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Resonance Potentials in Thin Films of Potassium Chloride

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Experiments have been conducted in which potassium chloride films have been bombarded with slow electrons. Electron absorption and backscattering were studied as a function of bombarding energy. Discontinuities of slope were obtained at characteristic bombarding energies, and these were interpreted in terms of decomposition and excitation energies. Three different experimental arrangements were utilized; a triode with a rotating dynode in which the electrons describe a simple straight-line path from source to target to detector, a device wherein both the primary and backscattered electron beams followed a cycloidal path due to external magnetic field, and an apparatus containing a magnetic velocity analyzer to limit the energy spread of the primary beam. General agreement was found in the data regardless of the type of apparatus used. The work function for inserting an electron into the potassium chloride film was estimated to be in the neighborhood of 0.3 ev.

It has been suggested that the technique of slow-electron bombardment may be used as a tool for analysis in thin-film studies and as a means of identifying band structure.

I. INTRODUCTION

DURING the past few years, research in secondary emission phenomena has indicated that the band scheme in solids might be studied experimentally. A rather comprehensive survey article by Marton *et al.*[1] discusses characteristic energy losses in solids due to electron bombardment. The various theories dealing with this phenomenon are summarized.

In the work of Rudberg, Haworth, and Harrower[2] it was found for the case of surfaces bombarded with electrons in the energy range of one hundred to several thousand electron volts, inelastic scattering of primary electrons could be observed. The data indicated that the scattered electrons had suffered well-defined losses of energy, these losses being independent of the primary energy and characteristic of the target material.

In still another approach to the problem of studying the band scheme by electron bombardment techniques, a group of experimenters have bombarded surfaces with low-energy electrons. In the work reported by Hilsch,[3] Wright,[4] and Bruining[5] experiments were conducted in which low velocity electrons were used to bombard surfaces such as potassium chloride, sodium chloride, sodium fluoride, calcium fluoride, and barium oxide deposited on metal targets. The ratio of backscattered current to bombarding current was measured as a function of bombarding energy. In all of these cases, a decrease in emitted electrons was noted at a critical energy for each particular chemical surface. For instance, for potassium chloride, at about 7.0-ev bombarding energy, the emitted electron current decreased, indicating absorption of primaries at this particular energy. From optical absorption techniques, it has been found that the exciton level in potassium chloride crystals is approximately 7.0 ev.

In the report by Wright, other critical energies were described for various materials, and it was pointed out that in addition to the exciton level, a correspondence could be found in the threshold of secondary emission and the optical absorption of an electron raised from the filled band to the conduction band. Leder, Mendlowitz, and Marton[6] point out a correspondence between x-ray fine structure and characteristic energy losses in various solids.

In the experiments to be described, the low-velocity primary electron beam technique was further explored. By utilizing more refined methods, discontinuities in dynode current and in the collector current due to inelastically scattered electrons, as a function of incident electron energy, are compared with optical absorption data and heat of formation energy. The results obtained appear to confirm previous results, indicating that the band structure of potassium chloride may be obtained by electron bombardment. In using electron bombardment techniques it was found, in addition, that new information relating to the structure of solids appeared.

II. EXPERIMENTAL METHOD, TRIODE STRUCTURE

During the course of these experiments, three types of apparatus were used. These included (1) a simply constructed triode with a rotating dynode, (2) a tube in which the primary electrons were deflected in a cycloid path by means of a magnetic field and in which inelastically scattered electrons were measured directly, and (3) a tube containing a magnetic velocity analyzer for the primary electron beam.

The first type is illustrated in Fig. 1. The purpose of using this construction was to confirm previous meas-

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[1] Marton, Leder, and Mendlowitz, *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. VII, p. 183.

[2] E. Rudberg, Phys. Rev. **50**, 138 (1936); L. J. Haworth, Phys. Rev. **48**, 88 (1935); G. A. Harrower, Phys. Rev. **102**, 340 (1956).

[3] R. Hilsch, Z. Physik **77**, 427 (1932); O. Krenzien, Z. Physik **126**, 365 (1949).

[4] D. A. Wright, Brit. J. Appl. Phys. **5**, 108 (1954).

[5] H. Bruining, *Physics and Application of Secondary Electron Emission* (Pergamon Press, London, 1954), p. 93.

[6] Leder, Mendlowitz, and Marton, Phys. Rev. **101**, 1460 (1956).

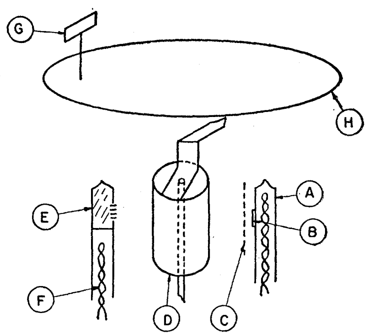

FIG. 1. Experimental triode: (A) indirectly heated cathode sleeve; (B) oxide-coated cathode; (C) wide meshed grid; (D) rotating dynode; (E) potassium chloride to be evaporated; (F) nickel sleeve and heater for potassium chloride evaporation; (G) getter; (H) mica shield.

urements by Wright and others. In addition, a structure such as this, if proven valid, could be used to explore rapidly a great variety of materials because of its inherent simplicity.

At exhaust, the cathode was activated and grid and dynode further cleaned by induction heating. The cathode-contaminated region of the dynode was rotated in front of the potassium chloride container and the container was degassed to the point of some evaporation of the potassium chloride. After this treatment, the contaminated portion of the dynode was rotated back in front of the cathode, and the cathode, grid, and dynode were again heated until they were clean and degassed rather completely. The getter was then evaporated and the tube sealed from the vacuum system.

The uncontaminated part of the dynode was then rotated in front of the cathode and control runs were carried out bombarding the metal dynode. The cathode was set at ground potential, the (6.3 v) filament at about 3 volts, the grid at 150 volts, and the dynode potential varied from 0 to +25 volts, with respect to the grounded cathode.

Following the control run, the bombarded area of the dynode was rotated in front of the potassium chloride container and the container was heated at successively higher temperatures in order to evaporate the potassium chloride onto the dynode. This area was bombarded between each heating. In this manner it was found that characteristic dynode current *vs* voltage curves developed with increasing thickness of the potassium chloride film.

It should be pointed out that the films deposited could not be seen by eye but could only be detected electrically. The film thickness during the experiments was estimated to be between 10 and 100 atomic diameters. If the film thickness increased to the point of interference colors (10^{-5} cm) the characteristics lost reproducibility and displayed signs of surface charging.

In Fig. 2, we see the results of the control run and some of the characteristics displayed by the potassium chloride film. Here, the ordinate is the fraction of the cathode current measured in the dynode circuit $[(I_D/I_C)\times 10^3]$, where I_D is the measurement of electrons going into the dynode and I_C is the cathode current.

The abscissa represents the energy of bombarding electrons.[7] In Fig. 3 further results are indicated. To provide additional checks on the results, repeat runs were made where the voltages were fixed for various lengths of time (i.e., 2 to 15 seconds). Always, the data were confirmed.

In comparing the data obtained in the control run on the uncontaminated dynode with the data measured on potassium chloride films, the presence of the potassium chloride films lowers the entire number of electrons going into the dynode. Another difference exists in the shape of the curves. Whereas the curve for the control run is relatively smooth, the curves for the potassium

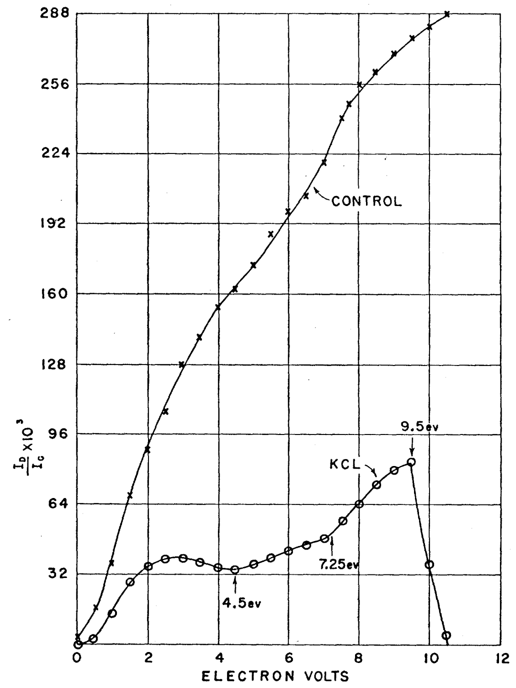

FIG. 2. Electron bombardment of a KCl surface using the triode structure. The fraction of the cathode current measured in the dynode circuit is plotted as a function of incident electron energy.

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[7] The method of correction for contact potential and thermal energies was as follows: At any particular range in current, the minimum detectable changes in absorption or secondary emission was observed. The dynode was then biased so that the voltage giving this amount of current at the start of the voltage run was assumed to be zero. For instance, if the readings were made so that one microampere of rising or falling current could be detected, the zero voltage was assumed to exist at that voltage where one microampere change could first be detected. If the scale used was such that the minimum detectable change was 10^{-9} ampere, then the voltage at which 10^{-9} ampere could first be detected was considered as the zero voltage. This method, admittedly empirical, did provide consistent results as illustrated in the data. The average correction was approximately 0.5 volt.

chloride films display certain discontinuities at characteristic bombarding energies. At about 2.5 ev the transmission of electrons through the potassium chloride film decreases. At about 4.4 ev there is an increase in the number of electrons entering the dynode circuit. At 7.25 ev there is another increase of electrons in the dynode circuit. At 9.0 ev to 9.5 ev there is a strong reversal in current interpreted as the threshold of secondary emission, for upon further increasing the bombarding energy, the number of electrons transmitted through the film decreases rapidly and finally the current reverses itself to the point where more electrons are leaving the dielectric film than entering.

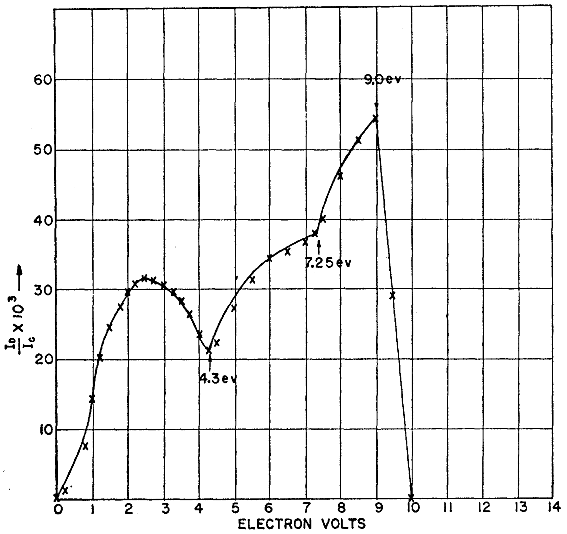

FIG. 3. Electron bombardment of a KCl surface with the triode structure using a dc method (voltages fixed for from 2 to 15 seconds). The fraction of the cathode current measured in the dynode circuit is plotted as a function of the incident electron energy.

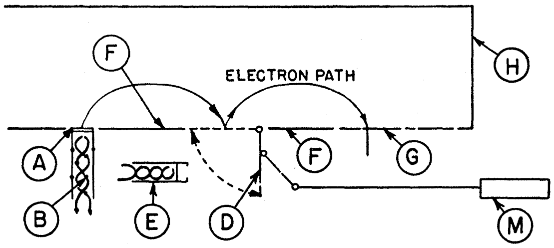

FIG. 4. Cycloid path electron tube: (A) indirectly heated oxide-coated cathode; (B) cathode heater; (D) first target which was coated with potassium chloride; (E) potassium chloride evaporator; (F) shields at the same potential as the cathode; (G) second target for collecting electrons reflected from D; (H) accelerating anode; (M) iron slug used to rotate the target, D, magnetically.

At this point, one can make the following tentative interpretation. The current, I_D, represents the measurement of electrons originating from the cathode and losing energy in the potassium chloride film in order to enter the dynode circuit. A decrease in I_D would indicate that electrons are being backscattered from the dynode surface film because of the mechanism of inelastic collisions. On the other hand, an increase in I_D indicates more electrons are entering the potassium chloride film in order to reach the dynode circuit. This also could be due to inelastic collisions. For instance, suppose that at about 7.25 ev, the electron energy is absorbed due to the "exciton" level of potassium chloride. Because of this absorption, the electron is no longer scattered from the surface but loses its energy in the surface film and then moves on to the dynode circuit. There are two such marked regions of increase in I_D, one at 4.5 ev and one at about 7.25 ev. The first could be due to absorption of the energy of the electron in decomposing some of the potassium chloride, the heat of formation of which is 4.5 ev. The second could be due to the absorption of the bombarding electron energy due to an exciton level in the potassium chloride film. In order to test this hypothesis further, a "cycloid tube" was constructed in which the backscattered electrons could be measured directly at the same time that the absorbed electrons were being studied.

III. CYCLOID BEAM EXPERIMENTS

In this phase of the experiments, by means of an external magnetic field, both the primary beam and scattered beam had cycloid trajectories and could be measured directly. The design of this tube is illustrated in Fig. 4.

The target, D, could be rotated by means of a magnetic system utilizing an iron slug. In the open position, potassium chloride could be evaporated onto the metal surface by means of the potassium chloride evaporator, E. Following this, D could be closed so that relatively uniform electrostatic fields existed between the bottom of the structure F, A, and D and the accelerating anode, H. A second target, G, was inserted in the tube for collecting electrons reflected from the target D in a second cycloid path.

During the run, the cathode was set near ground potential through a microammeter. The potential at the potassium chloride target, D, could be varied from near 0 to +25 volts. The potential at the second target, G, could also be varied from 0 to +25 volts. The anode, H, was maintained at a fixed potential of 200 volts.

The electrons entering D were measured as a function of bombardment voltage, and characteristic changes in absorption (electrons going into the D circuit) and backscattering (less current going into D) were observed. Simultaneously the second target, G, was maintained at a small fixed positive voltage. An increase in the absorption of bombarding electrons by potassium chloride could now be doubly demonstrated. For instance, if the dynode, D, were at 7 volts and G at 3 volts the only electrons which could reach G were those which were scattered from the potassium chloride by

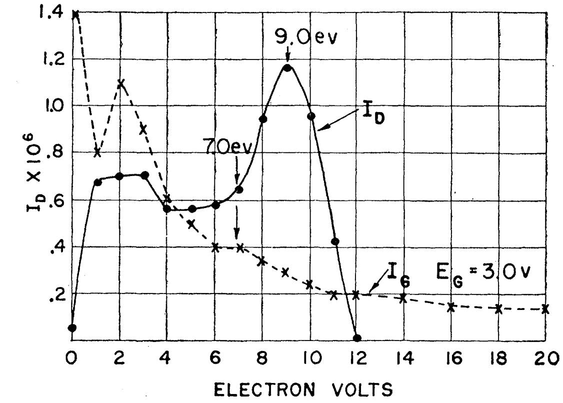

FIG. 5. Electron bombardment of a KCl surface using the cycloid structure with the secondary target at 3.0 volts. The currents flowing into the first target, *D*, and second target, *G*, are plotted as a function of the energy of the primary electron beam.

inelastic collisions. If an energy loss occurred, the electrons would leave with low initial velocities, and since *G* is more negative than *D*, secondary electrons or electrons which suffer energy loss could not be measured in the microammeter in series with the target, *G*. Thus, an increase in the number of electrons going through *D*, and a decrease in the electron current flowing through *G* would indicate that the primary beam was suddenly being absorbed by the potassium chloride and the number of scattered electrons had decreased.

In Fig. 5, the electron currents flowing into *D* and *G* were simultaneously plotted as a function of the energy of the primary beam striking *D*. In this case, the target, *G*, was set at three volts positive with respect to ground potential. The current penetrating the potassium chloride target (I_D) reaches a maximum between two and three volts, reversing its trend abruptly at four volts and between six and seven volts shows increased absorption. At nine volts the secondary emission threshold appears and if the voltage is further increased, the current becomes negative. Here the target will be operating in the region of true secondary emission, since the number of electrons leaving the target is greater than the number of electrons entering. The number of electrons entering the second target (I_G, the scattered current) shows a slight decrease in the region of seven volts, thus verifying the hypothesis that the increase in current I_D was due to absorption by potassium chloride.

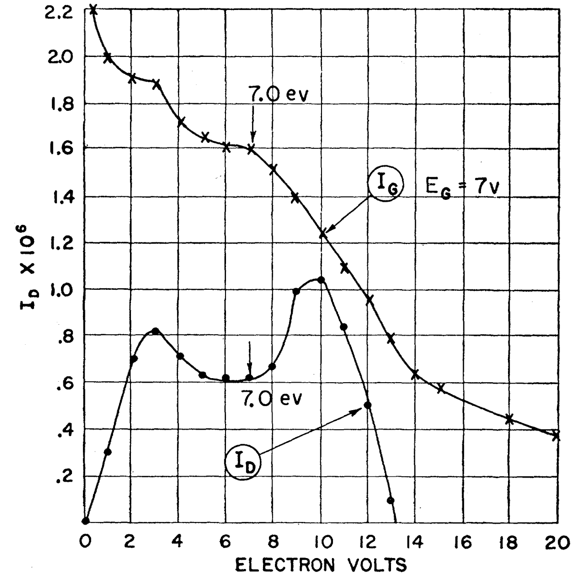

FIG. 6. Electron bombardment of a KCl surface using the cycloid structure with the second target at 7.0 volts. Currents flowing into the first target, *D*, and second target, *G*, are plotted as a function of the energy of the primary electron beam.

In Fig. 6, the voltage on the second target was set at seven volts positive with respect to ground. At three volts both backscattered and absorbed current decrease. This may indicate that electrons were scattered from the target film, but lost a small amount of energy and were not able to reach *G*. This region will be studied in more detail. Again at seven electron volts primary energy, we see an increase in absorption of the primary beam and a simultaneous decrease in current in the scattered beam.

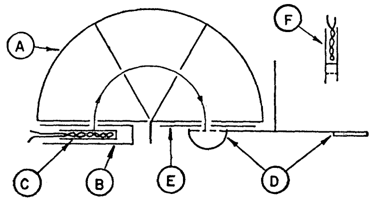

FIG. 7. Velocity analyzer tube: (A) semicylindrical velocity-analyzing chamber; (B) a focusing and accelerating grid; (C) indirectly heated cathode; (D) three rotating targets, a carbidized tantalum electron collector box, and two platinum targets; (E) limiting aperture focusing disk; (F) potassium chloride evaporator.

To summarize, these experiments demonstrate that at about seven electron volts, there is a sharp increase in absorption of electrons by the potassium-chloride-coated target and that a measurement of the back-scattered electrons can be used to substantiate this conclusion.

IV. VELOCITY ANALYZER STRUCTURE

In the third type of experimental tubes, use was made of a magnetic velocity analyzer.[8] This provided a more monoenergetic beam of primary electrons and at the same time arrangements could be made to shield the cathode rather completely from the target film. The schematic diagram for this experimental tube is indicated in Fig. 7.

The opening in *A*, *B*, and *E* consisted of slits 0.015 in. in width and 0.187 in. in length. During the secondary emission run, the analyzer voltage was maintained at

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[8] W. B. Nottingham, Phys. Rev. **55**, 203 (1939).

about 22 volts, the accelerating grid voltage near 30 volts, and the cathode filamentary voltage at 4 volts. A control run was made using the carbidized tantalum chamber as the target, during which I_D, the electron current into the target, was measured as a function of bombarding energy.

In Fig. 8, a bombardment run is demonstrated for the case of a clean platinum target.[9] Following this, successive layers of potassium chloride were deposited on the platinum until the characteristic curves of the potassium chloride appeared. One can conclude that the presence of the potassium chloride increased the reflection of electrons in the energy range above one electron volt. In addition, the discontinuities at 3.2 ev, 4.75 ev, 6.25 ev, 7.25 ev, and 9.25 ev appear.

In a modification of this magnetic deflection structure, another group of experimental tubes was constructed, similar to that described in Fig. 7, except that slits were larger in size and during bombardment the voltage on A was maintained at 358 volts. This arrangement, although it sacrificed the velocity selection, still provided the shielding of the target from the cathode, and in addition, because of the higher accelerating velocity provided more flexibility in the temperature of the cathode. In some instances, see Fig. 9, the data were taken with a technique in which the voltage was held at each point for approximately 15 seconds. In others, the data were obtained by an instantaneous method, that is, applying the voltage just long enough to take the reading and then switching off the power. The results were similar indicating that no effects of drift were involved in the measurements.

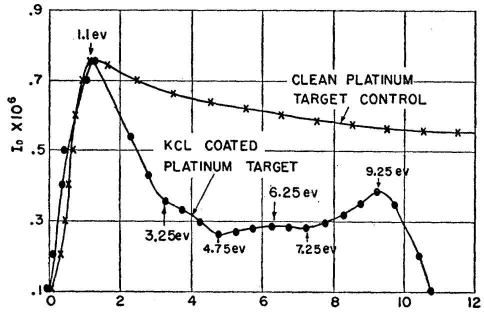

FIG. 8. Electron bombardment of a KCl surface using the velocity-analyzer tube. The current in the target circuit is plotted as a function of the energy of the primary electron beam.

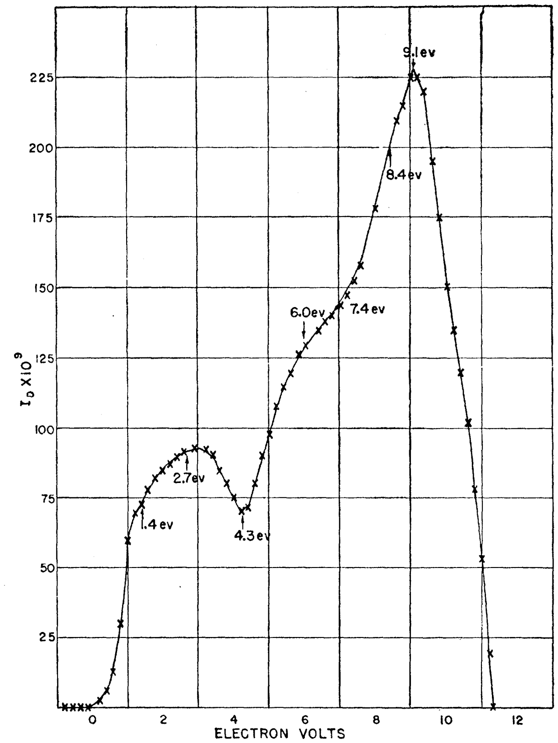

FIG. 9. Electron bombardment of a KCl surface using the velocity-analyzer tube with a dc method (voltage held at each point approximately 15 sec). The current in the target circuit is plotted as a function of the energy of the primary electron beam.

V. CONCLUSIONS

In some of the thin films coated on the dynode surface of the triodes where the films were not thick enough for high secondary emission ratios, evidence of further discontinuities was observed at approximately 10 and 11.5 ev. As the thickness of the film was increased these discontinuities were masked by the 9.2-ev peak. In Table I, there is listed a summary of the observed energies of discontinuities. It should be noted that for each energy value, the average deviation is less than 0.6 ev.

It is felt that the results are valid and consistent since regardless of the type of apparatus used, the spectrum is repeated within experimental error. The presence of the potassium chloride increases the inelastic scatter of electrons from the target. The low-energy changes need further study, but the 2.7-ev backscatter may be related to the absorption of light by F centers, a phenomenon discussed by Hilsch and Pohl, and by Seitz.[10] At 4.5 ev a strong absorption starts. Since the heat of formation of potassium chloride is of the same magnitude, we might expect the potassium chloride to start decomposing at this energy.[11]

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[9] It should be noted that the data reported here agree with that reported by Hilsch and Krenzien.[3] However, in their platinum control run the lower energy portion shows a gradual slope which indicates a spread in energy for the electrons at these low energies. This spread may very easily mask any inelastic collision effects in the potassium chloride film below 5 ev. We do not find the characteristic energy losses at 6.5 ev and 10 ev in platinum reported by E. Rudberg, Proc. Roy. Soc. (London) **A127**, 111 (1930). Rudberg's experiments were performed with incandescent targets and with higher incident energies than those reported in our work.

[10] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 567.

[11] H. Jacobs, J. Appl. Phys. **17**, 596 (1946); H. Jacobs and D. Dobischek, Phys. Rev. **81**, 1019 (1951).

TABLE I. Observed energies of bombarding electrons for which discontinuities are observed in dynode current, *vs* voltage characteristics.

Triode structure		Cycloid structure		Magnetic velocity analyzer	
Average energy at which discontinuity is observed (ev)	Number of runs out of total of 13 in which discontinuities are observed	Average energy at which discontinuity is observed (ev)	Number of runs out of total of 3 in which discontinuities are observed	Average energy at which discontinuity is observed (ev)	Number of runs out of total of 7 in which discontinuities are observed
1.1±0.5[a]	5	1.1±0.6	3	1.4±0.4	4
2.8±0.2	11	3.0±0.1	3	2.9±0.4	6
4.5±0.2	12	4.3±0.6	3	4.3±0.4	7
6.1±0.1	3	···	0	6.0±0.3	7
7.5±0.2	12	7.2±0.3	3	7.3±0.2	7
8.1±0.3	4	···	0	8.4±0.2	4
9.2±0.3	12	9.3±0.6	3	9.1±0.1	6
10.3±0.3	7	···	0	···	0
11.5±0.5	5	···	0	···	0

[a] Root-mean-square deviation is used throughout the table.

However, Wright and Woods[12] point out that this correlation is not necessary. The process of decomposition occurs over a small range of energies rather than at a sharp energy like that of the heat of formation. During the process of decomposition electrons are absorbed rather than backscattered, and the electron flow through the target film will increase.

Another strong absorption of electrons occurs near 7.2 ev. This is probably due to the exciton level of absorption discussed by Wright, Hilsch and Pohl, Krenzien, and Bruining. Near 9.2 ev the current reverses itself abruptly, indicating that here we have the threshold of secondary emission. When the films are thin, other breaks downward indicate that deeper levels are being tapped which contain a high density of electrons.

For the correspondence of optical and electron bombardment techniques to hold, one must require the work function for inserting an electron in the material to be small, since the electron in entering the film is accelerated by this potential. It so happens that for the alkali halides, calculations indicate that the work function for inserting the electron is small.[13] In this experiment with electron bombardment, the band gap is estimated at an average of 9.2 ev while measurements of photon absorption indicate 9.49 ev. Therefore, the work function for inserting an electron must be in the neighborhood of 0.3 ev. In addition, it is to be noted that the position of the calculated energy of the exciton level is 7.6 ev. By electron bombardment techniques the average level is near 7.3 ev. This furnishes further evidence that the work function for electron insertion is about 0.3 ev, and serves as a verification of the theoretical calculations which show the value to be very small.

Another point worth considering is that this technique may be applicable in the analysis of unknown films. The electron-bombardment technique offers the advantage that in one experimental test a broad range of energies may be covered, i.e., from the infrared to the soft x-ray region.

ACKNOWLEDGMENTS

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[12] D. A. Wright and J. Woods, Proc. Phys. Soc. (London) **66**, 1073 (1953).

[13] See reference **10**, p. 400.