Two-Quantum Volume Photoelectric Effect in Sodium*

M. C. TEICH† AND G. J. WOLGA
Cornell University, Ithaca, New York 14850
(Received 15 February 1968)

Two-photon photoelectric emission has been observed from a freshly deposited sodium surface. The two-quantum yield for the process, $\Lambda(\lambda,T)$, was determined to be $\Lambda(8450\text{ Å}, 300°\text{K})\sim 8\times10^{-16}I_0$ A/W, where I_0 is the intensity of the incident radiation in W/cm². Previous work attributed the phenomenon to a surface effect. However, it now appears more likely that it arises from a volume effect. The two-quantum yields for various metals, semiconductors, and organic crystals are compared.

I. INTRODUCTION

WITH the development of the laser, double-quantum transitions of various types have been observed in the optical region of the electromagnetic spectrum. This paper reports the observation of double-quantum photoelectric emission from sodium metal.[1]

Several attempts have been made to experimentally observe the two-quantum photocurrent from a metal,[2,3] in order to establish the validity of a particular theoretical model,[2,4] but various experimental difficulties complicated the task. The effect was finally observed in sodium,[5] but the observations were made on a relatively thin surface which was not freshly deposited, and the magnitude of the double-quantum current was reduced below its true value for the bulk effect. It is not clear whether the observations cited in this earlier report were the result of a surface effect or of a volume effect from a thin film (in which the film thickness was much less than the photoelectron escape depth), although now it appears more likely that a volume effect was responsible for those results as well.

In this paper, we detail the observation of two-quantum photoelectric emission from a freshly deposited, relatively thick sodium surface of work function 2.3 eV, when irradiated by photons of energy 1.48 eV from a GaAs semiconductor injection laser. The two-quantum yield obtained from this surface is considerably larger than that reported previously.[5]

The effect is of second order, and is most easily observed in the absence of ordinary first-order, or single-quantum, photoemission. Double-quantum photoelectric emission therefore becomes important when $\frac{1}{2}e\varphi < h\nu < e\varphi$, where $h\nu$ is the photon energy and $e\varphi$ is the work function of the metal under consideration. A quantity suitable for describing the efficiency of double-quantum photoelectric emission is the "double-quantum yield," $\Lambda(\lambda,T)$ expressed in A/W.[6] Here, λ is the wavelength of the incident radiation and T is the temperature of the surface. Because a second-order effect is under consideration, Λ will be proportional to the intensity I_0 of the incident radiation. For double-quantum photoelectric emission from sodium metal, Λ has been experimentally found to be $\Lambda_{Na}(8450\text{ Å}, 300°\text{K})\sim 8\times10^{-16}I_0$ A/W, where I_0 is the intensity of the incident radiation at 8450 Å expressed in W/cm². The observed value is about 1000 times larger than the theoretically expected value calculated on the basis of the surface effect,[4] but it is of comparable magnitude with the experimental value for gold Λ_{Au} (3471 Å, 300°K)$\simeq 24\times10^{-16}I_0$ A/W recently obtained by Logothetis and Hartman.[7]

Double-quantum photoelectric emission has also been obtained in materials other than metals. Sonnenberg, Heffner, and Spicer[8] obtained two-quantum volume photoelectric emission from Cs_3Sb, a semiconductor. The source of radiation was a Nd-doped-glass laser which emits photons with an energy of 1.17 eV. The photoelectric threshold energy for the first-order effect in Cs_3Sb is about 2 eV, as it is in sodium metal. The observed double-quantum photoelectric yield from Cs_3Sb was Λ_{Cs_3Sb} (8450 Å, 300°K)$\simeq 1.1\times10^{-11}I_0$ A/W, where I_0 is the incident light intensity in W/cm². This result has been normalized to $\lambda=8450$ Å, so that it may be directly compared with the results obtained for sodium.[9] It is seen that $\Lambda_{Na}\sim 7\times10^{-5}\Lambda_{Cs_3Sb}$; the double-quantum yield from sodium is smaller than the double-quantum yield from Cs_3Sb, as in the case of single-quantum or ordinary photoelectric emission. In other work, Imamura *et al.*[10] have observed the energy

* Financial support for this study was provided by the Advanced Research Projects Agency through the Materials Science Center at Cornell University, Ithaca, N. Y.
† Present address: Columbia University, New York, N. Y. 10027.
[1] M. C. Teich, Ph.D. thesis, Cornell University, 1966 (unpublished).
[2] P. Bloch, J. Appl. Phys. **35**, 2052 (1964).
[3] H. C. Bowers, M.S. thesis, Cornell University, 1964 (unpublished).
[4] R. L. Smith, Phys. Rev. **128**, 2225 (1962).
[5] M. C. Teich, J. M. Schroeer, and G. J. Wolga, Phys. Rev. Letters **13**, 611 (1964).
[6] This quantity is called the efficiency, since it is very closely related to the number L of photoelectrons emitted per incident photon: $\Lambda=(e/h\nu)L$, where $h\nu/e$ is of the order of unity.
[7] E. M. Logothetis and P. L. Hartman, Phys. Rev. Letters **18**, 581 (1967).
[8] H. Sonnenberg, H. Heffner, and W. Spicer, Appl. Phys. Letters **5**, 95 (1964).
[9] The correction from 1.06-μm radiation [as used by Sonnenberg, Heffner, and Spicer (Ref. 8)] to 0.84 μm radiation was small. It was obtained by simply evaluating the equation for the two-photon volume photoelectric current density for a semiconductor j_v given by Jha (Ref. 8), for both 1.17 eV photons (1.06 μm) and 1.48 eV photons (0.84 μm). The following ratio was obtained: $j_v(Cs_3Sb, 1.48\text{ eV})/j_v(Cs_3Sb, 1.17\text{ eV})=0.55$.
[10] S. Imamura, F. Shiga, K. Kinoshita, and T. Suzuki, Phys. Rev. **166**, 322 (1968).

distribution of electrons emitted from a photocathode of Cs_3Sb undergoing double-quantum photoemission, and have measured the two-quantum yield of K_3Sb as well. Recently, Logothetis[11] used a laser in conjunction with a variable-frequency incoherent source to perform two-photon photoelectric spectroscopy in CsI.

In an experiment utilizing a Millikan oil-drop apparatus, Pope, Kallmann, and Giachino[12] have measured the double-quantum photoelectric emission from organic single crystals of anthracene, tetracene, and perylene. These authors used a 1000-W Hg-Xe incoherent light source, having its highest output intensity at 3650 Å. For anthracene, the experimentally determined value of double-quantum yield at this wavelength was Λ_{anthr} (3650 Å, 300°K)$\simeq 6\times10^{-8} I_0$A/W, where I_0 is expressed in W/cm^2. It is seen that $\Lambda_{\text{Na}}\sim10^{-8}\,\Lambda_{\text{anthr}}$; the large value in anthracene arising from the energy storage capability of the intermediate state. In spite of the large two-quantum yield for anthracene, the photocurrents measured were extremely small because of the low light power incident on each particle. With the authors' apparatus, currents $\sim10^{-20}$ A have been measured.

The two-quantum yield measurements available to date from various materials are compared in Table I. A clustering of the yield values is observed within each group (metals, semiconductors, aud organic single crystals), in analogy with observations for single-quantum photoemission. It has been shown that the double-quantum yields induced by thermal sources and multiple-mode lasers are expected to be approximately a factor of two greater than those induced by single-mode lasers operated well above threshold.[13] Thus the individual entries in the table may vary by a factor of 2 as a result of the different statistical nature of the inducing radiation.

It is noted that the two-quantum photoeffect is of particular interest because the two-quantum process occurs in the radiation-detecting device itself. In addition to information about the higher-order physical process occurring in the detector, an opportunity is available to gain information about the properties of the incident radiation field, a topic of considerable interest.[14] For a two-photon detector, the counting rate is expected to be proportional to a second-order correlation function,[13,15] while for the usual square-law detector, the counting rate is proportional to a first-order correlation function (and thus proportional to the intensity of the incident beam). An analysis has also been given[13] in which it is shown that the two-photon effect may be used as a self-integrating Hanbury Brown–Twiss-type photon correlation experiment by permitting two superimposed radiation beams to be incident on the detector, one of which is time-delayed with respect to the other.

TABLE I. Double-quantum yield $\Lambda(\lambda,T)$ for various materials. Λ is given in A/W when I_0 is expressed in W/cm^2. No correction has been made for the varying statistical nature of the different radiation sources, which could change an individual entry by a factor of 2.

	Material	λ	T	$\Lambda(\lambda,T)$
Metals	Sodium[a]	8450 Å	300°K	$8\times10^{-16}\,I_0$
	Gold[b]	3471 Å	300°K	$24\times10^{-16}\,I_0$
Semiconductors	Cs_3Sb[c]	10 600 Å	300°K	$2\times10^{-11}\,I_0$
	Cs_3Sb[d]	10 600 Å	300°K	$6\times10^{-11}\,I_0$
	K_3Sb[d]	6943 Å	300°K	$0.04\times10^{-11}\,I_0$
Organic single crystals	Anthracene[e]	3650 Å	300°K	$6\times10^{-8}\,I_0$
	Tetracene[f]	3650 Å	300°K	$(0.6\text{–}6)\times10^{-8}\,I_0$
	Perylene[f]	3650 Å	300°K	$(0.6\text{–}6)\times10^{-8}\,I_0$

[a] This work.
[b] Reference 7.
[c] Reference 8.
[d] Reference 10.
[e] Reference 12.
[f] M. Pope (private communication).

II. EXPERIMENT

A. Choice of Sodium

Sodium metal was chosen as the material to be investigated for the following reasons: (1) ample data is available on the photoelectric and other solid-state properties of sodium, (2) it is a simple metal with a spherical Fermi surface, which would minimize complications in a comparison of experimental results with a theoretical model, and (3) the work function (2.3 eV as determined by a Fowler plot) is ideal for the observation of two-photon photoemission using incident radiation at 8450 Å (1.48 eV). The work function is sufficiently low so that two photons may overcome the surface potential, and yet sufficiently high so that single-quantum photoemission from the Fermi tail[16] will not swamp the double-quantum photoemission.

B. Experimental Method

The apparatus used for the experimental measurement of the double-quantum photoelectric effect is shown in the block diagram of Fig. 1. The radiation source was a pulsed GaAs semiconductor injection laser operated at 77°K and emitting a peak radiation power of 400 mW at 8450 Å. A translation stage supporting a lens permitted the laser radiation to be focused onto a vapor-deposited sodium surface in a specially constructed photomultiplier tube. A photomultiplier was used rather than a simple phototube in order to gain the advantage of "noise-free" electron multiplication. The glass envelope containing the photomultiplier structure, as well as the dynode material and the

[11] E. M. Logothetis, Phys. Rev. Letters **19**, 1470 (1967).
[12] M. Pope, H. Kallmann, and J. Giachino, J. Chem. Phys. **42**, 2540 (1965).
[13] M. C. Teich and G. J. Wolga, Phys. Rev. Letters **16**, 625 (1966).
[14] L. Mandel and E. Wolf, Rev. Mod. Phys. **37**, 231 (1965).
[15] R. J. Glauber, Phys. Rev. **130**, 2529 (1963); **131**, 2766 (1963); U. M. Titulaer and R. J. Glauber, *ibid.* **140**, B676 (1965).
[16] M. C. Teich and G. J. Wolga, J. Opt. Soc. Am. **57**, 542 (1967).

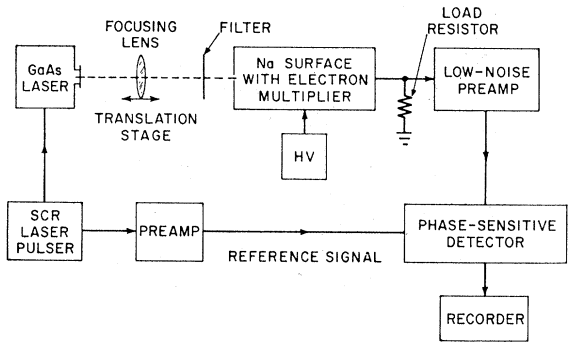

FIG. 1. Block diagram of experimental apparatus.

structure itself were the same as those used in a conventional Dumont type 6911 tube. In our apparatus, however, no translucent photocathode was present. Instead, sodium metal was deposited on one element of the structure, that which is generally used as the first dynode in the standard tube. The cathode substrate material was grade-A nickel.

The photomultiplier assembly contained a "thermal generator" so that sodium could be deposited on the cathode at any time. This generator consisted of a small, cylindrical (~2-mm diam by 1.5-cm long) grade-A nickel collar containing reagent-grade sodium chromate and silicon. External leads fed through the glass envelope permitted the collar to be heated by means of an electric current which caused the silicon to reduce the sodium chromate, thereby liberating sodium vapor. The vapor deposited on the (relatively cold) cathode. Experiments were carried out on a portion of the cathode surface which was flat, and lay perpendicular to the incident radiation. A spot was generally chosen in a region parallel to, but in from the edge of, the cathode by about 1–2 mm. The sensitivity of the sodium surface to white light was determined to be $\simeq$1–2 μA/lm. The gain of the photomultiplier was measured to be 50 000 when operated with a high voltage of 2000 V, which was the standard voltage used. A fresh coating of sodium was deposited on the cathode approximately two hours prior to the experimental runs reported here. The film thickness was estimated to be of the same order as the photoelectron escape depth (~800 Å at $2h\nu\simeq$4200 Å, as reported by Piepenbring).

The electron-multiplied current was passed through a 100-kΩ load resistor which fed a low-noise preamplifier followed by a lock-in amplifier. Phase-sensitive detection was performed at 2.2 kHz, which is the fundamental repetition frequency of the pulsed-laser output. The reference signal for the phase-sensitive detector was obtained directly from the specially constructed power supply[17] used to drive the laser.

In performing an experiment, filters calibrated at 8450 Å on a Cary spectrophotometer were inserted into the beam to provide known decrements of light power. Output voltage measurements were then recorded for each radiation power level. Using the known over-all gain of the system, which was 1×10^{-13} mho, the fundamental-frequency component of the cathode photocurrent was obtained. It was found that ordinary glass filters could not be used to provide the decrements of light intensity, because refraction in the glass caused the imaged-spot size and position to change. Thin gelatin (Kodak Wratten) filters, however, were found to be quite suitable.

C. Experimental Results

By plotting the measured photocurrent versus the measured radiation power on a log-log plot, a linear dependence of photocurrent on radiation power appears as a straight line of slope unity, while a quadratic dependence appears as a straight line of slope 2. The results of a typical experimental run (using the procedure described in Sec. II B) for a freshly deposited sodium surface are shown in Fig. 2, where the measured photoelectric current has been plotted against the peak radiation power incident on the *face* of the sodium surface photomultiplier tube. From Fig. 2, it is seen

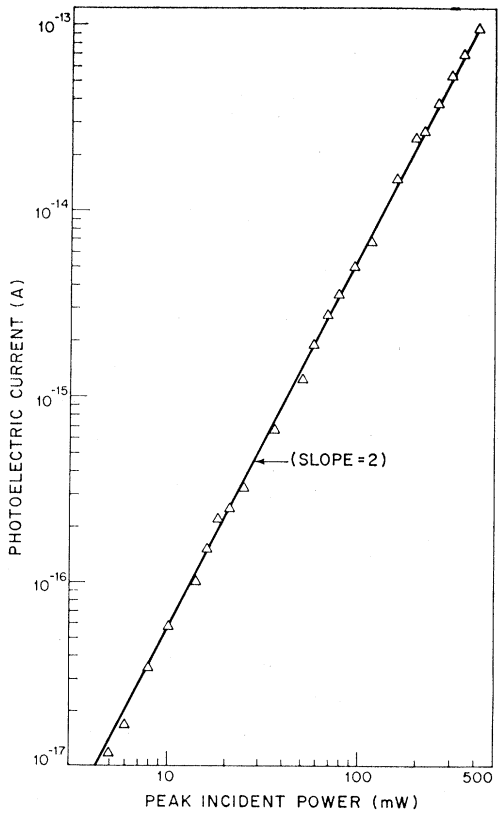

FIG. 2. Fundamental frequency component of photoelectric current versus peak radiation power incident on face of sodium surface photomultiplier. Because of absorption at the face of the photomultiplier, the radiation power incident on the sodium surface is less than the value shown above (see text).

[17] M. C. Teich, D. A. Berkley, and G. J. Wolga, Rev. Sci. Instr. **36**, 973 (1965).

that the experimental points fall on a line of slope 2. This quadratic dependence of the photoelectric current on the incident radiation power, signifying two-quantum photoelectric emission, extends for over four orders of magnitude of the photocurrent. This is a considerably greater range for the effect than observed previously.[5]

In order to compare the magnitude of the two-quantum effect in various materials, the double-quantum yield Λ is calculated. To obtain Λ, the observed photocurrent must be divided by the first Fourier coefficient of the square of the incident laser-radiation waveform, $p(t)$. This Fourier coefficient has been estimated to be $\simeq 0.1$ for the particular laser-output pulse shape and width used in these experiments. To obtain the peak radiation power incident on the sodium surface, which is also necessary to calculate Λ, a correction must be made for absorption and reflection at the face of the sodium surface photomultiplier. In these experiments, only about 40% of the measured radiation power has been estimated to impinge on the sodium photocathode (by visual comparison with neutral-density filters in a transmission experiment), the remainder being lost through absorption in the thin residual film of sodium on the photomultiplier window and through reflection.

The maximum observed photocurrent was 1×10^{-13} A (corresponding to 1×10^{-12} A referenced to cw laser radiation) occurring at a maximum peak radiation power of 400-mW incident on the photomultiplier face (corresponding to 160-mW incident on the sodium surface). Estimating the area of the focused laser spot[1] on the sodium surface as 2×10^{-5} cm^2, this corresponds to a double-quantum yield Λ_{Na} (8450 Å, 300°K) $\sim 8\times10^{-16} I_0$ A/W. Owing to uncertainties in the parameters used to estimate this quantity, it may be considered to be reliable only to within a factor of 3.

At the maximum incident radiation power, the double-quantum photocurrent was sufficiently large to be directly observed on an oscilloscope. Figure 3 shows a trace of the double-quantum photocurrent, $p(t)$ [or $i^{(2)}(t)$], directly above a trace of the incident-radiation waveform $l(t)$. Under ideal conditions, the function $p(t)$ should be equal to $l^2(t)$. Thus, if $l(t)$ were precisely hemispherical, which is a good approximation to the waveshape shown in Fig. 3, then $p(t)$ would be expected to be parabolic. It is seen, however, that the double-quantum waveform is not precisely the square of the single-quantum waveform. This may be understood to arise from variations in the spatial *intensity* distribution at the sodium surface as a function of time. Since the quadratic intensity dependence of the double-quantum current weighs higher-intensity regions more heavily than lower-intensity regions, an inhomogeneous intensity distribution in space and time enhances the nonlinear effect. Thus the changing mode structure of the laser output, resulting from laser heating during the current pulse, is responsible for this effect. Similar

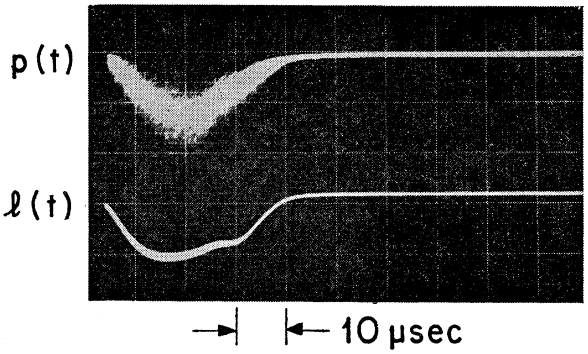

FIG. 3. Oscilloscope trace of double-quantum photocurrent waveform $p(t)$ shown above trace of incident laser radiation waveform $l(t)$.

observations for other two-photon processes have been reported.[18]

Finally, it should be mentioned that qualitative verification for the inverse area dependence expected for a two-quantum process[19] has been experimentally obtained: A large, but gradual rise in output current was observed while the lens was adjusted to image the laser-emitting region on the sodium surface.

D. Other Effects

In the discussion to follow, it will be shown that several other possible effects yielding electron emission do not contribute to the observed current, and that the experimental data presented in Fig. 2 may therefore be attributed to double-quantum photoemission. The following effects are discussed in order: (1) thermionic emission, (2) harmonic generation in the laser, and (3) harmonic generation at the metallic surface.

The following experiment was performed to enable the magnitude of the thermionic emission current to be estimated: The 400-mW laser beam used in the previously described experiments was focused onto a chromel-alumel thermocouple which registered an (average) temperature increase of 2°C. Using a model for pulsed-laser-induced metallic heating,[3] which is based on the one-dimensional classical diffusion equation, the temperature rise at the peak of the laser pulse was estimated to be less than 10°C. Convection effects were of minor importance in this estimate. This corresponds to a maximum thermionic emission current smaller than 10^{-26} A (from the Richardson equation), which is many orders of magnitude less than the lowest current observed. The four decades of quadratic dependence of photocurrent on the incident light intensity is further evidence that the emission was not thermionic.

---

[18] N. Bloembergen, *Nonlinear Optics* (W. A. Benjamin, Inc., New York, 1965), p. 131.

[19] If J is the current density, A the area of the focused laser spot on the cathode, I_0 the intensity of the radiation, and P the incident radiation power, then $J\propto I_0^2$, and therefore $i^{(2)}\propto I_0^2 A$. Since $I_0=P/A$, however, $i^{(2)}\propto P^2/A$ and the resultant inverse area dependence of the two-quantum current.

Another possible cause of electron emission was the second-harmonic generation of blue light (4225 Å) in the laser itself. This emission would cause a photocurrent of unity slope, since the decrements in incident radiation power were provided by inserting calibrated filters, rather than by changing the laser power itself. Therefore, this effect could not masquerade as the double-quantum emission (which is of slope 2). To experimentally ascertain that second-harmonic generation in the laser was of no importance, the single-quantum yield from the sodium phototube, $Y(\lambda,T)$, was measured[16] with and without a blue attenuating filter in the laser beam. No difference in the behavior of the current could be detected, indicating that blue light from the laser was not producing an observable current.

The emission of second-harmonic radiation at an illuminated metallic boundary has been considered by several authors. In particular, Brown, Parks, and Sleeper[20] have measured the second-harmonic radiation from an evaporated silver surface, illuminated by a ruby laser producing pulses of 1-MW peak power. They have estimated the harmonic generation efficiency at about 10^{-15}. This will provide an upper limit to the efficiency for the case under consideration, since the maximum intensity of $\sim 10^4$ W/cm^2 is well below that used by Brown *et al.* Considering an incident radiation power of $\simeq 0.4$ W, the blue light generated at the sodium surface should therefore have a power below 5×10^{-16} W. If all of this harmonic radiation were absorbed to create photoelectrons from the sodium, this effect would provide an electron current less than 5×10^{-16} W$\times 10^{-4}$ A/W$\sim 5\times10^{-20}$ A, which is well below detectability with our apparatus.

III. THEORY

A theoretical treatment of the double-quantum *surface* photoelectric effect in a metal was first given by Smith[4] in 1962. Smith used the Sommerfeld model of a metal, and used a second-order perturbation theory calculation to obtain the photocurrent. In 1964, Adawi[21] obtained a more general formulation of the two-quantum surface photoelectric effect by using the steady-state method of scattering theory, which is equivalent to the time-proportional transition method. In the limit of the step surface potential, the photocurrent obtained by Adawi reduced to Smith's result. Numerical estimates of the photocurrent arising from this mechanism, however, are three orders of magnitude less than the observed current in our experiments.

A theoretical treatment of the double-quantum *volume* photoelectric effect in a metal was given by P. Bloch,[2] also in 1964. In the volume effect, transitions occur between energy bands within the bulk of the material rather than at the surface. Just as Smith's second-order treatment of surface photoemission was based on the earlier first-order treatment given by Mitchell,[22] Bloch's second-order treatment of volume photoemission was likewise based on the earlier first-order treatment given by Fan.[23] In the case of both surface and volume photoelectric emission, the theoretically predicted double-quantum photocurrent is proportional to the square of the incident radiation power, and inversely proportional to the area irradiated.[19]

Bloch calculated the two-quantum current using a model for the interband mechanism, and by considering only **k**-conserving transitions in a simple metal. Within this framework, however, Bloch's calculation was inadequate in the following respects: (1) the electron-escape depth was not considered to be a function of the electron energy as has been shown necessary by Mayer and Thomas[24] (who used a model not too different from that of Fan), and also by Piepenbring[25]; (2) the effect of radiation reflection at the metallic surface was neglected; (3) considering the perturbation Hamiltonian $\mathcal{H}' = -e\mathbf{A}\cdot\mathbf{p}/mc + e^2A^2/2mc^2$ in which double-quantum transitions may take place either in second order through the $\mathbf{A}\cdot\mathbf{p}$ term, or in first order through the A^2 term,[26] Bloch tacitly attributed the effect to the term in A^2 by assuming that the oscillator strength arising from this transition was of the order of unity. The $\mathbf{A}\cdot\mathbf{p}$ term, however, may contribute heavily to the two-quantum transition probability[27–30]; and (4) Bloch's matrix elements were too large by a factor of $(2\pi)^{1/2}$.

Bloch's corrected result is recorded below, with the matrix element included in a factor defined as ρ. This factor, which is proportional to the spatial part of the two-quantum transition probability,[31] should replace the expression in square brackets in Eq. (7) of Bloch's paper. The corrected two-quantum photocurrent is

$$i^{(2)} = \pi e\rho\left\{\frac{2N-1}{N}\right\}\left[\frac{dr_0{}^2mc^2(\beta P)^2}{(2\pi)^2 2(h\nu)^3 \nu A}\right] \times\left[\frac{4\pi}{3}\left(\frac{E_F}{2h\nu}\right)k_F\left(1+\frac{e\varphi}{E_F}-\frac{2h\nu}{E_F}\right)^{3/2}\right]. \quad (1)$$

[20] F. Brown, R. E. Parks, and A. M. Sleeper, Phys. Rev. Letters **14**, 1029 (1965); see also F. Brown and R. E. Parks, Phys. Rev. Letters **16**, 507 (1966).

[21] I. Adawi, Phys. Rev. **134**, A788 (1964).

[22] K. Mitchell, Proc. Roy. Soc. (London) **A146**, 442 (1934); **A153**, 513 (1936).

[23] H. Y. Fan, Phys. Rev. **68**, 43 (1945).

[24] H. Mayer and H. Thomas, Z. Physik **147**, 419 (1957).

[25] F. J. Piepenbring, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Co., Amsterdam, 1966), p. 316.

[26] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), 2nd ed., p. 254.

[27] W. L. Peticolas and K. E. Rieckhoff, Phys. Letters **15**, 230 (1965).

[28] R. Guccione and J. Van Kranendonk, Phys. Rev. Letters **14**, 583 (1965).

[29] E. Corinaldesi, Phys. Rev. Letters **15**, 335 (1965).

[30] A general discussion of the various contributions to an arbitrary multiple-photon process has been given by S. Kielich, Acta Physica Polon. **30**, 393 (1966).

[31] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), p. 201–205.

The symbols have the following interpretation: $i^{(2)}$ is the two-quantum photocurrent, r_0 is the classical electron radius (e^2/mc^2), P is the incident radiation power, A is the area of the illuminated spot, $e\varphi$ is the work function of the material, E_F is the Fermi energy of the material, k_F is the wave number of an electron at the Fermi surface, N is the number of modes in which the laser is oscillating, ν is the frequency of the incident radiation, d is the escape depth or photoelectron range, β is 1 minus the reflectivity, and ρ is the two-quantum "oscillator strength."

The first factor in curly brackets $\{(2N-1)/N\}$ has been included to take into account the multimode operation of the laser. This factor arises from random phase contributions from different mode pairs, which enhances the double-quantum current. Bloembergen has discussed this factor in connection with second-harmonic generation and other nonlinear processes.[18]

A conclusion concerning the applicability of this model may not be drawn, nevertheless, because the appropriate matrix elements cannot be easily estimated and are quite difficult to calculate.[32] A very crude estimate of this quantity yields a current which appears to be considerably below the observed current, however.

For the alkali metals, Piepenbring,[25] Thomas,[33] and others[24,34,35] have given clear experimental evidence indicating that first-order photoelectric emission is purely a volume effect. For photon energies well above the threshold, photoemission studies on copper and silver have shown the data to be completely consistent with a volume effect. Furthermore, *nondirect* optical transitions have been shown to be stronger than direct ones for both Cu and Ag in this region.[36] Thus, as has been emphasized by Spicer,[37] the conservation of crystal momentum ($\mathbf{k}$) need not be an important selection rule in the photoelectric process. Recent work on the alkali metals has emphasized the importance of nondirect optical transitions in these materials as well[32,38–40] although it appears that direct transitions may play some part in the single-quantum photoelectric properties of these "simple" metals (that is, metals in which transitions are from s- and p-derived bands).[41,42] In view of these results for the one-quantum effect, it is reasonable to suggest that the two-quantum process may likely involve nondirect transitions, in which case Bloch's model would not be appropriate since it is based upon a direct-transition premise.

In summary, it appears that no adequate theory exists as yet, although the two-quantum yields for metals observed to date are consistent insofar as they are of the same order of magnitude.

IV. CONCLUSIONS

Double-quantum photoelectric emission has been observed from sodium metal. The two-quantum yield for the process Λ_{Na} (8450 Å, 300°K)$\sim 8\times 10^{-16} I_0$A/W is smaller than the yield from Cs_3Sb (a semiconductor) by a factor of about 10^4, and is about 10^8 times smaller than the yield from (organic) anthracene. The yield values within each group (metals, semiconductors, and organic single crystals) cluster at different orders of magnitude. The observed yield in sodium is about three orders of magnitude larger than that predicted on the basis of the surface effect. A reasonable comparison with the volume photoeffect is not possible with the present theory. It is noted that two-quantum photoemission is a nonlinear process of particular interest since observation of the effect does not require an external detector.

[32] S. J. Nettel, Phys. Rev. **150**, 421 (1966).
[33] H. Thomas, Z. Physik **147**, 395 (1957).
[34] H. Mayer, R. Nossek, and H. Thomas, J. Phys. Radium **17**, 204 (1956).
[35] A. Meessen, J. Phys. Radium **22**, 308 (1961).
[36] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030 (1964); **136**, A1044 (1964); C. N. Berglund, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Co., Amsterdam, 1966), p. 285.
[37] W. E. Spicer, Phys. Rev. Letters **11**, 243 (1963); Phys. Letters **20**, 325 (1966).
[38] J. C. Phillips, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Co., Amsterdam, 1966), p. 22.
[39] J. A. Appelbaum, Phys. Rev. **144**, 435 (1966).
[40] A. Overhauser, Phys. Rev. **156**, 844 (1967).
[41] H. Mayer and B. Hietel, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Co., Amsterdam, 1966), p. 47.
[42] W. E. Spicer, in *Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965* (North-Holland Publishing Co., Amsterdam, 1966), p. 296; see discussion with J. Friedel following this paper.

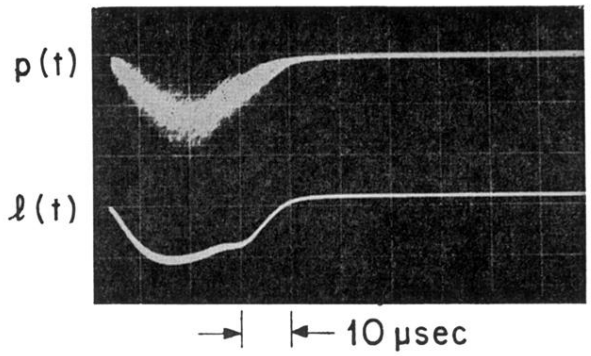

FIG. 3. Oscilloscope trace of double-quantum photocurrent waveform $p(t)$ shown above trace of incident laser radiation waveform $l(t)$.