Photoelectric Emission Phenomena in LiF and KCl in the Extreme Ultraviolet*

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The photoelectric emission from films of LiF and KCl and sheet Ni due to extreme ultraviolet radiation of 8 photon energies from 10 to 50 eV has been studied with a planar-potential retarding analyzer. Current-voltage diagrams which provide an analysis of the "normal" energy of the emitted electrons have been obtained. Photons of energies greater than twice the depth of the filled band below vacuum potential produce an effect which may be interpreted as two-electron emission. The results suggest this is an Auger process rather than being due to strong electron scattering. The results also indicate that the emission from LiF and KCl is preferentially in the forward direction.

INTRODUCTION

IN recent years, there has been increased interest in photoelectric phenomena in the extreme ultraviolet (xuv) region. The photoelectrons emitted due to radiation are those which occupy the valence and conduction bands of the material. Photoelectric phenomena in a solid are thus intimately involved with the electronic structure of the solid. In this region where the so-called volume photoelectric effect[1] becomes dominant, the photoelectric emission yields of all materials become quite high, exceeding 10%.[2] Therefore, photoelectric studies in the xuv are of interest not only for learning more about solids but also for improving detection techniques of xuv radiation through these high yields. The detection of xuv radiation is of interest for studies of such fields as solar radiation and plasma phenomena.

When the volume photoelectric effect sets in, insulators as well as metals become good electron emitters. Indeed, yields reported for insulators are frequently greater than those of metals.[3] This is not too surprising, since secondary electron emission yields of nonmetals are often greater than those of metals. In many respects the volume photoelectric effect is closely related to secondary emission, since, in both effects, the electrons emitted are those originating from levels and bands associated with an infinite crystal rather than with surface states as in the conventional surface photoelectric effect. Also, an electron of an insulator, if excited into the conduction band, will not be scattered so readily as is an electron of a metal, because of the very low free-electron density in insulators.

Lukirskii *et al.*[3] reported photoelectric emission yields of 61% for LiF for 110-eV photons. Taylor and Hartman[4] measured the yields of LiF and KCl for a photon energy range between 8 and 21 eV. They also measured the total energy distribution of photoelectrons emitted from KCl at four photon energies between 10 and 21 eV. Because of this earlier work, LiF and KCl were chosen for the present studies. To provide comparison with a metal, nickel was also investigated. The experiments were designed to examine the "normal" energy distributions of photoelectrons emitted under the influence of photons of 10 to 50-eV energy.[5]

APPARATUS

The experiment consists essentially of exposing a photocathode to monochromatic radiation in vacuo and measuring the photoelectric current as the potential difference between the photocathode and the retarding grid is varied. Sensitivity is obtained by using a 10-stage Be-Cu electron multiplier behind the retarding grid. The photocathodes are easily interchangeable. The original detector has been described in detail.[6] Figure 1 shows the present detector. This has been modified from the original design by introducing the light trap. This is an opening in the electrostatic shield directly opposite the aperture which admits the incident radiation. As a result, most of the light reflected from the cathode is prevented from causing photoelectric emission at the shield. This improvement has increased the useful sensitivity by a factor of 50 to 100.

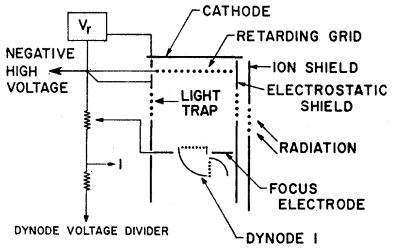

FIG. 1. Schematic drawing of the windowless photon detector combining a planar retarding potential analyzer with a 10-stage Dumont Be–Cu electron multiplier. The retarding potential between the retarding grid and cathode is established with a battery supply.

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[1] I. Tamm and S. Schubin, Z. Phys. **68**, 97 (1931).

[2] G. L. Weissler, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, Part I, p. 304 (note especially Sec. 27).

[3] A. P. Lukirskii, M. A. Rumsh, and L. A. Smirnov, Opt. Spectry. (USSR) **9**, 265 (1960).

[4] J. W. Taylor and P. L. Hartman, Phys. Rev. **113**, 1421 (1959).

[5] A brief report of this work has been presented to The American Physical Society [Bull. Am. Phys. Soc. **8**, 198 (1963)].

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

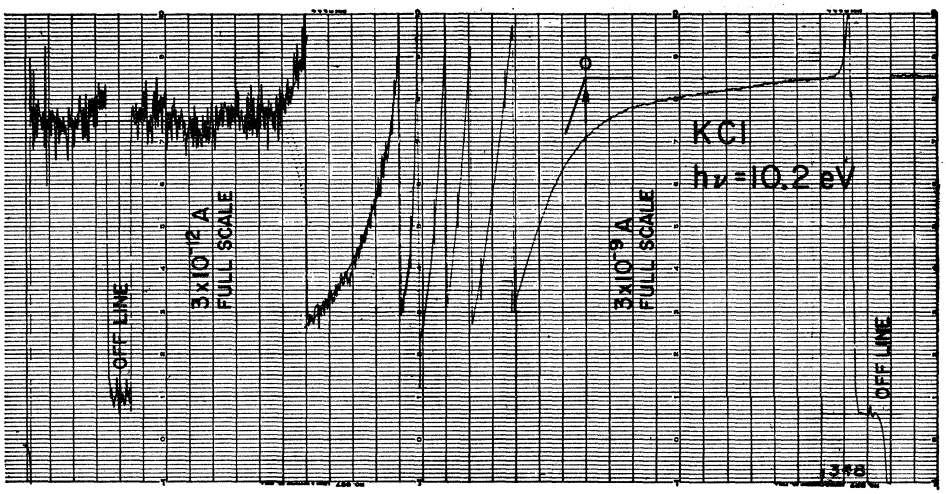

FIG. 2. Original uncorrected current-voltage record obtained from a KCl photocathode (2000 Å thick) irradiated with 10.2-eV photons. The ratio of saturation signal to the fully retarded signal is ~1200. The corrected zero is indicated by the arrow.

A modified Schueler lamp[7] was the light source. This provided emission lines from 1216 to 256 Å depending on the discharge gas. A 3-meter grazing incidence vacuum monochromator with a 15 000 line/in. grating with an 86° angle of incidence was used. The pressure in the neighborhood of the detector was about 10^{-5} Torr.

The detector was used in dc operation with a Beckman Model V micromicroammeter and an L&N Speedomax recorder. The multiplier was used at gains between 10^3 and 10^4 depending on the intensity of the specific emission line.

Films of KCl and LiF were evaporated onto stainless steel disks by Thin Film Products, Incorporated. For each alkali halide, four thicknesses were investigated: 2000, 1000, 500, and 250 Å. The thicknesses were measured interferometrically and are known to within 20%. Between evaporation and use in vacuum they were stored in a desiccator over silica gel. The nickel cathode was untreated commercial grade A nickel.

EXPERIMENTAL DETAILS

The detector was placed behind the exit slit of the monochromator. The cathodes were 42 mm in diam. The illuminated area was 1 mm wide and 10 mm high, centered in the middle of the cathode. The light struck the cathode at an angle of 45°. Since the electron emission originated at the center, fringe effects were avoided.

Pin holes are frequently associated with evaporated films. To determine their effect, measurements of the emission from an uncoated stainless steel cathode were made. The resulting current voltage diagrams (CVD's) were atypical of the KCl and LiF films but did resemble closely those of the nickel cathode. This is in keeping with the measurements of Heroux and Hinteregger[6] who found nearly identical results with nickel and tungsten.

There was no evidence of charge-replacement difficulties during the measurements. The maximum current drawn from the films was about 10^{-13} A for a 14 cm² area. From the work of Taylor and Hartman,[4] current densities of at least 10^{-11} A/cm² are required before appreciable potential drops occur within the films. The use of an open-structure multiplier of low noise allowed measurements to be made over a wide dynamic range, even for low intensity-emission lines such as the He II line at 256 Å.

As stated earlier, the alkali halide films were stored in a desiccator between evaporation and measurements. There was no sign of deterioration of the films, and measurements made several months apart were identical within experimental error. By "identical," it is meant that the same discharge pressures and power inputs produced the same photocurrents. This result is confirmed by the work of Lloyd[8] who has measured photoelectric yields of LiF for photon energies between 10 and 21 eV. He observed changes with time in the yields for photon energies between 10 and 12 eV but reproducibility for energies greater than 12 eV. These changes he ascribed to a gradual contamination of the surface, even at pressures as low as 10^{-6} Torr. As is expected from earlier work on the volume photoelectric effect,[2] the state of the surface is negligible after the onset of the true volume effect.

CURRENT-VOLTAGE DIAGRAMS

A typical sample of original data is shown in Fig. 2 and represents a current-voltage record of 2000-Å thick KCl, irradiated with 10.2 eV photons. There are two off-line points–one at saturation and one at full retardation. These are a measure of the multiplier output, when the exit slit of the monochromator is moved away from the position on the Rowland circle corresponding to the wavelength of the exciting radiation. This off-line background is due to scattered light and thermal noise. The saturation signal is $\sim 2.4\times10^{-9}$ A and the fully retarded signal is $\sim 2.0\times10^{-12}$ A, a factor of 1200.

[7] R. G. Newburgh, L. Heroux, and H. E. Hinteregger, Appl. Opt. **1**, 733 (1962).

[8] J. N. Lloyd, thesis, Cornell University, Ithaca, New York, 1963 (unpublished).

TABLE I. LiF cathode (2000-Å thick). Anode signal (expressed in percentage of saturation signal) for particular values of retardation voltage V_r and for illumination of the cathode with several monochromatic wavelengths.

	Photon energy or wavelength							
V_r	10.2 eV (1216 Å)	11.8 eV (1048 Å)	13.5 eV (920 Å)	16.7 eV (744 Å)	21.2 eV (584 Å)	26.9 eV (460 Å)	40.7 eV (304 Å)	48.4 eV (256 Å)
0	100	100	100	100	100	100	100	100
−1	47.5	37.5	63.5	73.0	82.5	79.0	80.5	69.0
−2	11.5	15.5	33.0	50.5	65.0	59.0	63.5	49.0
−3	2.10	4.0	16.0	35.0	51.5	42.5	42.0	36.0
−4	0.275	1.05	6.0	23.0	40.0	32.0	30.0	26.5
−5	0.06	0.315	2.25	13.0	31.0	24.5	22.0	19.5
−6	0	0.115	0.45	7.80	23.5	19.0	16.0	14.0
−7		0.02	0.085	3.90	17.5	14.5	12.0	10.0
−8		0	0	1.95	13.0	11.5	8.50	6.75
−10				0.425	5.0	7.25	3.60	3.80
−12				0.060	1.25	4.60	2.05	2.10
−14				0	0.22	2.80	1.35	1.20
−16					0.020	1.50	0.91	0.835
−18					0	0.60	0.675	0.62
−20						0.155	0.540	0.495
−22						0.023	0.440	0.405
−26						0	0.295	0.275
−30							0.160	0.180
−34							0.043	0.0795
−38							0	0.0385
−42								0.005
−46								0

To obtain the retardation curve for 48.4-eV photons was slightly more complicated. The light source contained helium and produced both 584- and 304-Å radiation in addition to the 256-Å line of 48.4-eV energy. The intensity of the 256-Å line was about 5 to 10 times less than those of the 304 and 584-Å lines. Since the grating scattered the longer wavelengths quite strongly, it was necessary to make an off-line retardation scan as well. This scan was subtracted from the on-line scan and the corrected retarding plot synthesized. The stability of the discharge was checked and was completely adequate for this procedure. The signal at a given wavelength remained constant within 1% for hours, after the discharge had been allowed to run for 30 to 60 min.

All current-voltage diagrams shown in Figs. 3–8, and summarized in Tables I, II, and III, represent corrected original data. The background on-line signal remaining at full retardation has already been subtracted. All results were normalized to saturation current and replotted.

TABLE II. KCl cathode (2000-Å thick). Anode signal (expressed in percentage of saturation signal) for particular values of retardation voltage V_r and for illumination of the cathode with several monochromatic wavelengths.

	Photon energy or wavelength							
V_r	10.2 eV (1216 Å)	11.8 eV (1048 Å)	13.5 eV (920 Å)	16.7 eV (744 Å)	21.2 eV (584 Å)	26.9 eV (460 Å)	40.7 eV (304 Å)	48.4 eV (256 Å)
0	100	100	100	100	100	100	100	100
−1	55.0	63.0	72.0	80.5	57.5	69.5	60.0	71.5
−2	20.0	31.5	47.5	62.5	28.0	43.5	32.5	44.0
−3	3.20	11.5	28.5	44.5	12.5	25.5	17.5	25.0
−4	0.275	2.5	15.5	31.0	7.00	15.5	9.25	12.5
−5	0.084	0.355	6.50	21.0	5.00	9.00	6.5	8.35
−6	0.022	0.085	2.00	13.5	3.80	5.00	4.25	6.25
−7	0.001	0.0205	0.23	8.50	2.95	2.60	2.90	4.80
−8	0	0	0.030	4.75	2.25	1.65	2.10	3.60
−10			0	0.80	1.15	0.965	1.30	2.00
−12				0.006	0.43	0.680	0.90	1.45
−14				0	0.10	0.455	0.76	1.15
−16					0.0095	0.260	0.625	0.955
−18					0	0.110	0.52	0.790
−20						0.036	0.43	0.665
−22						0.001	0.345	0.570
−26						0	0.210	0.425
−30							0.115	0.285
−34							0.0325	0.150
−38							0	0.068
−42								0.0095
−46								0

TABLE III. Solid nickel cathode. Anode signal (expressed in percentage of saturation signal) for particular values of retardation voltage V_r and for illumination of the cathode with several monochromatic wavelengths.

	Photon energy or wavelength							
V_r	10.2 eV (1216 Å)	11.8 eV (1048 Å)	13.5 eV (920 Å)	16.7 eV (744 Å)	21.2 eV (584 Å)	26.9 eV (460 Å)	40.7 eV (304 Å)	48.4 eV (256 Å)
0	100	100	100	100	100	100	100	100
−1	22.5	42.5	56.0	77.0	70.0	62.0	65.0	62.5
−2	5.00	17.5	29.0	53.0	47.0	39.5	42.5	42.5
−3	0.725	4.5	12.5	36.0	34.0	27.0	28.5	29.0
−4	0.11	1.15	4.75	22.5	26.5	19.0	20.0	20.0
−5	0	0.27	1.60	14.0	21.0	14.5	14.0	14.5
−6		0.055	0.30	7.25	16.5	11.0	11.5	11.0
−7		0	0.075	4.00	13.0	9.50	9.25	8.15
−8			0	1.75	9.5	8.20	7.30	6.85
−10				0.15	5.00	6.00	5.00	5.05
−12				0	1.60	4.40	3.65	3.90
−14					0.275	2.95	2.85	3.15
−16					0	1.80	2.20	2.65
−18						0.70	1.80	2.30
−20						0.23	1.50	2.00
−22						0.022	1.20	1.70
−26						0	0.750	1.05
−30							0.400	0.745
−34							0.120	0.465
−38							0	0.245
−42								0.090
−46								0

To establish the point of zero retardation, the following, admittedly somewhat arbitrary, procedure has been used. At the point of maximum slope of the current-voltage diagram, a straight line having this slope is extrapolated until it intersects the line parallel to the voltage axis corresponding to saturation signal. This point of intersection establishes zero retardation. Such a correction minimizes the significance of contact potential differences and facilitates comparison of different current-voltage diagrams.

RESULTS AND DISCUSSION

Since the photocathode and retarding grid have plane parallel geometry, the electric field is essentially normal to the emission surface. The retardation, therefore, affects only the normal component of electron velocity. As a result, retardation energies refer to the kinetic energy "associated" with this velocity component. This has been commonly termed the "normal" energy and must be clearly distinguished from the actual kinetic energy of the electron. It must be emphasized that the experiment described here analyzes this "normal" energy only.

If the maximum kinetic energy of the emitted electrons determined by the photon energy is E_0, the distribution of energies of the electrons is described by the function, $f(E)$ normalized to represent a probability

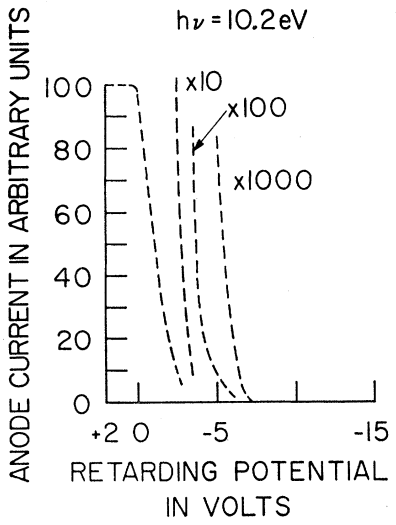

FIG. 3. Current-voltage diagram for photoelectric emission from KCl illuminated with 10.2-eV photons.

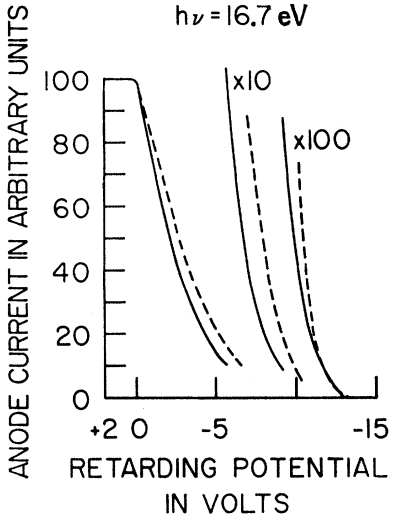

FIG. 4. Current-voltage diagrams for photoelectric emission from LiF (solid line) and KCl (dashed line) illuminated with 16.7-eV photons.

density per unit energy interval such that

$$\int_0^{E_0} f(E)dE=1. \tag{1}$$

For a total energy analyzer the electron current collected as a function of retarding voltage is

$$I(E_R)=I_0\int_{E_R}^{E_0} f(E)dE, \tag{2}$$

where I_0 is the saturation current and $E_R=eV_R$ is the energy corresponding to the retarding voltage.

For a planar analyzer the expression is quite different. Any determination of the relation between the normal and total energy distribution requires knowledge of the angular distributions of the emission velocities. Let θ designate the angle between the surface normal and the electron velocity. For a given energy of emission, E, and direction of emission, θ, the "normal" energy is given by

$$E_{\text{norm}}=E\cos^2\theta. \tag{3}$$

For a given retarding energy E_R, only those particles with "normal" energy greater than E_R can be collected, a condition expressed as

$$E\cos^2\theta \geqslant E_R. \tag{4}$$

Electrons emitted with energy $E \geqslant E_R$ to be collected must have a direction of emission lying within the cone whose half-angle θ is determined by Eq. (4), i.e.,

$$\theta=\cos^{-1}(E_R/E)^{1/2}. \tag{5}$$

For a planar analyzer the relation for collected current as a function of retarding energy which corresponds to Eq. (2) for a total analyzer is

$$I(E_R)=I_0\int_{E_R}^{E_0} f(E)\left\{\int_{\cos\theta=1}^{\cos\theta=(E_R/E)^{\frac{1}{2}}} h(\theta)\sin\theta d\theta\right\}dE. \tag{6}$$

The term $h(\theta)$ is the angular distribution function and would be equal to unity for isotropic emission.

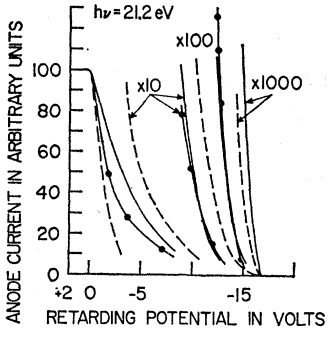

FIG. 5. Current-voltage diagrams for photoelectric emission from LiF (solid line) KCl (dashed line) and Ni (solid line with dots) illuminated with 21.2-eV photons.

This brief discussion of measurements with planar analyzers shows their complicated nature and should be kept in mind in an interpretation. The results for the 2000-Å films of LiF and KCl as well as nickel are shown in Figs. 3–8 and summarized in Tables I, II, and III. These results have all been normalized as described above. Several features are noticeable in the curves. If one considers the ×1 and ×10 branches, small retardation voltages affect the LiF less than KCl or nickel for photon energies below 16.7 eV. For 40.7 and 48.4-eV photons, the LiF comes closer to the nickel whose ×10 branch exceeds that of LiF. At 16.7 eV the KCl is least affected but at 21.2 eV is most strongly affected.

Consider the voltages for which the collected current is 10% of saturation. One might expect that increasing photon energies would always shift the 10% point to higher retarding energies. However, this is not observed. For KCl irradiated with 16.7-eV photons, this point is at 6.6 V, for 21.2-eV photons it is at 3.2 V. For LiF though, the two points are at 5.7 V for 16.7-eV photons and 8.7 V for 21.2-eV photons. For 26.9-eV photons though, the 10% point has decreased to 8.4 V and for 40.7-eV photons to 7.6 V. This is contrary to our expectation. Such an effect has been observed with[9] Cs_3Sb and with[4] KCl. If the top of the filled band of an insulator is at an energy W below vacuum potential, this effect occurs for exciting radiation $h\nu>2W$. For KCl the Cl^-3p valence band is 8–9 eV below vacuum[4,10] and for LiF the value for the analogous band is somewhere between 12 and 13 eV.[4] Therefore, the effect in LiF should be apparent for photons of energy between 24 and 26 eV. This is indeed the observation.

It is significant that this effect is so pronounced even with a planar detector. There is a similar shift for nickel but not quite so marked. This is not surprising since, for temperatures above absolute zero, metals have no discontinuity in the energy of occupied states. Apker *et al.*[9] have interpreted this phenomenon as being most likely a strong scattering of the excited electrons by

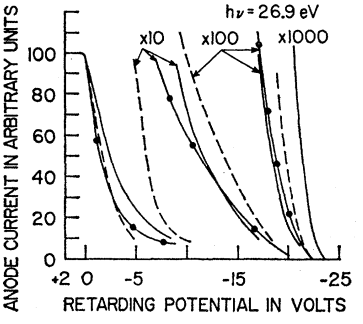

FIG. 6. Current-voltage diagrams for photoelectric emission from LiF (solid line) KCl (dashed line) and Ni (solid line with dots) illuminated with 26.9-eV photons.

[9] L. Apker, E. Taft, and J. Dickey, J. Opt. Soc. Am. 43, 78 (1953).

[10] L. G. Parratt and E. L. Jossem, J. Phys. Chem. Solids 2, 67 (1957).

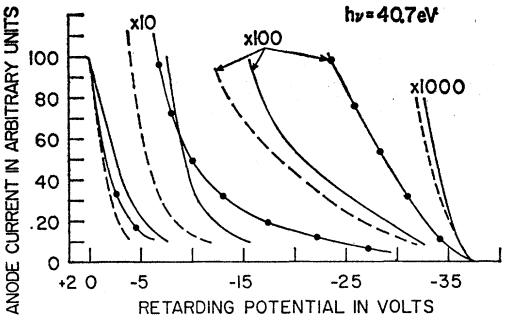

FIG. 7. Current-voltage diagrams for photoelectric emission from LiF (solid line) KCl (dashed line) and Ni (solid line with dots) illuminated with 40.7-eV photons.

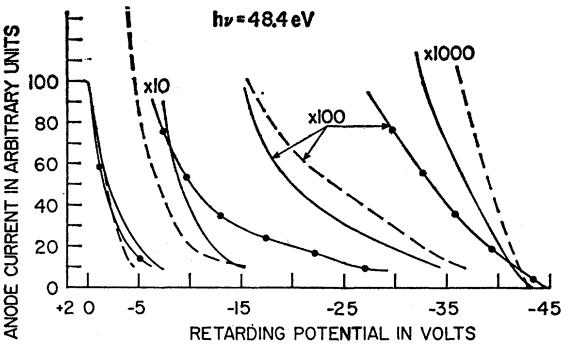

FIG. 8. Current-voltage diagrams for photoelectric emission from LiF (solid line) KCl (dashed line) and Ni (solid line with dots) illuminated with 48.4-eV photons.

the valence electrons in the filled band. They also mention the possibility of a double-electron excitation by the absorbed quantum. In the present study the photon energies have been as much as 6 times the value of W for KCl and 4 times that for LiF. Yet, the only energy at which the effect was observed was for $h\nu \approx 2W$. There was no evidence for a three-electron process such as might be expected if strong scattering occurred. On the other hand, Auger electrons have been observed experimentally in secondary electron emission studies with metals,[11] where, however, the characteristic energies have been considerably higher than those observed here. Therefore, a simple explanation may be in the first excited electron's leading to an Auger process with a second. It does appear definite that at least one type of two-electron processes is involved.

In Table I, an absorption effect is apparent. The values for the 11.8-eV excitation of LiF show a strong reduction in the energy of emitted electrons as compared with the values for 10.2- and 13.5-eV excitation. This can be explained by the strong photon absorption of LiF at this energy.[12]

Striking effects of film thicknesses were observed only with LiF irradiated with 10.2-eV photons. The photoelectric emission from the 250-Å film of LiF exposed to 10.2-eV radiation was down by a factor of 500 as compared with the thicker LiF films. For higher photon energies all four films were comparable. Apparently there is no appreciable absorption of the 10.2-eV photons in the thinnest film, so that the photoelectrons are produced in the substrate. But the film is too thick to allow the emission of these electrons. This result has been applied in a rocket-borne grazing-incidence monochromator flown on 2 May 1963 to record the 55- to 315-Å region of the solar spectrum.[13] The cathode of a Bendix multiplier was coated with a 300-Å film of LiF to minimize its response to the very intense 1216-Å solar radiation.

Lukirskii *et al.*[3] have reported photoelectric yields of 61% for LiF exposed to 100-eV radiation. The present work extended only as far as 50 eV. A preliminary evaluation of photographic and photoelectric records from the present work indicates yields at 50 eV to be between 5 and 10%. There is not an adequate basis for a comparison of absolute values at the present time.

Even though no angular distribution measurements were made in the present study, a tentative conclusion can be drawn from the observations of a marked two-electron effect. Since the analysis was of normal energy only, the implication seems to be that the emission from LiF and KCl is preferentially in the forward direction. Were this not so, the marked two-electron effect would not be apparent, unless every photon with energy greater than that of the threshold created two low-energy electrons.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge stimulating discussion of this work with D. E. Bedo and H. E. Hinteregger of this laboratory, and with P. L. Hartman of Cornell University.

[11] J. J. Lander, Phys. Rev. **91**, 1382 (1953).
[12] A. Milgram and M. P. Givens, Phys. Rev. **125**, 1506 (1962).
[13] H. E. Hinteregger, L. A. Hall, and W. Schweizer (to be published).