 50 nsec per division.

[14] L. Heroux and H. E. Hinteregger, Appl. Opt. 1, 701 (1962).

[15] S. F. Pellicori, Appl. Opt. 3, 361 (1964).

the illuminated area of the sample. In this calculation it is assumed that the intensity is uniform over the cross section of the beam. This was tested by successively decreasing the beam dimensions and measuring the energy of the pulse. The results indicated that indeed the intensity was uniform for small-beam cross sections (about 0.5 cm^2). It should be stressed, however, that this test is inherently an averaging measurement and therefore cannot exclude the existence of "hot" or "cold" spots on the area of the beam arising from imperfections in the optical parts of the laser. Some calculations were carried out in order to investigate the effect of beam nonuniformities. It was found that while such nonuniformities cannot change the intensity dependence of the electron emission, the numerical coefficients in a relation like $J=bI^2$, for example, can be different from those calculated under the assumption of a uniform light beam.

The absolute value of the electron current emitted from the samples was determined by two methods: first, by using the known gain of the electron multiplier and second, for large enough currents, by measuring them directly without the use of the electron multiplier.

The shape of the electron pulse is very important because it depends on the nature of the process that results in electron emission. For example, if the intensity dependence of the electric current is $i=aI^n$, where $I=I_p e^{-t^2/\Delta^2}$, then the electron pulse is also Gaussian $i=i_p e^{(-t^2/\Delta'^2)}$ with $\Delta'=\Delta/\sqrt{n}$. Therefore, much information may be obtained from the shape and duration of the electron pulses. For this reason, special care was taken to keep the reaction time of the measuring circuits as small as possible. Finally, the limiting factor was the 7-nsec rise time of the 547 Tektronix oscilloscope.

The sensitivity of the detection system, i.e., the combination of the electron multiplier and the oscilloscope, was 10^{-9}-Å peak current ($\approx$200 electrons per pulse) with a signal-to-noise ratio of 10.

For intensities up to the highest ($\approx$15 MW/cm^2) used in these measurements only electron emission was observed. Negative or positive ions were never observed.

All measurements were made at room temperature.

1. *Stainless Steel*

The stainless-steel mirrors were polished mechanically.[16] Before being installed in the photoelectric cell they were cleaned with acetone and alcohol.

Figure 4 shows the dependence of the electron current emitted from stainless steel on the incident laser intensity for the case of the 6943 and 10 600 Å radiations. These plots are the results of several series of measurements. It is not possible to draw a single straight line through the experimental points. However, if one draws a sort of average straight line, its slope is close to 7. It is very important to notice in Fig. 4 that both radiations give very similar results.

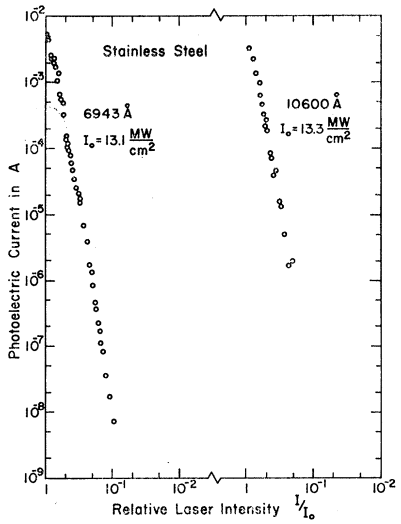

FIG. 4. Photoelectric current from stainless steel versus relative intensity of the 6943 and 10 600 Å laser radiations.

The results for the 3472 Å radiation are shown in Fig. 5. The experimental points fit a straight line with slope 2, indicating a second-order process.

Electron pulses resulting from the three radiations are shown in Figs. 3(d)–3(f). They were very reproducible. In the case of the 3472 Å radiation, the electron pulse is

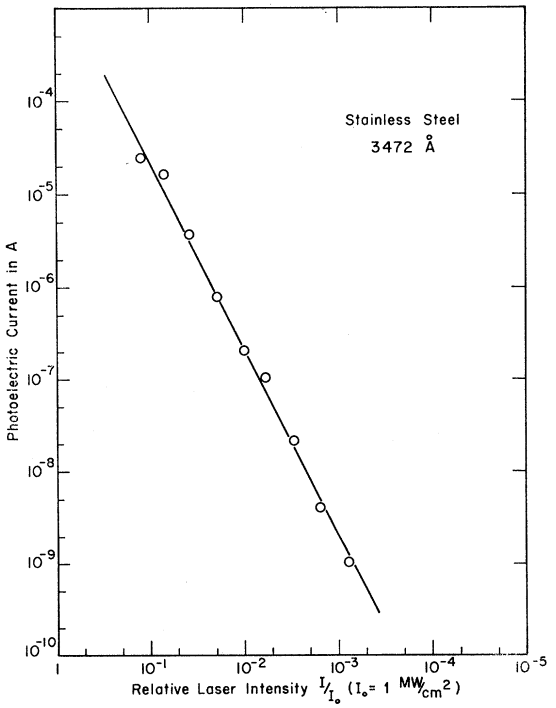

FIG. 5. Photoelectric current from stainless steel versus relative intensity of the 3472 Å laser radiation.

[16] The mirrors were polished by Mrs. Newton of the Crystallographic Laboratory of Cornell University.

approximately Gaussian with duration of about 20 nsec. Since the light-pulse duration is about 27 nsec, $\Delta^2/\Delta'^2 \sim 2$, a further indication of a second-order process.

2. Au[12]

The Au films (several thousand Å thick) were evaporated in an external evaporation chamber and were transferred into the photoelectric cell and under vacuum within 3 min after evaporation. Only a very slight degree of contamination of the Au films is expected during the short exposure to the atmosphere. Moreover, the Au films were probably somewhat cleaned and annealed inside the cell in allowing the full intensity of the 6943 Å radiation to hit them. Experiments in the past[5] and conclusions drawn from this experiment (Sec. V) show that surface heating to very high temperatures results when light intensities of the order of several MW/cm² are incident on a metal surface.

Figure 6 shows the electron current from Au as a function of the 6943 Å radiation. The datum points are the results of measurements on two different Au films. It is evident from Fig. 6 that the electrons originate in two distinct processes for two different intensity ranges. For intensities higher than about 1 MW/cm² the current is as strongly dependent on the light intensity as that from stainless steel for the 6943 and 10 600 Å radiations, while at lower intensities, the experimental points fit a straight line of slope 3, i.e., the current here is given by $i=bI^3$, a third-order process. The shape and duration of the electron pulse [Fig. 3(c)] is also consistent with a third-order process.

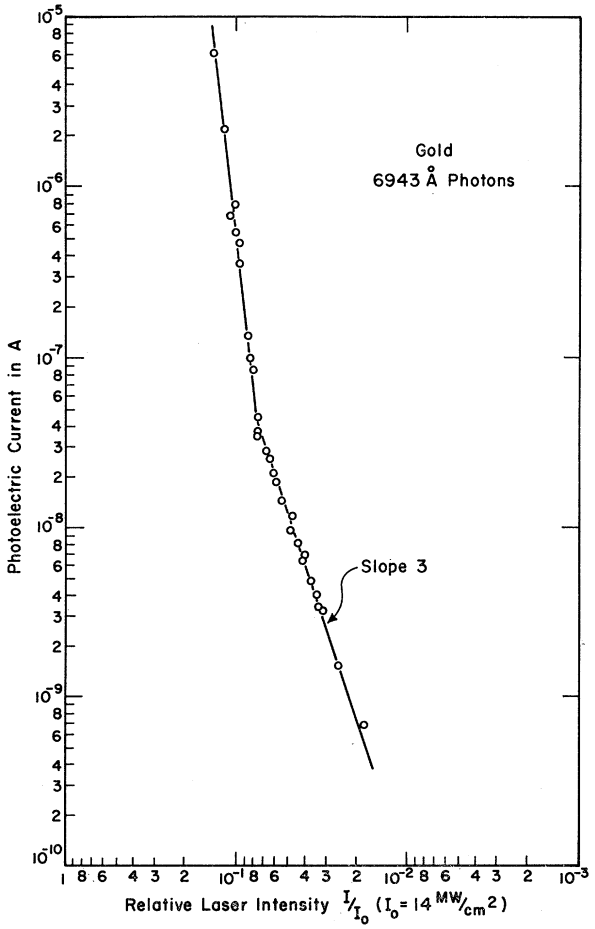

FIG. 6. Photoelectric current from Au versus relative intensity of the 6943 Å laser radiation. The light-beam diameter was 4.6 mm.

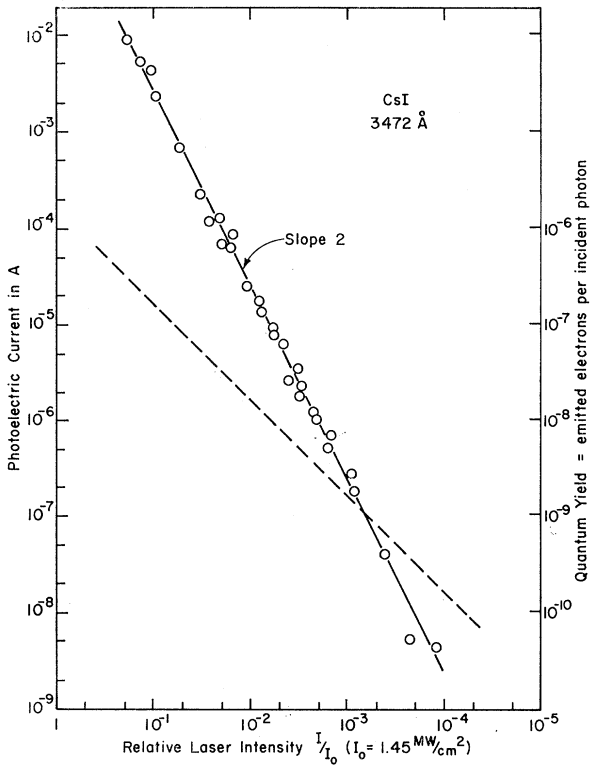

FIG. 7. Photoelectric current from CsI evaporated films versus relative intensity of the 3472 Å laser radiation (solid line). The light-beam diameter was 6 mm. The quantum yield is also plotted as a function of the light intensity (dotted line).

In the case of the 3472 Å radiation the current from Au showed a square-law dependence on the intensity[12] indicating a second-order process.

3. Alkali Halides

Among the alkali halides, CsI, KI, and KCl were chosen for study. At room temperature CsI and KI have a one-photon photoelectric-emission threshold of about 6.2 and 7 eV, respectively; they are therefore candidates for a two-photon photoelectric effect with the 3472 Å (3.57 eV) radiation. KCl, on the other hand, has a one-photon threshold at about 8 eV, so that a two-photon effect with this radiation was not expected, contrary to results.

The three alkali halides were studied in the form, first, of thin films evaporated on the stainless-steel mirror. From all of them, the 3472 Å radiation resulted in an electron-emission current which was proportional to the square of the light intensity over seven orders of magnitude of the photocurrent (Figs. 7–9).

The effect of the 6943 Å radiation was also investigated. At low-light intensities, films evaporated outside the photoelectric cell and then transferred into the cell exhibited an electron current which depended linearly on the intensity, indicating a one-photon effect (Fig. 10) in spite of the fact that pure alkali halides do not absorb light in the 6943 Å range. At higher intensities, the signal became very strongly intensity dependent, as it did for stainless steel and Au (Figs. 4 and 6), but it was highly irreproducible from pulse to pulse, and the

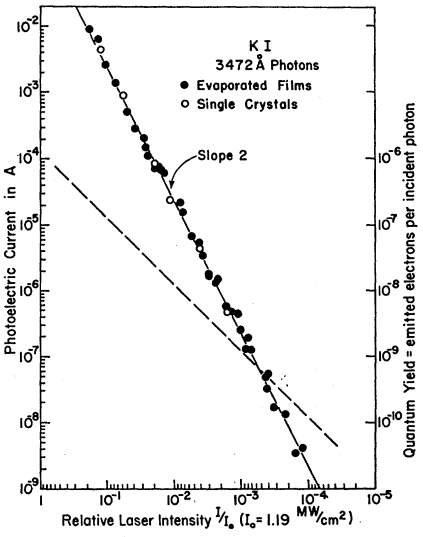

FIG. 8. Photoelectric current from KI versus relative intensity of the 3472 Å laser radiation (solid line). The beam diameter was 6 mm. The quantum yield is also plotted as a function of light intensity (dotted line).

electron pulses were wide and irregular. Finally, at the highest laser intensities the films were destroyed, as was observed visually. On the other hand, films evaporated inside the photoelectric cell did not show a consistent behavior to the 6943 Å radiation. Some of them exhibited the linear intensity dependence of the electron emission while others did not, even after exposure to the atmospheric air. At high intensities all films showed the strongly intensity-dependent signal and were destroyed at the highest intensities.

In trying to understand further the behavior of the alkali halides, the measurements were extended to single crystals, both KI and KCl being studied. The crystals were cleaved outside the cell and mounted onto the stainless-steel mirror. Special precautions were taken to block the escape of electrons liberated from the stainless-steel mirror when light passing through

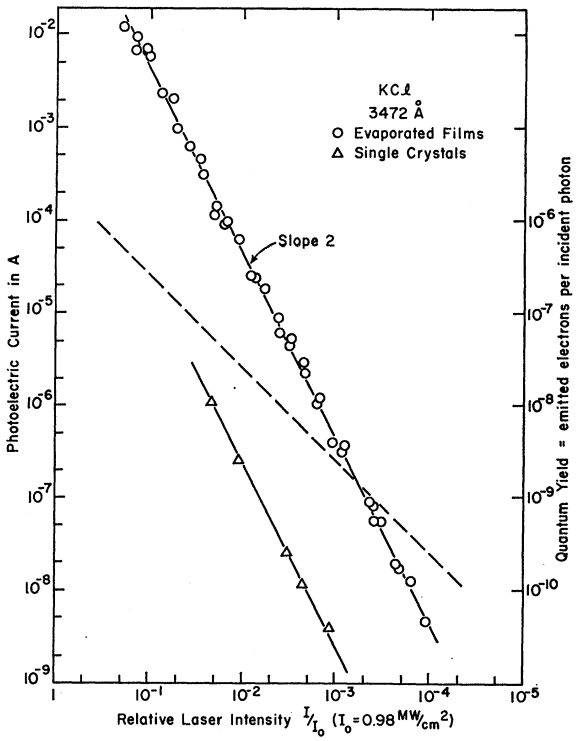

FIG. 9. Photoelectric current from KCl versus relative intensity of the 3472 Å laser radiation (solid lines). The beam diameter was 6 mm. The quantum yield is also plotted as a function of the light intensity (dotted line).

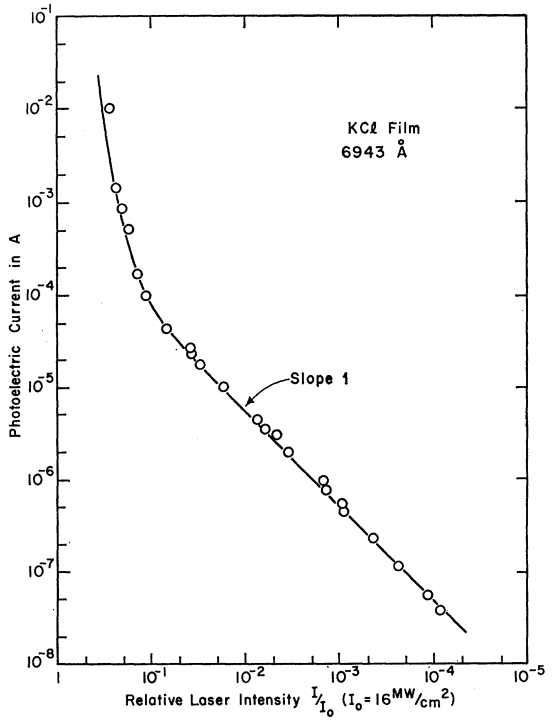

FIG. 10. Photoelectric current from KCl evaporated films versus relative intensity of the 6943 Å laser radiation.

the crystal was incident on the mirror. Results on the single crystals for the 3472 Å radiation are shown in Figs. 8 and 9. On both KI and KCl the electron-emission current exhibited a square dependence on the light intensity. For KI the magnitude of the effect was precisely the same as that observed on evaporated KI films. In KCl single crystals, however, the effect was more than two orders of magnitude weaker than that found on evaporated KCl films.

The effect of the 6943 Å radiation on single alkali-halide crystals was also explored. A KCl crystal 2 mm thick mounted on the mirror was examined. The electron emission was extremely small, about 5×10^{-9} A at 5 MW/cm^2, an intensity for which the evaporated alkali-halide films were destroyed.

B. Energy Distribution of Emitted Electrons

The energy distribution of the emitted electrons was measured using the planar and spherical analyzers described in Sec. II. The retarding voltage was changed in steps of 0.1–0.05 V.

The planar analyzer was used in studying the electron emission from the metals under the influence of the 6943 Å radiation. As described in Sec. III A, this electron emission depends very strongly on the light intensity. Because of the existing knowledge on the electron emission from metals (Sec. I), one is inclined to interpret this emission as thermionic rather than as a seven- or eight-photon photoelectric effect. However, this is not a sufficient reason to dismiss the possibility of a many-photon photoelectric effect, especially in view of some recent claims of a five-photon photoconductivity effect.[17] There is, nevertheless, a unique test in differentiating between thermionic and photoelectric emission: this rests in measurements of the normal energy distribution of the emitted electrons. If the electrons are due to thermionic emission their normal to the emitting surface energy distribution should be exponential.[18] This normal energy distribution was measured with the planar analyzer for stainless steel and Au.

Figure 11 shows some results on stainless steel. The retardation curves have been normalized to the saturation current. Each experimental point is the average of at least two measurements (two laser shots). It is evident that for the 6943 Å radiation the experimental points for retarding voltages fit a straight line, supporting the thermionic origin of the electrons. For accelerating voltages the current shows saturation. To further ascertain the thermionic origin of these electrons, the planar analyzer was used in carrying out retardation measurements on stainless steel irradiated by the 3472-Å radiation, which presumably produced a two-photon

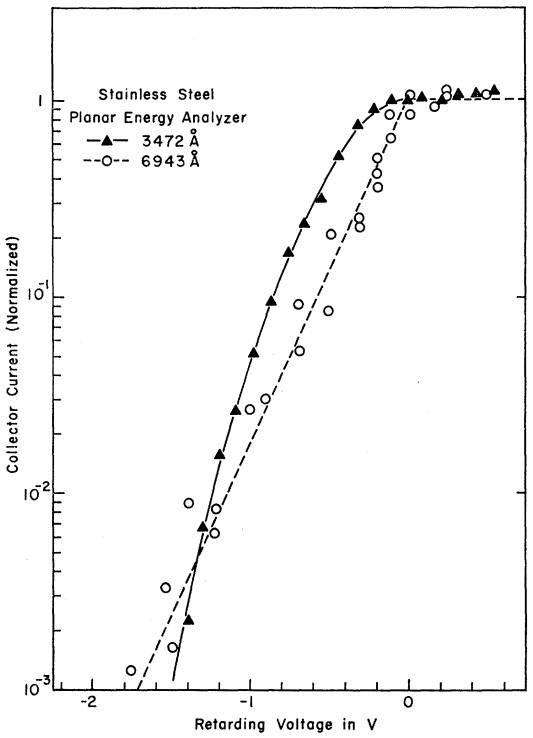

FIG. 11. Collector current versus retarding voltage for stainless steel for the 6943 and 3472 Å laser radiations (planar analyzer).

photoelectric effect (Fig. 5); the retardation curve of photoelectrons is expected to be very different from that of thermionic electrons. As seen in Fig. 11, there is a pronounced difference between the two retardation curves showing the different origin of the electrons in the two cases.

The measurement of the normal energy distribution of thermionic electrons is of special interest since the slope of the retardation curve gives the temperature of the emitting solid, as will be discussed later. The retardation curve in Fig. 11 for the 6943 Å radiation was taken for a laser intensity of 5.9 MW/cm^2 and the saturation current was 6×10^{-4} A.

Similar measurements were made on Au with similar results.

In the case of the 3472 Å radiation, all five solids exhibited a square-intensity–dependent electron emission. Thermionic emission was not observed for this light at the intensities employed here (less than 1 MW/cm^2). In such a case one is interested in the total energy distribution of the emitted electrons; it was measured with the spherical energy analyzer. As an example, the retardation curve for KI is presented in Fig. 12. Again each experimental point is the average of at least two laser shots. The retardation curves were measured more than once with a very high degree of reproducibility. Differentiation of these curves furnishes the electron energy distributions shown in Fig. 13.

[17] V. Dneprouskii, D. Klyshko, and A. Penin, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 3, 385 (1966) [English transl.: Soviet Phys.—JETP Letters 3, 251 (1966).

[18] A. J. Dekker, *Solid State Physics* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960), pp. 221-222.

Because of the high potential differences between the various electrodes of the energy analyzer, deviation from perfect spherical geometry may result in an appreciable distortion of the energy distribution curves. To investigate this problem, the normal to the surface energy distributions of the electrons emitted from stainless steel and KI were measured with the planar analyzer. If $f(E)$ is the total energy distribution and E_0 the maximum electron energy, then the collector current of the planar analyzer at the retarding voltage E_R is

$$I(E_R)=I_0\int_{E_R}^{E_0} f(E)\left(\int_{\cos\theta=1}^{\cos\theta=(E_R/E)1/2} h(\theta)\sin\theta d\theta\right)dE,$$

where $h(\theta)$ is the angular distribution of the electrons and θ is the angle between the initial velocity of an electron and the normal to the cathode surface.

From the measured function $f(E)$ the normal to the surface energy distribution was calculated from the above integral for three different angular distributions: (i) $h(\theta)=1$, isotropic; (ii) anisotropic, $h(\theta)=\cos\theta$ (forward emission); and (iii) $h(\theta)=\sin^2\theta$ (forward emission is zero). These were compared with the measured normal energy distributions (planar analyzer). It was found that the isotropic distribution resulted in a very good agreement between calculated and measured distributions indicating that the spherical analyzer is functioning correctly and the angular distribution is closely isotropic.

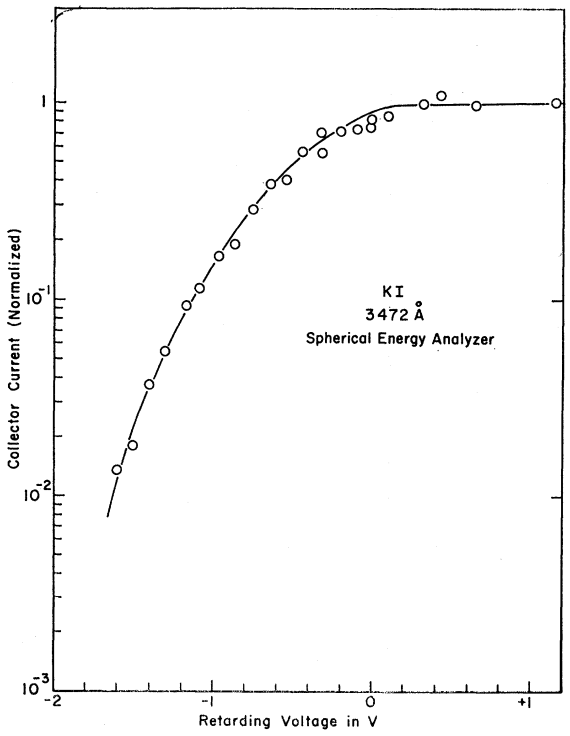

FIG. 12. Collector current versus retarding voltage for KI for the 3472 Å laser radiation (spherical analyzer).

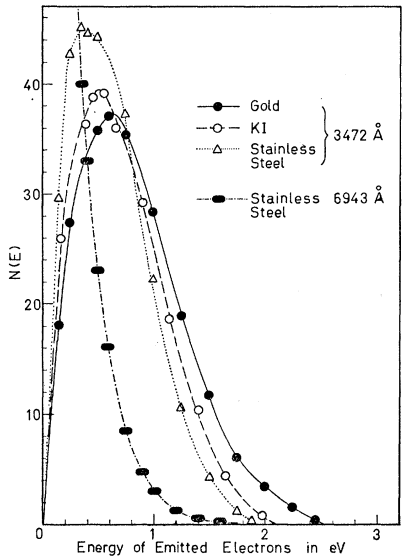

FIG. 13. Energy distribution of photoelectrons emitted from Au, KI, and stainless steel.

The effect of the laser intensity on the electron energy distribution was also studied: (1) For a given set of voltages on the electrodes of the energy analyzers the current was measured as a function of the laser intensity. In all cases, the intensity dependences obtained in Sec. III A were reproduced. (2) Retardation curves were obtained for more than one intensity. For the 3472 Å radiation (photoelectric effects) the retardation curves for different intensities, when shifted vertically (semilogarithmic plots), coincided. For the 6943 Å radiation in stainless steel (thermionic effect) the slope of the straight line (Fig. 11) depended on the intensity in the correct manner, i.e., larger at lower intensities (lower temperatures).

C. Two-Photon Photoelectric Spectroscopy

The results of the measurements in Sec. III A indicated that it might be possible to perform two-photon photoelectric spectroscopy in KI and CsI using a laser beam and a variable-wavelength incoherent light source.[19] In these measurements only the 6943 Å laser radiation could be used, since the 3472 Å radiation resulted in a second-order electron emission by itself.

The incoherent light source was an EG&G FX42A-3 flash lamp which gave light pulses of about 50-μsec duration. The light from the flash lamp was passed through a Bausch & Lomb Model No. 33-86-40 grating monochromator with 1-mm slits (resolution about 33 Å) and then focused on the stainless-steel mirror. The two pairs of windows of the photoelectric cell were used for the passage of the two light beams. The two light pulses were synchronized so that the short laser pulse coincided with the peak of the long uv light pulse.

[19] E. M. Logothetis, Phys. Rev. Letters **19**, 1471 (1967).

Thin KI and CsI films evaporated on the stainless-steel mirror inside the photoelectric cell were investigated. The laser intensity was kept at about 0.1 MW/cm² in order to avoid electron emission from the 6943 Å radiation alone.

When the laser and the uv beams were incident on a KI film an electron emission pulse was observed with the following characteristics: (1) The shape and duration of the pulse was the same as that of the laser pulse; (2) this electron emission was observed only for uv wavelengths shorter than about 250 mμ; (3) spatial coincidence of the two light beams on the KI film was required for electron emission; (4) temporal coincidence of the two light pulses was not necessary; in particular, the same electron pulse was not only observed when both light pulses coincided in time but also when the laser pulse alone was incident on the KI film, provided that previously the uv pulse had been allowed to be incident on the film.

The last experimental fact clearly shows that this electron emission from KI is not a two-photon photoelectric effect. It seems rather that the uv light "activates" the KI film, and that the laser light subsequently causes a (one-photon) electron emission. Subsequent laser pulses (alone, uv beam blocked) continued to give similar electron pulses, but with a constantly decreasing amplitude. It was found that this "deactivation" of the KI film was not a function of time but rather of the number of laser pulses. In fact, the amplitude of the electron pulses was roughly an exponential function of the number of laser shots with a "decay constant" the number of photons per laser pulse (about 10^{16} photons).

The situation was different in CsI. When both light beams were incident on a CsI film an electron-emission pulse was observed with the following characteristics: (1) The shape and duration were the same as the laser pulse; (2) spatial and *temporal* coincidence of the two light beams on the CsI was required for the electron emission to occur; (3) this electron emission was observed for uv wavelengths shorter than about 270 mμ; (4) the signal was proportional to the laser intensity I_L and to the uv intensity I_{uv}. These characteristics are exactly what one expects from a two-photon photoelectric effect. The peculiar effect observed in KI was almost absent in CsI (it accounted for only 5% of the total electron emission).

Figure 14 shows the relative two-photon quantum yield (emitted electrons per incident uv photon) as a function of the total (uv plus laser) photon energy. The quantum yield was obtained by dividing the electron current at a given total photon energy by the photon flux of the uv light corresponding to this total photon energy. The relative uv light intensity was measured with a 7664 DuMount photomultiplier, corrected for the spectral response of the photocathode.

Four different films several thousand Å thick were studied with very reproducible results.

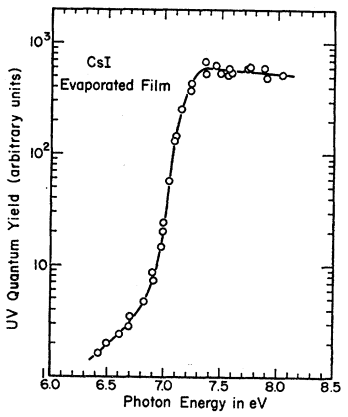

FIG. 14. Two-photon quantum yield of CsI versus total (laser plus uv) photon energy. Laser intensity = 8×10^{-2} MW/cm².

An attempt was made to measure the absolute quantum yield of the two-photon photoelectric effect in CsI, although an accurate value was not expected to be obtained because of difficulties in the geometry of the system. This was accomplished by measuring the absolute intensity of the variable light source at one wavelength (550 *mμ*) with an SD-100 photodiode. From this result and the relative intensity distribution of the uv source, the absolute quantum yield of the electron emission was calculated to be about 10^{-4} electrons per uv photon at 7.14 eV for a laser intensity of 0.08 MW/cm².

An attempt was made to perform similar two-photon spectroscopy in the metals, but no electron emission was observed.

IV. DISCUSSION

The electron emission from Au, stainless steel, KI, CsI, and KCl for laser radiations of 1.17-, 1.29-, and 3.57-eV photon energy at intensities lower than about 15 MW/cm² can be explained in terms of two fundamental processes: thermionic emission and many-photon photoelectric effects. However, several experimental results cannot be definitely explained and require further experimental and theoretical work.

A. Thermionic Emission

The high level and very strongly intensity-dependent segment of the electron emission from the solids investigated here with the 6943- and 10 600-Å laser radiations (Figs. 4 and 6) can definitely be identified as thermionic emission. This is in agreement with existing understanding of laser-induced electron emission from metals and may indeed be characteristic of all solids under such circumstances. A seven- or eight-photon photoelectric effect, as might be suggested from the measured intensity dependence of the emission current (which in fact is not exactly either seventh or eighth power) seems very unlikely. The probability of such an

effect should be extremely small,[20] very many orders of magnitude lower than the one observed. On the other hand, a photoelectric effect is selective in the sense that it depends on the photon energy and the band-structure characteristics of the solid. The measurements here, however, have established that both metals studied (with different band structures) exhibit the same dependence on intensity of the electron emission. In addition, this emission does not depend on the photon energy of the 6943 and 10 600 Å radiations (Fig. 4).

The most conclusive evidence for the thermionic origin of the emission lies in the results of the electron energy distribution measurements. The normal to the surface velocity distribution of thermionic electrons should be Maxwellian[18] with the collected current as a function of retarding voltage V_R given by

$$I(V_R)=I_0e^{-V_R/kT}.$$

The results shown in Fig. 11 clearly show such a functional relationship. In addition, at higher incident light intensities the experimental slopes of such retardation curves decrease as expected since the temperature of the solid is increased (Sec. III).

From the data of Fig. 11 the surface temperature of the stainless steel was calculated to be 2500±200°C at a laser intensity of 5.9 MW/cm², close to that found by Ready[5] in W under similar conditions. It is, however, near or a little higher than the melting point of stainless steel. From a rough measurement of the absolute value of the emitted current, the work function was calculated from the Richardson relation to be 6 eV, which seems rather high for stainless steel.[21] Many reasons may account for such discrepancies, i.e., uncertainties in the value of the coefficient A in the Richardson relation and in the values of measured current density and the influence of possible beam nonuniformities which may become very important for the strongly intensity-dependent electron emission.

The rest of the experimental observations pertinent to this part of the electron emission are also consistent with the interpretation of the effect as thermionic emission. The shape of the electron emission pulse [Fig. 3(d)], especially the existence of a relatively long tail, is in agreement with what one intuitively expects from a heating effect and with the theoretical calculations of Ready.[5] The alkali halides here do not absorb the 6943 Å radiation and, therefore, a heating effect should not result. Indeed, a single KCl crystal 2 mm thick did not emit any electrons with this radiation. In the case of thin alkali-halide films at very high laser intensities (>1 MW/cm²) evaporation and electron emission occurs as a secondary effect, the primary effect being that of heating the stainless-steel substrate. One should be reminded that the melting point of alkali halides is in the range of 700–900°C.

No attempt was made to investigate the thermionic effect further, since this work was oriented more toward photoelectric effects, and since thermionic emission has been investigated in great detail elsewhere.[7] It is sufficient for the purpose of these experiments here to have established the part of the electron emission discussed above as thermionic emission.

B. Many-Photon Photoelectric Effects

The solids studied here were chosen because their band-structure characteristics are such that a given laser radiation should not cause the same many-photon photoelectric effect in all of them. In this way, one should be able to give a definite interpretation to the electron emission.

Table I gives for the five solids the band-structure characteristics pertinent to the photoelectric effect and the order of the many-photon photoelectric effect that might be expected for each solid and laser radiation. Those with a circle are the processes that were observed.

The 10 600-Å radiation did not give any of the possible photoelectric effects in any of the materials studied. The same is true of the 6943 Å radiation except in the case of Au (Fig. 6) where a third-order process was observed. It would take at least a fourth-order process to produce photoelectrons from such photons in the other materials. It is therefore not surprising that nothing was seen in them, for the probability of a four-photon effect should be very small. A comparison between the two-photon and three-photon photoelectric effects (see Sec. IVC1) suggests that the constant d in a relation $J=dI^4$ should be smaller than 10^{-11} (A/cm²)/(MW/cm²)⁴, making the observation of a fourth-order effect impossible under the present experimental conditions.

1. *Theoretical Considerations*

Very little theoretical work has been done on the two-photon photoelectric effect. This is understandable, since such calculations involve, in addition to the initial and final electronic states, an intermediate state: Even if the complete band structure of a solid is known, the

TABLE I. Order of the many-photon photoelectric effects expected from the five solids and the three laser radiations. Those with a circle are the processes that were observed in this experiment.

	W = Work function		E = Valence-band–vacuum-level energy difference		
Laser	Au $W=4.8$ eV	Stainless steel $W=5$ eV	CsI $E=6.1$ eV	KI $E=7.0$ eV	KCl $E=8.0$ eV
10 600 Å 1.17 eV	5	5	6	6 or 7	7 or 8
6943 Å 1.786 eV	③	3 or 4	4	4	5
3472 Å 3.57 eV	②	②	②	②	3

[20] Compare the magnitudes of the two- and three-photon effects which were observed here and are discussed later.

[21] In fact a (photoelectric) work function of 5.1 eV was found from the energy distribution of the electrons emitted from stainless steel under the influence of the 3472 Å radiation.

task of calculating the two-photon absorption and from that the photoelectric current is very complicated. It should be mentioned that only recently[22] has quantitative information been obtained from the much simpler one-photon photoelectric effect.

Smith[23] and Adawi[24] have calculated the two-photon–surface photoelectric effect in metals, but their results are not applicable here since low-energy excitations very close to the work function of the metal are considered in these calculations. At the high-energy excitations involved here (≈ 7 eV), however, the volume photoelectric effect dominates. Following Fan's treatment[25] of the one-photon effect, Bloch[26] treated the two-photon photoelectric effect by a first-order perturbation calculation of the A^2 term of the perturbation Hamiltonian $\mathcal{H}'=-e\cdot\mathbf{A}\cdot\mathbf{p}/m+e^2\cdot A^2/2m$. The $\mathbf{A}\cdot\mathbf{p}$ term, however, when treated in a second-order perturbation calculation, may give a larger contribution to the two-photon probability; Teich and Wolga[11] have recently made a calculation using this term.

In the following, some results will be presented of an attempt to calculate the two- and three-photon photoelectric effects.

If α_m is the m-photon absorption constant then the m-photon photoelectric current density is

$$J_m=e\int_0^\infty I(x)p(x,E)\alpha_m dx,$$

where $I(x)$ is the light intensity at x, and $p(x,E)$ is the escape probability of an electron of energy E generated at a depth x in the solid.

a. Two-photon photoelectric effect. If $|j\rangle$, $|f\rangle$, and $|i\rangle$ are the initial, final, and intermediate electron states of a solid involved in a two-photon (of frequency ω_1 and ω_2) transition, the transition probability (using standard second-order perturbation theory for the term $\mathbf{A}\cdot\mathbf{p}$) is

$$W_f=\frac{h\pi}{2\epsilon_0^2\omega_1\omega_2\zeta_1^2\zeta_2^2}\frac{n_1}{V}\frac{n_2}{V}\delta(E_{fj}-h\omega_1-h\omega_2)\times\left|\sum_i\left(\frac{H_{fi}^{(1)}H_{ij}^{(2)}}{E_{ij}-h\omega_2}+\frac{H_{fi}^{(2)}H_{ij}^{(1)}}{E_{ij}-h\omega_1}\right)\right|^2, \quad (1)$$

where

$$H_{fi}^{(l)}=\langle f|-(e/m)[\exp(i\mathbf{K}_l\cdot\mathbf{r})]\xi_l\cdot\mathbf{p}|i\rangle,$$

$\mathbf{K}_l$ and ξ_l ($l=1, 2$) being the wave vector and polarization unit vector of lights 1 and 2, ζ_l the index of refraction at frequency ω_l, n_1 and n_2 the number of photons of frequency ω_1 and ω_2, respectively, and V the volume.

The total transition probability per unit time and unit volume from all possible initial states $|j\rangle$ to all possible final states $|f\rangle$ of the solid is then

$$W_2=\int W_f\frac{2}{(2\pi)^3}d\mathbf{k}. \quad (2)$$

If $\alpha_2(\omega_2)$ is the absorption constant for photons ω_2 in the presence of photons ω_1, then in the dipole approximation

$$\alpha_2(\omega_2)=\frac{h\pi e^4}{2\epsilon_0^2\omega_1\omega_2 cm^4\zeta_1^2\zeta_2^2}\frac{n_1}{V}\int\frac{2}{(2\pi)^3}d\mathbf{k}\delta(E_{fj}-h\omega_1-h\omega_2)\times\left|\sum\left(\frac{p_{fi}^{(1)}p_{ij}^{(2)}}{E_{ij}-h\omega_2}+\frac{p_{fi}^{(2)}p_{ij}^{(1)}}{E_{ij}-h\omega_1}\right)\right|^2, \quad (3)$$

where

$$p_{fi}^{(l)}=\xi_l\cdot\mathbf{p}_{fi},\quad l=1, 2.$$

To make further progress one has to consider a specific model. In the case of insulators the simplest model is the one shown in Fig. 15. The filled valence band v is taken as the initial state, the usual conduction band c as the intermediate state, and a second conduction band l with its bottom coinciding with the vacuum level as the final state. If all three bands are assumed to be parabolic, then the two-photon absorption constant is the same as that calculated by Braunstein and Ockman.[27] In the case of only one light beam ($\omega_1=\omega_2$) one has

$$\alpha_2(\omega)=\frac{e^4E_aE_gf_{lc}f_{cv}}{4\pi\epsilon_0^2c^2h^3\omega^3m^{1/2}\zeta^2}\frac{(2h\omega-E_0)^{1/2}}{(E_a-h\omega)^2}I, \quad (4)$$

where $E_a=E_0-E_g$ is the electron affinity of the insulator and f_{ij} the oscillator strength for the ij transition. The photoelectric current density is then given by

$$J_2=\frac{e^5E_aE_gf_{lc}f_{cv}}{4\pi\epsilon_0^2c^2h^4\omega^4m^{1/2}\zeta^2}\frac{(2h\omega-E_0)^{1/2}}{(E_a-h\omega)^2}\times\int_0^\infty I^2(x)p(x,E)dx. \quad (5)$$

When one-photon absorption is not concurrent with the two-photon effect (metals are excluded therefore), and $p(x)=e^{-x/D}$, where D is the average escape depth

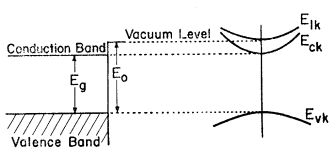

FIG. 15. Energy-band model used to calculate the two-photon photoelectric effect in semiconductors. E_g—band gap, E_0—work function.

[22] W. C. Spicer, Phys. Letters **20**, 326 (1966), and references therein.
[23] R. L. Smith, Phys. Rev. **128**, 2255 (1962).
[24] J. Adawi, Phys. Rev. **134**, A788 (1964).
[25] H. Y. Fan, Phys. Rev. **68**, 43 (1945).
[26] P. Bloch, J. Appl. Phys. **35**, 2052 (1964).
[27] R. Braunstein and N. Ockman, Phys. Rev. **134**, A499 (1964).

of the electrons, one finds that

$$J_2=\frac{e^5E_aE_gf_{lc}f_{cv}D}{4\pi\epsilon_0^2c^2h^4\omega^4m^{1/2}\zeta^2}\frac{(2h\omega-E_0)^{1/2}}{(E_a-h\omega)^2}I^2. \quad (6)$$

This equation is very similar in form to the one quoted in Ref. 9; presumably, the same model was used.

The applicability of the model is questionable for most solids, especially because of the assumption that the bottom of the final band coincides with the vacuum level.

In view of the complexity of the problem it will be satisfactory for this work to obtain an estimate of the two-photon photoelectric effect rather than an exact value. This can be done conveniently by expressing $\alpha_2(\omega)$ in terms of $\alpha_1(2\omega)$, the one-photon absorption constant at 2ω; this is given by

$$\alpha_1(2\omega)=\frac{\pi e^2hf_1'}{2\epsilon_0cm\zeta'}\int\frac{2}{(2\pi)^3}d\mathbf{k}\delta(E_{fj}-2h\omega), \quad (7)$$

where f_1' is the oscillator strength for the transition from initial state to final state separated by $2\hbar\omega$, and ζ' the index of refraction at 2ω. Equation (3) can be written as

$$\alpha_2(\omega)=\frac{\pi he^4}{2\epsilon_0^2c\omega^2m^4\zeta^3}\frac{n}{V}\left|\sum_i\frac{2p_{fi}p_{ij}}{E_{ij}-h\omega}\right|^2\times\int\frac{2}{(2\pi)^3}d\mathbf{k}\delta(E_{fj}-2h\omega). \quad (8)$$

Combining Eqs. (7) and (8) gives

$$\alpha_2(\omega)=\frac{\zeta'e^2}{\epsilon_0\omega^2m\zeta^3}\frac{n}{V}\frac{f_d}{f_1'}\alpha_1(2\omega), \quad (9)$$

where a pseudo-oscillator-strength[28] has been defined as

$$f_d=\frac{1}{m^2}\left|\sum_i\frac{2p_{fi}p_{ij}}{E_{ij}-h\omega}\right|^2. \quad (10)$$

In terms of intensity, $\alpha_2(\omega)$ becomes

$$\alpha_2(\omega)=\frac{e^2\zeta'}{\epsilon_0h\omega^3cm\zeta^3}\frac{f_d}{f_1'}\alpha_1(2\omega)I, \quad (11)$$

and the two-photon photoelectric current density is

$$J_2=\frac{e^3\zeta'D}{\epsilon_0h^2\omega^4cm\zeta^3}\frac{f_d}{f_1'}\alpha_1(2\omega)I. \quad (12)$$

b. Three-photon photoelectric effect. In this case only the $\mathbf{A}\cdot\mathbf{p}$ term can give a contribution when the perturbation is carried in third order. If $|j\rangle$ and $|f\rangle$ are the initial and final states and $|g\rangle$ and $|j\rangle$ the two intermediate states, then the transition probability is

$$W_{fj}=\frac{\pi h^2}{4\epsilon_0^3\omega_1\omega_2\omega_3\zeta_1^2\zeta_2^2\zeta_3^2}\frac{n_1n_2n_3}{V^3}\delta(E_{fj}-h\omega_1-h\omega_2-h\omega_3)\times\left|\sum_{ig}\left(\frac{H_{fg}^{(1)}H_{gi}^{(2)}H_{ij}^{(3)}}{(E_{gj}-h\omega_2-h\omega_3)(E_{ij}-h\omega_3)}+5\text{ similar terms}\right)\right|^2, \quad (13)$$

where

$$H_{fg}^{(a)}=\langle f|-(e/m)\mathbf{A}_a\cdot\mathbf{p}|g\rangle=-(e/m)\xi_a\cdot\mathbf{p}_{fg},\quad a=1,2,3. \quad (14)$$

In the case of a single laser beam ($\omega_1=\omega_2=\omega_3$), the transition probability W_3 per unit time per unit volume (involving the absorption of three photons) from all possible initial states $|j\rangle$ to all possible final states $|f\rangle$ of the solid is

$$W_3=\frac{9\pi h^2e^6}{\epsilon_0^3\omega^3m^6\zeta^6}\left(\frac{n}{V}\right)^3\int\frac{2}{(2\pi)^3}d\mathbf{k}\delta(E_{fj}-3h\omega)\times\left|\sum_{ig}\frac{p_{fg}p_{gi}p_{ij}}{(E_{gj}-2h\omega)(E_{ij}-h\omega)}\right|^2, \quad (15)$$

and the absorption constant is

$$\alpha_3(\omega)=\frac{9\pi e^6h^2}{\epsilon_0^3c\omega^3m^6\zeta^5}\left(\frac{n}{V}\right)^2\int\frac{2}{(2\pi)^3}d\mathbf{k}\delta(E_{fj}-3h\omega)\times\left|\sum_{ig}\frac{p_{fg}p_{gi}p_{ij}}{(E_{gj}-2h\omega)(E_{ij}-h\omega)}\right|^2. \quad (16)$$

To consider a four-band model for the solid would be unrealistic at this time. Thus, in order to obtain an order-of-magnitude estimate of α_3, this absorption constant is expressed again in terms of the one-photon absorption constant at $3\hbar\omega$. One then obtains

$$\alpha_3(\omega)=\frac{18e^4\zeta'}{\epsilon_0^2c^2h^2\omega^6m^2\zeta^3}\frac{f_d}{f_1'}\alpha_1(3\omega)I^2, \quad (17)$$

where a pseudo-oscillator-strength has been defined again as

$$f_d=\frac{h\omega}{m^3}\left|\sum_{ig}\frac{p_{fg}p_{gi}p_{ij}}{(E_{gj}-2h\omega)(E_{ij}-h\omega)}\right|^2. \quad (18)$$

The three-photon photoelectric current density is then given by

$$J_3=\frac{18e^5\zeta'D}{\epsilon_0^2c^2h^3\omega^7m^2\zeta^3}\frac{f_d}{f_1'}\alpha_1(3\omega)I^3. \quad (19)$$

2. Discussion of Experimental Results on Many-Photon Photoelectric Effects

For all the materials studied here, the 3472 Å radiation resulted in an emission current which depended on

[28] An order-of-magnitude calculation gives $f_d\approx1$.

the square of the laser intensity. The shape and duration of the photoelectric pulse is also consistent with a second-order process. A square-intensity dependence, however, does not necessarily mean that it is a true two-photon effect. There are other possibilities, among which probably the most important are: (a) generation in the material of second-harmonic radiation (7.14 eV), which subsequently causes a one-photon photoelectric effect; (b) an excited-state absorption process due to some kind of impurity or defect in the crystal, i.e., the electrons of such centers are first pumped to a (real) excited state and subsequently, during the lifetime of the excited state, absorb a second laser photon reaching a final state above the vacuum level.

The second-harmonic generation (SHG) can be excluded for the following reasons: (i) SHG is not possible in alkali halides since they have a center of symmetry; (ii) SHG due to plasma oscillations is possible in metals,[29] but the efficiency of conversion is of the order 10^{-5}, much smaller than the effects observed here; (iii) even if there were a SHG from the stainless-steel substrate, this could not cause the observed photoelectric effect in alkali halides which were evaporated on the mirror. The one-photon absorption constant of KI at 7.12 eV is about 5×10^5 cm^{-1}; therefore, in the case of a 1-mm-thick single crystal, the SHG photons leaving the stainless-steel substrate and entering the KI crystal would be absorbed within a few thousand Å and could not reach the exposed surface of the crystal. This implies that if SHG were a factor, there would be a difference in the magnitude of the photoelectric effect between thin KI films and single KI crystals, contrary to the experimental observations.

The case of defects and impurities is more complicated in the sense that these centers cannot be easily discounted as the origin of the observed photoelectric effects. If the concentration of such centers were of the order of 10^{15} cm^{-3}, they could cause an excited-state absorption which might result in a photoelectric emission with quantum yield of the same order of magnitude as the ones measured here.

There is, however, experimental evidence that the photoelectric effects here are true two-photon effects, except possibly in the case of KCl. It is known from one-photon experiments that the concentration of defects (vacancies, color centers, etc.) is larger in evaporated alkali-halide films than in single crystals. In addition, impurity atoms like oxygen may be introduced in the films during evaporation. It is expected, therefore, that if there is a defect or impurity excited-state absorption, this effect would be larger in films than in single crystals. It was found here that both single crystals and evaporated films of KCl exhibited a square-intensity–dependent current, but the quantum yield from films was more than two orders of magnitude larger than that from single crystals. In contrast, both types of KI samples showed a photoelectric effect with the same quantum yield. This suggests then that the effect is intrinsic in KI but possibly not in KCl. A supporting evidence for such an explanation is the behavior of thin alkali-halide films to the 6943 Å radiation. Some of them exhibited a linear-intensity–dependent photoelectric current (Fig. 10 for KCl), which may be explained as one-photon photoelectric effect from impurities or defects. In addition, the results of the attempt at two-photon photoelectric spectroscopy in KI also point to the existence of centers in evaporated films. Since, on the other hand, in all our materials except KCl the energy of two 3472 Å photons is larger than the vacuum-level–valence-band energy difference, it is concluded that the photoelectric effect observed in steel, Au, KI and CsI with the 3472 Å radiation is a true two-photon effect. The effect in KCl is probably not intrinsic, but is rather, related to structural defects or impurities.

The two-photon photoelectric effect may be expressed as $J=bI^2$, where b is a constant containing all physical information on the effect, i.e., the probability of two-photon absorption (of total energy 7.14 eV) and the electron-escape probability. From the present measurements the following values of b are found: 4.2×10^{-3}, 2.4×10^{-3}, 3.0×10^{-1}, and 3.2×10^{-1} (A/cm^2)/(MW/cm^2)^2 for stainless steel, Au, KI, and CsI, respectively. These values have not been corrected for reflections. The two-photon quantum yield (electrons per photon) is given by $\eta_2=3.6\times10^{-6}bI$, and has been plotted as a function of intensity in Figs. 7–9. In this relation for η_2, intensity I is in MW/cm^2, with b as stated above.

In comparing the experimental results with theoretical predictions one can compare either the photoelectric quantities (the constant b or the quantum yield η) or the absorption constant α_2. Both involve the same assumption about the escape probability of the photoelectrons. The comparison made here is in the absorption constant shown in Table II. The calculations were made for a laser intensity of 0.77 MW/cm^2. The second column gives α_2 as calculated from the three-parabolic-band model of Fig. 15. This model is completely unrealistic for the metals, so α_2 was not computed for Au and steel. The third column gives the values of α_2 calculated from Eq. (11). For an order-of-magnitude calculation, α_1 was taken to be 5×10^5 cm^{-1} for all solids. The fourth column gives the experimental values of α_2 calculated from the constants b.[30]

In view of the uncertainties and assumptions involved in the calculations, the agreement between experiment and theory is considered not bad. In the alkali halides the agreement is worse when the three-band model is

[29] F. Brown, R. Parks, and A. Sleeper, Phys. Rev. Letters **14**, 1029 (1965).

[30] In the case of metals the light beam is strongly attenuated with depth into the metal because of one-photon absorption. In this case, the two-photon absorption constant at the surface ($x=0$) for the incident intensity I is $\alpha_2=3.6\times10^{-6}(2\alpha_1+1/D)bI$, where α_1 is the one-photon absorption constant. For the alkali halides one still has $\alpha_2=3.6\times10^{-6}DbI$. Details of these and other similar calculations are contained in Ref. 13.

TABLE II. Many-photon photoelectric effects. Comparison between theory and experiment.

Solid	Theory Model 1 α_2 in cm^{-1}	Theory Model 2 α_2 in cm^{-1}	Experiment α_2 in cm^{-1}	Quantities used in calculating α_2 $I=0.77$ MW/cm^2
KI	1.4×10^{-3}	2.4×10^{2}	4.1×10^{-1}	$E_0=7$ eV $E_g=6$ eV $\alpha_1=5\times10^5$ cm^{-1}
CsI	2.2×10^{-4}	2.4×10^{-2}	4.2×10^{-1}	$E_0=6.3$ eV $E_g=6.2$ eV $\alpha_1=5\times10^5$ cm^{-1}
Au	...	2.4×10^{-2} 4.8×10^{-2}	2.2×10^{-2} 2.6×10^{-2}	$\alpha_1=5\times10^5$ cm^{-1} $\alpha_1=10^6$ cm^{-1} } $D=5\times10^{-7}$ cm
Stainless steel	...	2.4×10^{-2} 4.8×10^{-2}	3.6×10^{-2} 4.7×10^{-2}	$\alpha_1=5\times10^5$ cm^{-1} $\alpha_1=10^6$ cm^{-1} } $D=5\times10^{-7}$ cm
Au	...	$\alpha_3=1.4\times10^{-8}$	$\alpha_3=3.9\times10^{-7}$	

used, but examination of their band structure[31] shows that the use of this particular three-band model is really not justified.

In the case of Au, Bloch's formula[26] for the two-photon photoelectric effect as corrected by Teich and Wolga[11] was used to calculate the absorption constant. With the assumption that the oscillator strength is equal to 1, α_2 is found to be about 2×10^{-5} cm^{-1}, 3 orders of magnitude smaller than the experimental value. It is evident that much theoretical work on the two-photon photoelectric effect is necessary.

It is interesting to compare the results of the present work with those of other experiments on the two-photon photoelectric effect.

Teich and Wolga[11] investigated the two-photon photoelectric effect in Na using a GaAs laser (1.48 eV) and found a b value of 8×10^{-4} (A/cm^2)/(MW/cm^2)^2, which is of the same order of magnitude as the values n Au and steel measured here. Sonnenberg *et al.*[9] and Imamura *et al.*[11] performed similar measurements on Cs_3Sb and on Cs_3Sb and K_3Sb, respectively. They found b values in the range 8–4×10^{-1} (A/cm^2)/(MW/cm^2)^2 which compare well with the values measured here for the alkali halides.

The energy distributions of the emitted electrons are shown in Fig. 13. In the case of Au, the electron energy distribution is consistent with the band-structure characteristics of this material as obtained from one-photon experiments. Au has a photoelectric work function of 4.8 eV; thus, the maximum energy of the photoelectrons should be $2\hbar\omega-W=2.4$ eV. From Fig. 13 one obtains $E_{\max}=2.5$ eV. Such an agreement between one- and two-photon photoelectric effects is not completely unexpected, since in both effects the joint density of only the initial and final states is of importance; the density of intermediate states does not enter into the calculation. Therefore, provided that selection rules do not dictate otherwise, the same critical points in the density of states will determine the one- and two-photon effects.

The case of KI is more complicated. The maximum energy of the photoelectrons emitted from KI is about 2 eV, considerably larger than the difference between the energy of the two 3472-Å photons (7.2 eV) and the one-photon photoelectric threshold (7.0 eV). It should be noted, however, that most of the electrons have energy less than 0.8 eV and only 7% of them have energies higher than 1 eV. It is not possible to provide a definite explanation of this difference based solely on these experimental facts. In speculating, however, one may consider the following explanations: (i) There is a lowering of the vacuum level due to the absorption of impurity atoms on the surface of the KI films (the energy distributions were measured in films only). This, taken alone, is not a sufficient explanation because information from one-photon photoelectric studies of KI[32] suggests that the vacuum level in films cannot be lower than that of single crystals by more than 0.3 eV. (ii) These high-energy electrons may originate from valence band states higher in energy than the states involved in the one-photon effect. Current band-structure models of the alkali halides,[31] however, do not seem to substantiate such a conclusion. (iii) These high-energy electrons originate from impurity or defect centers. Such contributions to the one-photon photoelectric effect have been observed here (Fig. 10) and in other experiments.[33]

The results from KCl show a maximum electron energy of about 1.8 eV, where no photoelectric emission is even expected (photoelectric threshold is about 8.0 eV at room temperature and the two-photon energy is 7.2 eV). It is assumed, therefore, that the electrons originate from impurities or defects in the films.

In concluding, one may say that not all the electron-energy distributions are well understood and that further experimental work is needed in trying to under-

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[33] P. Petrescu, Phys. Status Solidi **29**, 333 (1968); **29**, K3 (1968).

stand the problems that arose from these measurements.

In Au the 6943 Å radiation resulted in an electron emission which followed a third-power dependence on the intensity (Fig. 6), strongly suggesting a three-photon photoelectric effect.[12,34] The work function of Au (4.8 eV) is much higher than the energy of two photons (3.57 eV), but lower than the energy of three laser photons (5.36 eV).

If J is the photoelectric current density, one may write $J=cI^3$, where c has a meaning similar to b in $J=bI^2$. From the data it was found $c=1\times10^{-7}$ $(A/cm^2)/(MW/cm^2)^3$. The quantum yield is given by $\eta_3=1.8\times10^{-6}cI^2$, where the intensity I is expressed in MW/cm^2, and η_3 in electrons/photon.

A very good approximate relation between η_3 and the three-photon absorption consistant α_3 (at the surface and therefore at the incident intensity I) is

$$\eta_3=\alpha_3/3\alpha_1+1/D.$$

Using the same values of α_1 and D as in the case of the two-photon effect, one obtains $\alpha_3=5\times10^{-7}$ cm^{-1} for an intensity $I=0.77$ MW/cm^2. From the theoretical formula derived [Eq. (17)], α_3 is found to be 1.5×10^{-8} cm^{-1}. In view of the assumptions involved in the calculations, the agreement between theory and experiment is considered fair.

It would have been very interesting to measure the energy distribution of these three-photon photoelectrons. Unfortunately, the signal was too small to allow such measurements.

In the two-photon photoelectric spectroscopy measurements (Fig. 14), it is obvious that in the case of KI the observed photoelectric emission is not a true two-photon effect since temporal coincidence of the 6943 Å and uv beams were not required. It is well known that irradiation at the first exciton peak of the alkali halides creates F centers and other centers.[35] It is therefore presumed that the initial uv pulse produces defect centers and the subsequent laser pulses cause photoelectric emission from these centers (by a one- or even two-photon effect). The resulting bleaching of these centers can account for the decrease of the electron emission from pulse to pulse.

In CsI the photoelectric emission exhibited all characteristics expected from a two-photon effect, especially the temporal coincidence of the uv and laser beams which was absent in the case of KI. It is concluded that this attempt at two-photon photoelectric spectroscopy was successful and that Fig. 14 does indeed show the two-photon photoelectric spectrum in the range 6–8.5 eV (for laser photon energy of 1.8 eV). The low-energy (<6.9 eV) component of the photoelectric emission correlates well with the two-photon absorption spectrum of Hopfield and Worlock[8]; it is suggested, therefore, that it is due to two-photon parity-forbidden transitions in the vicinity of the Γ point of the Brillouin zone. The high-energy component with a threshold at 6.9 eV is then attributed to parity-allowed two-photon transitions at some point of the Brillouin zone without inversion symmetry.

Because of experimental difficulties the quantum yield could not be measured accurately. An estimate is about 10^{-4} electrons/(incident photon) at 7.14-eV total photon energy for a 6943-Å laser intensity of 8×10^{-2} MW/cm^2. From the two-photon effect using the 3472-Å laser radiation, the quantum yield at 7.14 eV is calculated to be about 7×10^{-7} electrons/photon for a laser intensity equivalent to the ruby fundamental intensity of 8×10^{-2} MW/cm^2, i.e., a yield about 150 times smaller. The experimental uncertainty in the two values cannot account for more than a factor of 5 in this difference. The rest, a factor of about 30, seems to be real. A factor of 2 or more may be accounted for by the different statistical properties of the light beams[36] in the two experiments (incoherent uv beam versus coherent laser beams). So a factor of 10–15 still remains to be explained. Since different photon-energy light beams were used in the experiments (3.57+3.57 eV versus 1.79+5.35 eV), it is expected that the magnitude of the effect will be different in the two cases. Using the three-band model discussed previously, one expects a difference of a factor of 5. It is possible, therefore, that the factor of 10 to 15 may be fully accounted for when a more accurate model is used for the photoelectric effect in CsI.

V. CONCLUSIONS

The present study of electron emission from some solids has made it possible to differentiate between thermionic emission and many-photon photoelectric effects. The magnitude of the two- and three-photon effects observed here compare rather well with theoretical estimates, but existing detailed theoretical models predict appreciably smaller effects. More sophisticated theoretical calculations are therefore needed.

The success with the two-photon photoelectric spectroscopy in CsI may open a new way of obtaining additional information on the electronic properties of solids. This may be particularly true in the case of metals, in which two-photon absorption spectroscopy is not possible because of the simultaneous and much stronger one-photon absorption. However, in order to extract detailed information from such measurements rather advanced theoretical work is needed.

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