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Inelastic Scattering of Electrons from Solids

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The energy distribution of electrons scattered inelastically from solid targets has been studied for primary energies from 50 to 400 volts, using a method of magnetic deflection. Target surfaces of Cu, Ag and Au were deposited by evaporation in vacuum immediately before the measurements were made. For certain values of the energy loss suffered by the scattered electron the curves exhibit maxima, which are characteristic of the material of the target and independent of the primary voltage in the range studied. All three metals have two maxima below 10 volts, the most pronounced one being that for Ag at 3.9 volts. These maxima appear to correspond roughly to the regions of high optical absorption for the same substance. An estimate of the depth of penetration of the scattered electron was obtained from energy distribution measurements on films of Ca, CaO, Ba and BaO of known thickness, deposited on Ag. The results indicate, that the inelastic scattering is determined by the first few atomic layers near the surface. The fresh deposits of Ca and Ba show a very high rate of oxidation, even when the total pressure is $<10^{-7}$ mm; the distribution curves for the oxide are entirely different from those for the parent metal and exhibit a rather complicated structure. Measurements of the energy distribution of scattered electrons should in some cases prove a sensitive tool for the study of surfaces. A deposit of 5×10^{14} atoms/cm^2 of Ca on CaO—less than a monatomic layer in the Ca-crystal—is easily detected by this method.

IT is a well-known fact that when the molecules of a gas are bombarded by electrons of sufficient energy, there is a re-emission of electrons from the gas which can be regarded as composed of three different parts: Elastically reflected electrons, inelastically scattered electrons and low energy secondary electrons, resulting from ionizing collisions. Since the pioneer work of Franck and Hertz the energy distribution of the inelastically scattered electrons has been studied with the object of securing information about the energy states of the molecules in question, and the transitions between such states. In the same way the secondary emission from a bombarded solid may be described as consisting of elastically reflected electrons, inelastically scattered electrons and secondary electrons proper. Some years ago it was shown[1–3] that the energy distribution of the inelastically scattered electrons exhibited a structure of maxima and minima, characteristic of the solid surface under bombardment. These occurred at a constant distance from the peak caused by reflected electrons on the energy scale, independent of the primary voltage. If the zero of the energy scale is determined by the position of this reflection peak, the curves evidently represent the distribution of the energy losses suffered by the bombarding electrons. Such curves were obtained[4] from velocity distribution measurements by three different methods, employing focusing magnetic fields, a combination of magnetic and electric fields as well as focusing electrostatic fields. The targets studied were Cu, Ag, Au, Pt and the oxides MgO, CaO, SrO and BaO; some unpublished results have also been obtained for Ni. Later Haworth[5] has reported similar results for well outgassed Mo. As in the case of a gas, the maxima in these curves were regarded as indicating that definite excitation processes were taking place in the bombarded substance, the position of a maximum representing the energy involved in that particular excitation.

A possible way of accounting for these structures theoretically was indicated in some work by Kronig and Penney[6] and in the general theory of metals by Bloch;[7] certain general results which can be derived from Bloch's work were used by Fröhlich[8] in connection with a special model in a theory of secondary emission. The theory of inelastic collisions in solids is discussed in a following paper[9] by Professor Slater and the present writer.

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[1] Brown and Whiddington, Leeds Phil. and Lit. Soc. Proc. **1**, 162 (1927).

[2] Whiddington, Leeds Phil. and Lit. Soc. Proc. **1**, 242 (1928).

[3] Rudberg, K. Svenska Vet. Akad. Handl. **7**, No. 1 (1929).

[4] Rudberg, Proc. Roy. Soc. **A127**, 111 (1930).

[5] Haworth, Phys. Rev. **48**, 88 (1935); see also **37**, 93 (1931); **42**, 906 (1932).

[6] Kronig and Penney, Proc. Roy. Soc. **A130**, 499 (1931).

[7] Bloch, Zeits. f. Physik **52**, 555 (1928).

[8] Fröhlich, Ann. d. Physik **13**, 229 (1932).

[9] Slater and Rudberg, Phys. Rev., following article.

The early experimental work[4] was unsatisfactory because of the presence of vapor from a waxed joint in the tube; in order to keep the bombarded surface clean it was held at incandescence during the measurements. It now appears that this method, while successful in the case of the oxides, did not always give a well-defined surface in the case of metal targets. The present paper is a report on some work during the last few years, in which the distribution curves for Cu, Ag and Au have been remeasured under more satisfactory vacuum conditions.[10] In connection with the problem of the depth of penetration for inelastically scattered electrons, the scattering from films of Ca, Ba, CaO and BaO on Ag has also been studied.

APPARATUS AND METHODS

The essential features of the apparatus are indicated in Fig. 1. Most metal parts are made of sheet copper. A beam of electrons of nearly uniform speed, obtained from an electron gun G, is allowed to fall on the target T in question under an angle of incidence of about 45°. The target is surrounded by a cylindrical shield S to retain the bulk of the secondary emission. The total current to T and S thus measures the bombarding current and is kept constant during a run. A narrow beam of the re-emitted electrons from T escapes through a small opening in S, in a direction at right angles to the primary beam. Through a narrow slit it enters the deflection box B, where the energy distribution in the beam is analyzed. The entrance slit and two other slits in the box define a circular path, which electrons of the proper speed are made to follow by means of a magnetic field, perpendicular to the path. Two extra partitions with slits serve to trap electrons scattered from the walls of the box. The electrons emerging from the third slit are caught by the collector C. With this arrangement, the energy distribution can be measured in two different ways. In the first, the box is kept at the same potential as T and S, and the current i received by C is measured as a function of the magnetizing current I in the Helmholtz coils. The energy distribution is then given by i/I^2 *vs.* I^2, except for constant factors. In the second method, the magnetic field is kept constant at a suitable value, and i is measured as a function of a variable voltage v applied between the target and shield unit and the box. The disadvantage with the second method, which yields results on an energy scale directly, is that the effective volume within which the electron trajectories must fall inside S in order that the electrons may reach C, varies both in shape and size with the applied voltage v, in a way which is difficult to correct for. This is most serious for low bombarding voltages V, when the range over which v is varied is not negligible compared with V. Hence the first method has been used except for a few measurements on Ag, where small parts of the energy distribution were studied with a variable accelerating voltage v.

The primary voltage V, the primary current drawn by T and S, as well as the magnetizing current in the second method, were kept sensibly constant during each run, the constancy being checked by compensating devices with galva-

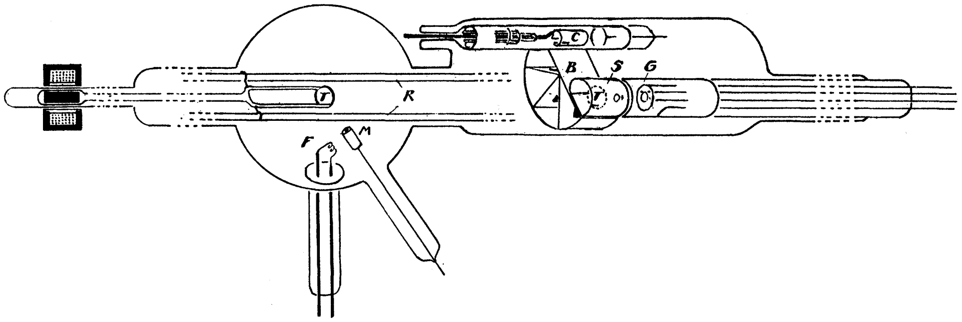

FIG. 1. Apparatus.

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[10] The material in this part of the paper was presented before the Washington Meeting of the Am. Phys. Soc., April 28, 1934. Phys. Rev. **45**, 764 (1934).

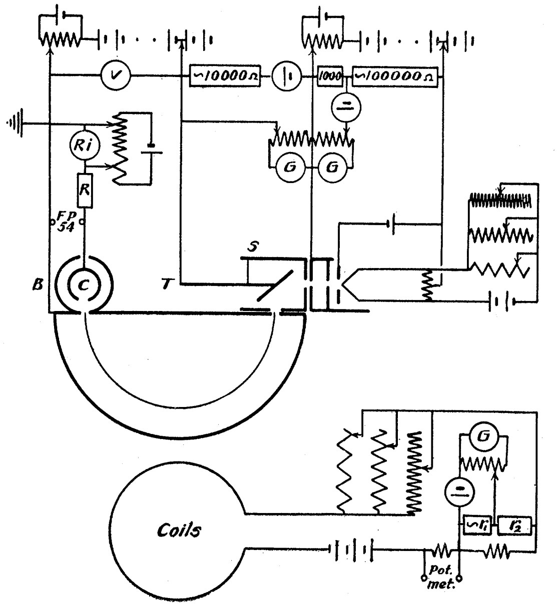

FIG. 2. Wiring diagram.

nometers. In the first method, I was measured with a potentiometer. The collector current i was determined by compensation of the drop produced in a high resistance R, with an FP-54 electrometer tube serving as null instrument. The electrical connections are shown in Fig. 2.

PREPARATION OF TARGET SURFACES

All the targets studied were prepared by evaporation in vacuum directly in the tube. A small disk T of sheet molybdenum is attached to a magnetically operated slider, Fig. 1, one end of which is resting on a track of glass rod R. Thus T can be withdrawn from the position for measurement inside S into the bulb to the left, where it can be outgassed by bombardment from the filament F or covered with a fresh evaporated layer of the metal to be studied. In the case of Cu, Ag and Au the metal is contained in a molybdenum crucible M, which can be heated by bombardment from F. Two such crucibles are provided.[11] The films obtained in this way were sufficiently thick, so that no effect of the backing substance could be detected. As a matter of fact the backing material soon became quite complex, since a new surface was frequently formed by evaporation and surfaces of different metals were often studied alternatingly. In one case such a target with alternate layers of Cu and Ag was heated to incandescence, so that a reaction took place. The resulting surface upon cooling gave distribution curves quite different from those for Cu and for Ag.

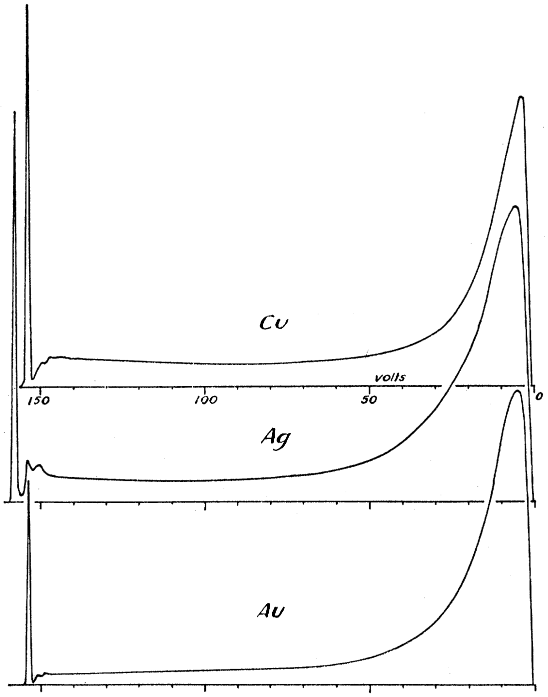

FIG. 3. Energy distribution of scattered electrons.

Ca and Ba were evaporated at accurately controlled temperatures from small molybdenum furnaces of a type described in connection with the measurement of the vapor pressures for these metals.[12, 13] The rate at which the material was deposited could therefore be computed from the geometrical arrangement and the known vapor pressure.

The apparatus was subjected to the customary outgassing by baking at 400°C and high frequency induction heating for the metal parts. It was pumped continuously. The pressure with the tube operating did not exceed the order of 1×10^{-7} mm, as measured with an ionization gauge, calibrated for air.

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[11] I am much indebted to Dr. H. W. B. Skinner and Dr. H. M. O'Bryan for valuable suggestions in regard to crucible design.

[12] Rudberg, Phys. Rev. **46**, 763 (1934).

[13] Rudberg and Lempert, J. Chem. Phys. **3**, 627 (1935).

RESULTS FOR Cu, Ag AND Au

Typical distribution curves for Cu, Ag and Au are shown in Fig. 3, for a primary energy of about 150 volts. The sharp peak to the left in each curve represents the elastic scattering. This serves to locate the zero of energy loss in the subsequent curves. The primaries themselves have a distribution, due to temperature and filament drop, about 0.5 volt wide (Halbwertsbreite). The width of the reflection peak is satisfactorily accounted for by this original distribution and the finite resolving power of the analyzer which corresponds to a width $\Delta V = 0.008\,V$ on an energy scale. It is evident that the bulk of the emission is made up of low energy secondaries which exhibit the broad maximum to the right for low energies. It is possible that a closer examination of this low energy part might reveal a structure such as has recently been reported by Haworth in the case of molybdenum after prolonged heat treatment.[5] Inelastic collisions are indicated by the part of the curve immediately to the right of the reflection peak. When the primary voltage is changed this part shifts bodily, whereas the low energy side of the curve remains essentially the same. In the following Figs. 4, 5 and 6 attention is confined to the inelastically scattered electrons. As may be inferred from Fig. 3 the top of the reflection peak would fall well outside the figures on this scale; this peak, although not indicated, was always measured in order to locate the zero position on the energy loss axis.

For reasons which are not quite clear it appears to be more difficult to obtain well-reproducible

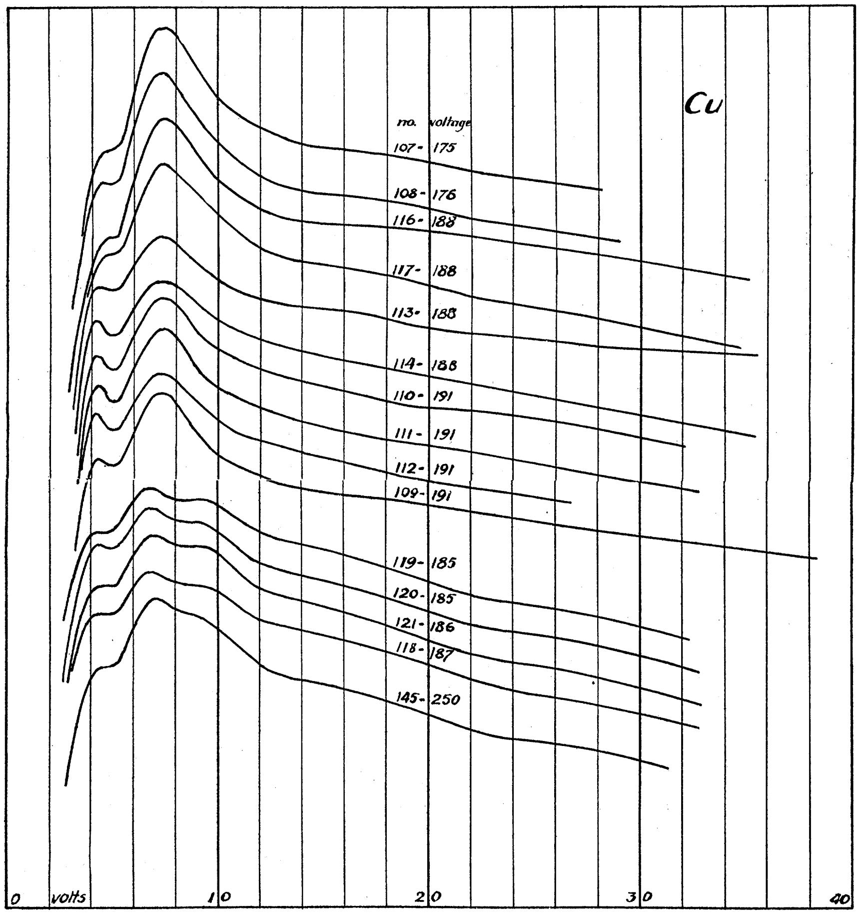

FIG. 4. Copper.

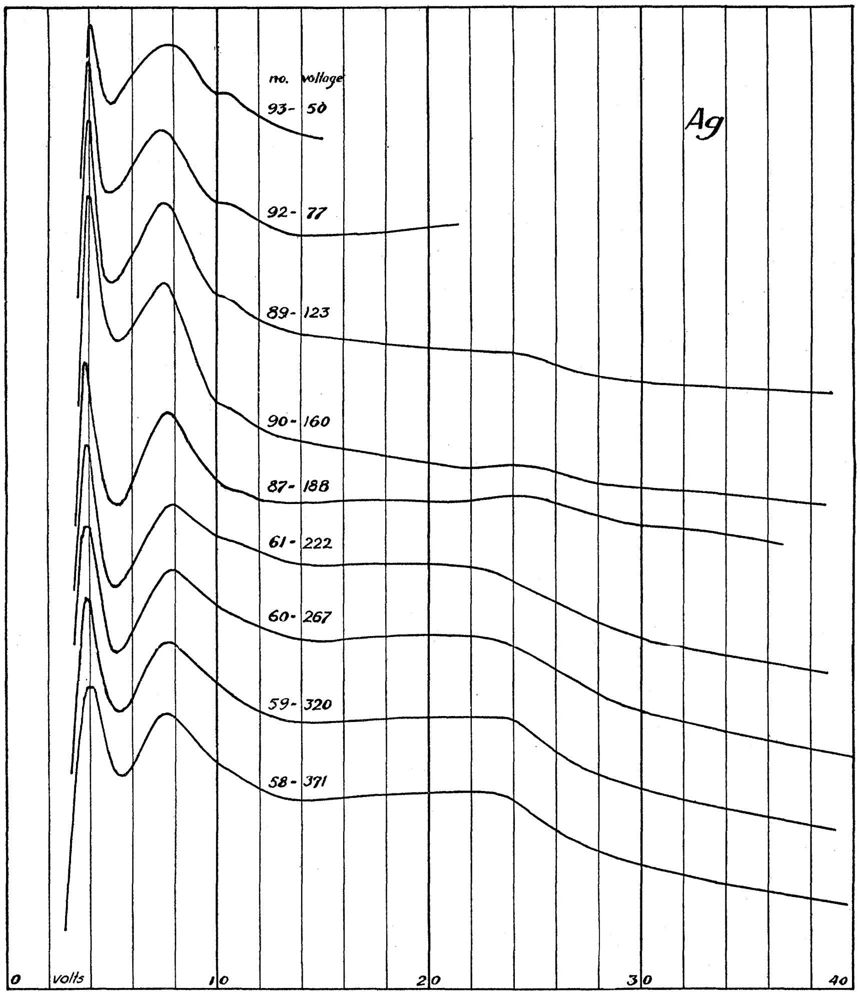

Fig. 5. Silver.

curves with copper than with the other metals, but Fig. 4 gives a fair representation of the results. The curves are labeled by the serial number and the primary voltage, the latter increasing downward. The base metal is silver, molybdenum or gold. The first hump is always present, the second is present but varies in importance and in some curves, like the group at the bottom of the figure, there is a third hump, which in the earlier stages of evaporation actually rose above the second maximum. This may possibly indicate that it is characteristic of some impurity distilling over with the metal.

Curves for silver are shown in Fig. 5. They exhibit the sharpest maximum found so far at 3.90 volts, and a broader maximum at about 7.8 volts. The range of primary voltage is from 50 to 370 volts. The broadening of the peak for higher voltages is of course due to the decreasing resolution of the velocity analyzer for higher energies.

In the case of gold, Fig. 6, there are again two main maxima, the first one for an energy loss of 3.05 volts. For this metal there is also a very broad hump around 24 volts. The relative proportion of higher energy losses is greater than for copper and silver. For high primary voltage, however, the gold curves bend down in this region like the others. The yield per primary, in the direction studied and for the voltage range employed, is less than for Cu and Ag by a factor of 2 to 4.

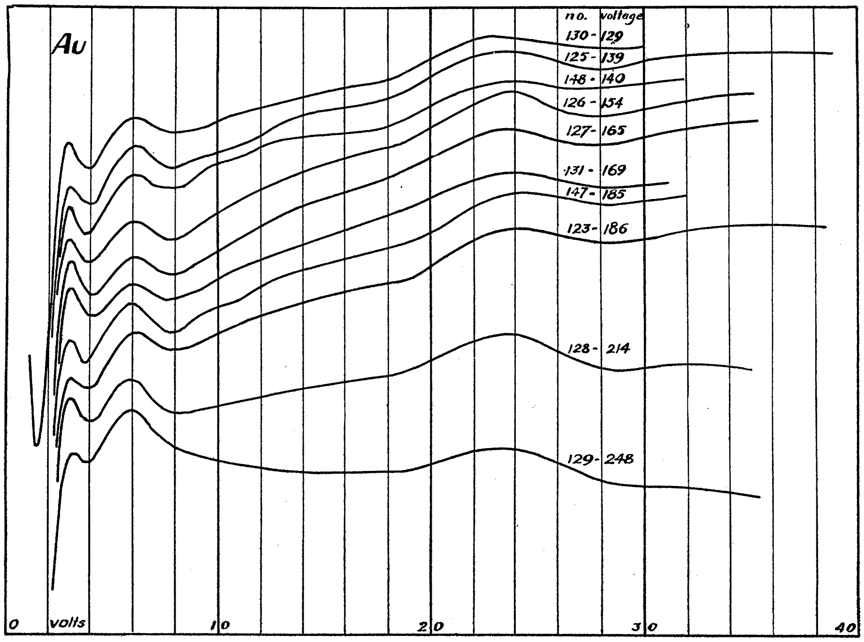

FIG. 6. Gold.

Typical curves for all three metals are collected in Fig. 7, which also illustrates the spacing of experimental points. Those for Cu and Ag have been shifted upwards by amounts indicated to the left. It will be seen that the curves for these three metals are similar in that there is a deep valley next to the reflection peak, which indicates the absence of inelastic collisions with small energy losses; this is followed by two main maxima. The positions of these in the case of Ag and Au are such that the second maximum could result from two of the processes giving rise to the first; however, the wide difference in shape, at least in the case of Ag, makes it very unlikely that this is the sole cause of the second maximum.

The fact that the position of these maxima is independent (in the range investigated) of primary voltage, of the potentials of other parts of the tube such as the electron gun, and of whether they are measured by a varied accelerating voltage or by a varied magnetic field—should prove conclusively, that these maxima are connected with characteristic transitions in the target. A separate experiment showed that the sharp silver maximum could be reproduced within 40 seconds after a fresh surface had been formed by distillation. At a pressure of 1×10^{-7} mm the formation of a monomolecular layer by the residual gas requires at least that time if every

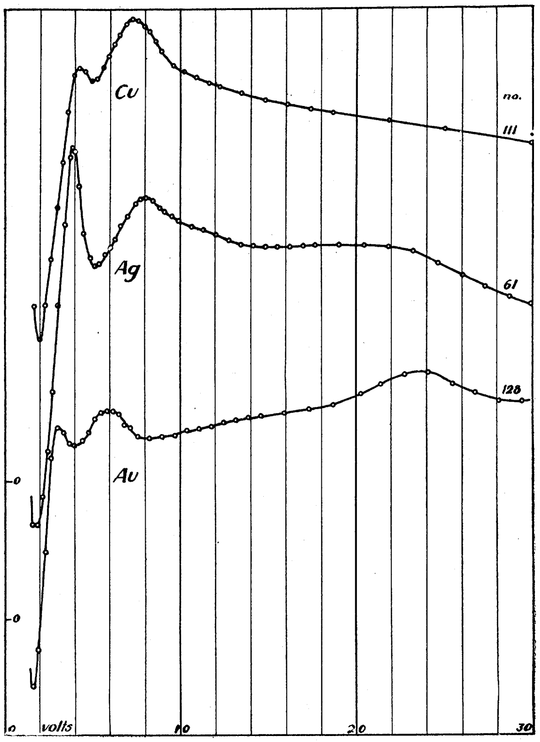

FIG. 7. Distribution of energy losses for Cu, Ag and Au.

TABLE I. *Values of the energy loss for the first maximum in silver and in gold.*

Target Ag			Target Au		
SER. NO.	VOLTAGE	ENERGY LOSS (volts)	SER. NO.	VOLTAGE	ENERGY LOSS (volts)
93	50	3.95	130	127	2.95
92	77	3.85	125	139	3.00
63	109	3.65	148	140	2.95
89	123	3.85	126	154	3.10
62	141	3.75	133	154	3.15
90	160	3.95	132	164	3.15
212	175	3.85	127	165	3.05
252	175	3.90	131	169	2.95
87	188	3.80	122	183	2.90
56*	194	3.80	144	185	3.10
57	194	3.75	123	186	2.95
64*	196	3.90	128	214	3.05
65*	196	3.90	124	217	2.95
66*	196	3.90	129	248	3.15
67*	196	3.85			
68*	196	3.90			
61	222	3.85			
232	250	4.10			
173	250	4.00			
174	250	4.05			
60	267	3.80			
88	296	4.10			
59	320	3.80			
58	371	3.90			
mean of 24 values		3.88	mean of 14 values		3.03
	or	3.90		or	3.05
probable error in mean ±0.05 volt					

* Measured by method of variable accelerating voltage.

hitting molecule sticks. Even granting that the pressure of residual gases during evaporation might have been somewhat higher than 10^{-7} mm this result makes it difficult to ascribe the maximum to adsorbed gases.

The values obtained for the position of the first maximum for silver and for gold are summarized in Table I.

COMPARISON WITH OPTICAL DATA

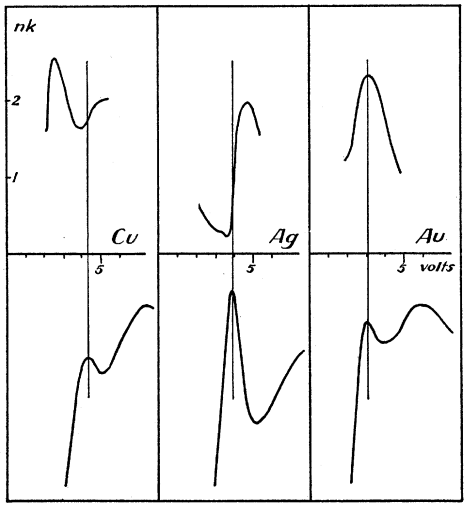

FIG. 8. Distribution of optical transitions (upper) and of electron energy losses (lower).

In a given system showing linear absorption, the number of transitions per second in unit frequency range at a frequency ν may be written as $T_\nu\overline{E_\nu^2}$ and the rate of absorption of energy as $h\nu T_\nu\overline{E_\nu^2}$, if E_ν is the electric vector of the radiation field. If the complex refractive index of the substance for this particular frequency is $n-ik$, the current density for the component in phase with the field is νnkE_ν, so that the rate of absorption of energy per unit volume is $\nu nk\overline{E_\nu^2}$. Hence T_ν is proportional to the product nk. Kronig[14] and others have shown, in the case of the Bloch-Sommerfeld model of a metal, that there exists a selection rule for the electronic transitions which can be produced by absorption of radiation. According to this rule, which results from the space periodicity of the lattice and therefore holds for crystalline solids in general, transitions can only take place between states having the same (3-fold) momentum quantum number: $\mathbf{k}_0'=\mathbf{k}_0$. The probability of such a transition is proportional to $L^2\overline{E_\nu^2}$, where L is the moment $\int\psi\mathbf{r}\psi'^*d\tau$ for the two states ψ and ψ' in question. Thus $T_\nu=\text{Const}\cdot\sum L^2$. It can be shown that, when the energy loss is very small compared with the energy of the bombarding electron, a similar selection rule should be approached for the case of excitation by electron impact, and that the probability of excitation is determined by L^2 also in this case.[9] Thus one would expect the curve for nk as a function of the energy $h\nu$ to be similar to the distribution curve for small energy losses for the same substance, at least when the bombarding voltage is high. Fig. 8 shows a comparison of nk and the energy loss curves for Cu, Ag and Au, the frequency being measured in equivalent electron volts. The constants used are those given by Minor[15] (Cu, Ag) and Meier[16] (Au), in all cases measured in air. It is known that optical constants vary considerably with the surface condi-

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[14] Kronig, Proc. Roy. Soc. **A124**, 409 (1929).

[15] Minor, Ann. d. Physik **10**, 581 (1903).

[16] Meier, Ann. d. Physik **31**, 1017 (1910).

tions, which probably accounts for the conflicting results often found by different observers. It is possible, therefore, that the constants used could refer to a material quite different from that for which the distribution of energy losses has been measured. This is more likely to be the case with copper than with the other two; the *nk*-curve given for this metal in Fig. 8 may actually be the curve for cuprous oxide. The other two metals show a fair agreement as to the position of the main peak, although the optical maximum appears shifted to higher energies for Ag. The optical measurements by Pfestorf[17] show for Au a maximum at a somewhat higher energy than that given by Meier's data, but his points are considerably more scattered. Pfestorf's data for Cu give indication of the minimum in the *nk*-curve of Fig. 8, but do not show the maximum.

EXPERIMENTS WITH FILMS OF CALCIUM AND BARIUM AND THEIR OXIDES

The theory of these collision processes, which is given in a following paper, is based on the model of the inside of a metal infinite in extent. In the experiments, however, electrons are shot into the metal (and escape from it to be measured) through the surface. It is therefore conceivable that the collisions take place in a region at the surface, where the wave functions are quite different from those in the interior of the metal. No satisfactory theory is available for this region at present.

In order to obtain some information about the depth of penetration, it was planned to cover a substance of well-defined energy loss characteristics, such as silver, with some other material, and study the changes in the energy loss curve as a function of the thickness of the latter. The cover substances chosen were calcium and barium, since the useful part of their vapor pressure curves appeared to fall in a range available for controlled evaporation, yet high enough so that one might expect the reflection from a clean, cold surface to be negligible. Special long exposure tests with the target withdrawn to such a position, that it could be reached by atoms reflected from the walls but not by the direct beam, actually indicated that such reflection was negligible. In the case of calcium, the target rested against the flat bottom of a reentrant tube (not shown in Fig. 1) during exposure to the atomic beam from the gun. Some of the films were deposited while this tube was cooled by CO_2-ice and acetone, others with the tube at room temperature. No difference could be detected.

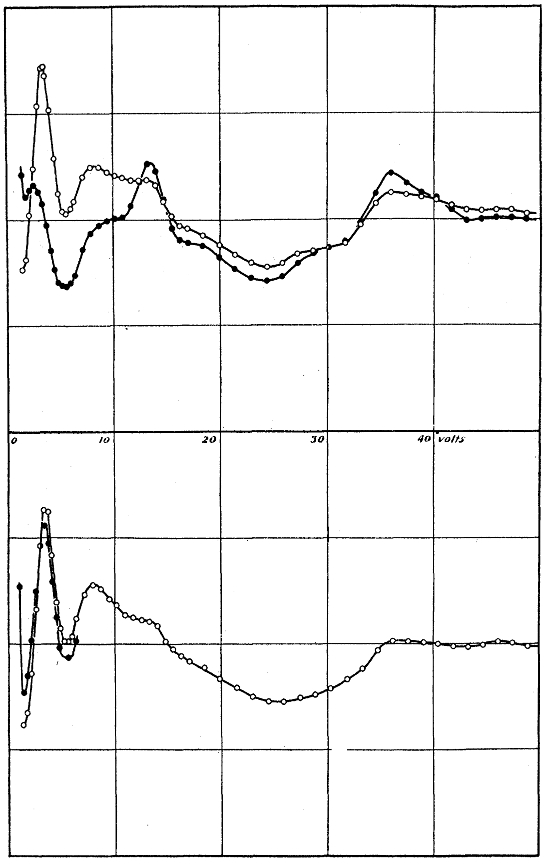

FIG. 9. Showing "aging" of Ca-deposits. White circles: fresh deposit, black: 30 minutes old. Lower curves with continuous Ca-evaporation.

For convenience the amount of metal per unit area has been expressed as the number of single layers to which it would correspond, if arranged as in the planes of closest packing in that particular metal, the (111)-planes for the face-centered Ca, the (110)-planes for Ba. It is not supposed that this is the actual arrangement of the deposits, the structure of which is as unknown as that of the underlying substance.

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[17] Pfestorf, Ann. d. Physik **81**, 906 (1926).

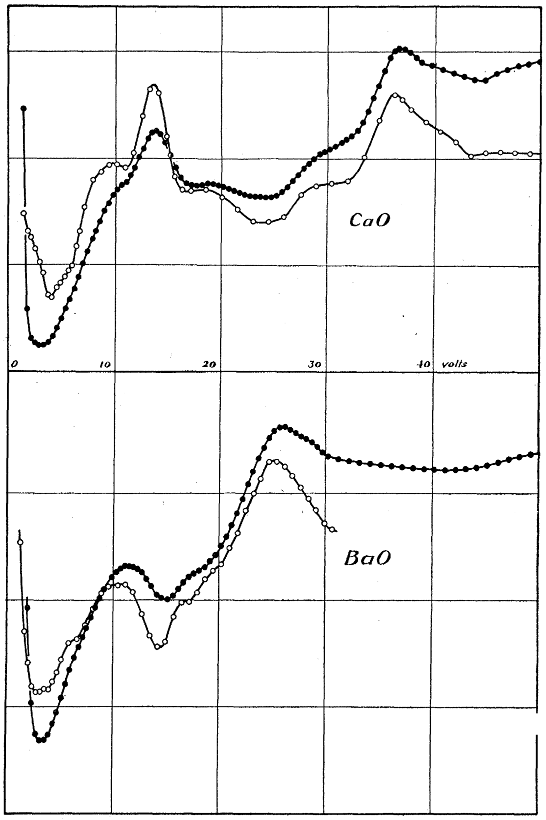


FIG. 10. Distribution curves for "aged" Ca- and Ba-deposits (white circles) compared with old data for CaO and BaO (black).

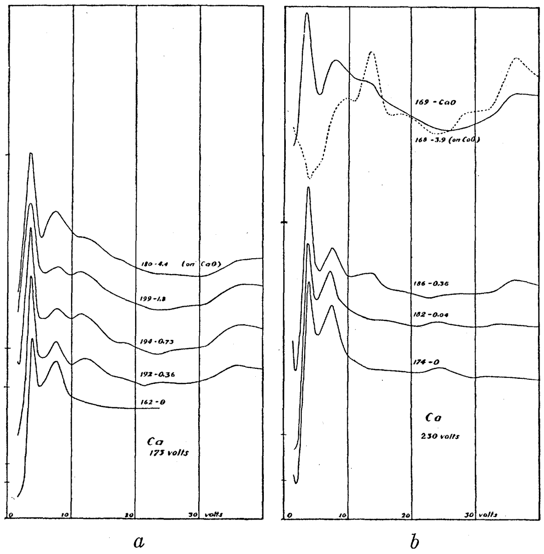
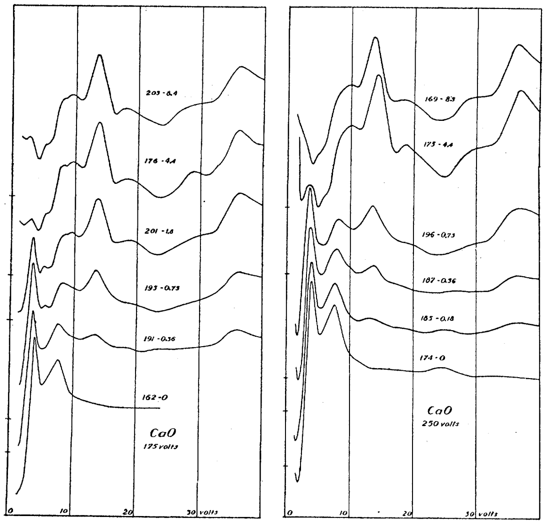


FIG. 11. Calcium on silver.

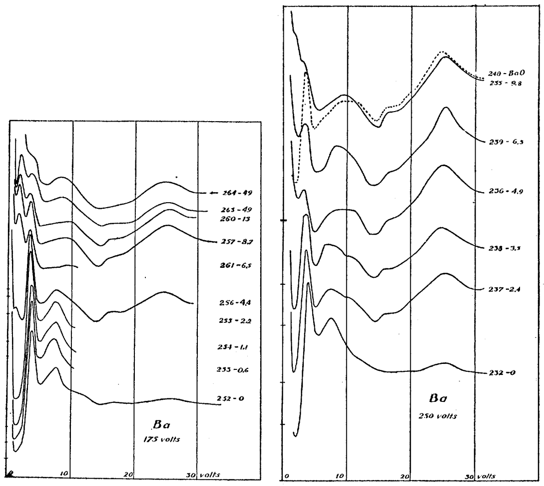
It was found both in the case of calcium and barium, that a fresh deposit gave a distribution curve quite different from that obtained from the same target after a few hours standing in a high vacuum. The change was quite noticeable even in the time (about 30 min.) required for a run; the curve obtained from a deposit a few hours old could be reproduced a week later, if no further evaporation took place. This behavior was suspected to be due to a reaction between the freshly distilled Ca- or Ba-metal and some constituent of the residual gas in the tube, at a pressure $\leq 10^{-7}$ mm, the distribution curve after "aging" being due to a compound. The following facts substantiate this hypothesis and are believed to prove that the compound formed is the oxide.

Fig. 9 shows two pairs of curves for deposits of Ca. The white circles represent measurements immediately after the film was formed, starting with low energy losses. The black points were measured 30 min. later, also from left to right. Conditions in the case of the upper pair were the same as when the lower pair was measured, except that in the latter case the Ca-gun was left on in the evaporation chamber during the measurement. In this way the walls of the chamber were continuously being covered with a fresh coating of Ca, which acted as a getter removing the active gas from the tube. This evidently greatly increased the "lifetime" of the first high peak, which is the most characteristic feature of the pure calcium curve. Several years ago energy distribution curves for CaO and BaO were measured with a different apparatus.[4] The nitrates were deposited on platinum, by evaporation of the water from aqueous solutions, and these converted into the oxides by further heating in air. Fig. 10 shows a comparison of the present measurements (white circles) on "aged" deposits of Ca and Ba and the old curves (black circles) for the corresponding oxides. The latter ones were measured according to the second method described (with an accelerating voltage v), which accounts for the gradual rise with increasing energy loss. Evidently every important feature of the old curves reappears in the present measurements on the "aged" deposits. These will therefore be called oxides.



a *b*

FIG. 12. Calcium oxide on silver.



a *b*

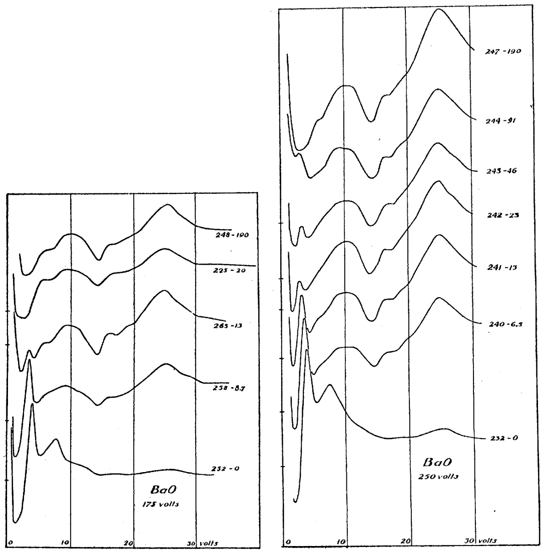
FIG. 13. Barium on silver.

In the measurements on Ca- and Ba-films the gun was usually kept at evaporation temperature to slow down the rate of reaction, and the curves were taken as fast as possible, starting, as a rule, from the end of low energy losses, where the peaks are sharper. In this way the distribution for higher energy loss will exhibit, to some degree, features characteristic of the oxide. These can be distinguished from those of the metal itself by measuring each particular part of the curve separately, immediately after evaporation. In a new apparatus, now under construction, it will be possible to have the target sprayed continuously with the metal during the measurements.

Fig. 11 shows results for Ca-films at two voltages. The curves are labeled by their serial number and the thickness of the film in the unit defined above (thickness $1=7.46\times10^{14}$ atoms/cm^2). The backing is freshly distilled Ag, except in the top curve in *a*, where the film is backed by an old oxidized Ca-deposit. The dotted curve No. 169 shows the result of "aging" on the film which yielded No. 168 immediately after evaporation. Evidently the strongest oxide peaks are already beginning to appear in the curve for the fresh deposit. It will be seen that Ca has a strong peak very near the position of the sharp Ag-maximum and a broader hump in the region of the second maximum for silver. This makes it impossible to state at what thickness the Ag-characteristics are obscured by the Ca-deposit, but it is evident that the film affects the distribution curve already for a thickness less than 1.

Energy loss curves for CaO on Ag are given in Fig. 12. The thickness values refer to the Ca-film before oxidation. In each case the deposit was allowed to "age" for a sufficiently long time before measurement, so that no further change in the curve would take place. The oxide maxima begin to appear for a thickness less than 0.5, but the sharp silver peak is not completely obscured by a thickness 10 times greater than this.

The results for Ba-films on Ag are shown in Fig. 13 (thickness $1=5.63\times10^{14}$ atoms/cm^2). These films appear to oxidize even more rapidly than the Ca-deposits. Thus the BaO-features appear in all the curves at higher energy losses. The curves were measured from left to right, so that the part for small energy losses, in which the characteristic features of Ba fall, is representative of Ba-metal. A thick deposit of Ba, or a film of Ba on BaO, shows no maximum near the silver peak, although thin films of Ba on Ag seem to enhance that peak. Ba has a low energy maximum at 1.7 volts; this is so close to the reflection peak, that the maximum is only resolved at low primary voltage. At 250 volts it is suppressed by overlapping from the strong reflection peak, except in the top curve, although its presence is indicated in the other curves by the trend in this



a *b*

FIG. 14. Barium oxide on silver.

TABLE II. *Measured energy losses corresponding to the top of Ag peak for Ca and Ba films on silver.*

THICKNESS	SER. NO.	VOLTAGE	ENERGY LOSS (volts)
	Ca film		
0.04	182	250	3.95
0.04	183	250	4.10
0.15	184	250	3.90
0.36	186	250	3.85
0.36	190	90	3.75
0.36	192	175	3.75
0.73	194	175	3.60
0.73	198	90	3.60
0.83	163	250	3.65
1.3	164	250	3.50
1.8	199	175	3.60
2.2	166	250	3.65
3.9	168	250	3.50
4.4	170	250	3.55
4.4	179	90	3.35
4.4	180	175	3.55
	mean of 10 values		3.56
		or	3.55
	CaO film		
0.18	185	250	3.95
0.36	187	250	3.80
0.36	188	175	3.75
0.36	189	90	3.60
0.73	195	175	3.50
0.73	196	250	3.60
0.73	197	90	3.45
1.8	200	175	3.50
1.8	201	175	3.50
2.2	165	250	3.40
4.4	175	250	3.60
	mean of 7 values		3.51
		or	3.50

THICKNESS	SER. NO.	VOLTAGE	ENERGY LOSS (volts)
	Ba film		
0.6	253	175	3.85
0.8	213	175	3.60
1.1	254	175	3.90
2.2	255	175	3.85
2.4	214	175	3.45
2.4	237	250	3.65
3.3	217	175	3.50
3.5	238	250	3.75
4.1	219	175	3.10
4.4	256	175	3.60
4.9	215	175	3.05
4.9	220	175	3.20
4.9	233	250	3.60
4.9	236	250	3.40
6.5	239	250	3.45
6.5	259	175	3.40
6.5	261	175	3.35
6.8	217	175	3.50
8.7	257	175	3.55
13	260	175	3.40
	mean of 16 values		3.43
		or	3.45
	BaO film		
4.9	216	175	3.05
6.5	240	250	3.45
8.7	258	175	3.35
13	241	250	3.30
13	265	175	3.45
23	242	250	3.05
46	243	250	3.40
91	244	250	3.15
	mean of 8 values		3.28
		or	3.30

TABLE III. *Energy losses for Ba targets.*

TARGET	THICKNESS	SER. NO.	VOLTAGE	ENERGY LOSS (volts)
Ba	4.1	219	175	1.80
	4.4	256	175	1.45
	4.9	215	175	1.75
	4.9	220	175	1.65
on BaO	6.5	249	175	1.70
	6.5	261	175	1.65
	8.7	257	175	1.70
on BaO	9.8	269	175	1.60
	13	260	175	1.75
	20	221	175	1.80
	49	263	175	1.45
	202	266	175	1.85
	202	267	175	1.50
		mean of 14 values		1.68
			or	1.70

region. The dotted curve shows the "aging" effect on the deposit of No. 239 and the extent to which BaO-maxima appear in the Ba-curves for higher energy loss. The Ag-peak shows up more strongly in No. 240 than in No. 239, indicating that the deposit becomes less opaque to the electrons when it is oxidized. Definite Ba-characteristics appear at a thickness about 4, although the enhancement of the Ag-peak can probably be noticed at a thickness of 2.

Fig. 14 shows energy loss curves for BaO on Ag. The oxide maxima appear for thicknesses less than the smallest one shown here.

The measured energy losses corresponding to the top of the Ag-peak and the peaks for Ca and Ba are collected in Table II and III.

DISCUSSION

In the cases where sharp maxima do not overlap, CaO, Ba and BaO on Ag, the results indicate that the excitation process responsible for the Ag-peak still takes place when the exciting (and scattered) electron has to penetrate a layer several atoms deep. If the penetration is of the same order in other materials as in these three substances, the distribution of small energy losses can not be determined entirely by the surface atoms, but must depend on the structure of the solid below. In that case a theory of these processes, based on the electronic model for the interior of a large crystal, would be expected to give a reasonable approximation to the actual situation.

It takes several layers of Ba before the 1.7-volt peak appears. The maxima for CaO are present in their proper places for a thickness <1 and show no appreciable change (other than a gain in strength) as the thickness is increased. These maxima, however, occur for higher values of energy loss and they are rather broad, though distinct. Thus they are possibly chiefly determined by the nature of the atom or molecule in question, and only to a lesser degree by the forces from neighboring elements in the structure; the shifts in energy due to changes in the latter are probably unimportant compared to the width of these maxima. The situation appears to be different in the case of Ca. For a thickness <1 of this metal on CaO the sharp peak, which in Fig. 11 is superposed on the prominent Ag-maximum, shows up in the same position as for thick films. This may indicate, that a backing of CaO happens to act in just the same way on a single layer of Ca, as a backing of metallic Ca. If the distribution of energy losses results from the cooperation of several atom layers below the surface, one would in general expect a difference between the curve for a single layer and that for the thick metal. However, if we imagine a solid of N^3 atoms gradually built up from free atoms, so that first N atoms are brought together to form a string, then N of these strings lined up to make a layer and finally N layers piled up in the proper way—then the greatest change in the electronic energy levels would be expected to take place in the first step, and a relatively small change in the last.

That the surface layer in general influences the position of the energy loss peak for the underlying substance is evident from Table II. In each case, all the values for films above a certain thickness (as indicated by a horizontal line) were included in the mean. The spread of the individual values is fairly wide, but the shift from the pure Ag-value of 3.90 volts is evidently much larger than the probable error in the mean, which is of the order ±0.05 volt. Since at least part of the peak with Ca-films represents a characteristic energy loss for this substance, there is definite evidence of the effect in question only for films of CaO, Ba and BaO, where the shift is of the same magnitude, but increasing in this order. It is believed that this represents a general shift in the energy levels of the underlying silver target, due to the forces exerted by the adsorbed film. This may be in the nature of a general change of the potential field in the target, or may result from a change in the interatomic distances, produced by the presence of the film. For "nearly free" electrons in a crystal the energy associated with a given set of quantum numbers, and therefore the energy difference for two states of given quantum numbers, is inversely proportional to the square of the lattice spacing. If the energy shift of 10–15 percent for the Ag-peak is to be accounted for in this latter way, it would indicate a linear expansion of 5–8 percent. A calculation by Lennard-Jones and Dent[18] for ionic crystals shows that the lattice spacing at the free surface should be smaller than that in the interior by an amount of the order of 5 percent. It is possible that a contraction of the same order exists at the surface of a metal. When this is covered by some other substance, so that it is no longer free, the lattice at the surface may effectively approach an interior lattice, with a corresponding increase in spacing.

In the preceding discussion it was assumed, that the evaporated deposits are spread uniformly over an area comparable with the apparent surface area of the target. This must certainly be true at the moment the deposits are formed, since there is no reflection. It is conceivable that patches of high concentration, separated by large bare regions, are subsequently formed by the process of surface migration. While this can not be disproved, it does not appear likely in view of some of the experimental results. Thus it is hard to understand the high yield of CaO-collisions with deposits <1, if the greater part of the surface is bare. The rate of migration over a bare surface can not be high at the temperature used. In some experiments the back of the target was exposed to the metal gun, so that a deposit several units thick should have been formed. The front side, however, when tested always gave the curve characteristic of Ag, showing the absence of migration round the edge. On the other hand the apparent electron

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[18] Lennard-Jones and Dent, Proc. Roy. Soc. **A121**, 247 (1928).

transmission through thick BaO-deposits (Table II) may indicate the presence of thin regions, formed in the process of oxidation of thick Ba-films. That these regions are not bare is evidenced by the shift of the Ag-peak.

The distribution of energy losses appears to offer a new, sensitive tool for the study of surfaces and surface layers. If the substance of the film has a distribution curve reasonably different from that of the backing material, layers only a few atoms thick can be detected. This test appears to be somewhat more sensitive, and less likely to alter the conditions studied, than present electron diffraction methods employing high voltages.[19] In the case of Ca, the metal can be detected in a thickness decidedly <1 on a backing of the oxide. This is now being used to study the surfaces of thermionic emitters made from CaO and BaO. For the detection of small amounts of foreign material on a surface this method is probably never as sensitive as thermionic measurements, but in favorable cases it has one great advantage compared with these: it not only detects, it identifies.

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[19] The diffraction beams obtained with single crystals at low bombarding voltages appear to be even more sensitive than the energy loss distribution to a small coverage of foreign material on the surface: Farnsworth, Phys. Rev. **49**, 605 (1936).

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Theory of Inelastic Scattering of Electrons from Solids

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The general properties of the single electron wave functions for a crystal are discussed, and an expression derived for the probability of excitation by electron bombardment as a function of the two electronic levels involved in the transition. When the excitation energy is small compared with the energy of the bombarding electron, the relative transitions probabilities approach those for excitation by radiation. A detailed calculation has been carried out for the case of solid copper, for which the energy levels are now known from other work. Approximate wave functions—of the atomic type for the lower state, free-electron-like for the upper state—were used to evaluate the transition integrals. The calculated distribution curve for the inelastically scattered electrons is in fair agreement with the experimental curve in the region of small energy losses: the rapid rise from small values and the following two maxima exhibited by the experimental curve are all reproduced in their proper positions. The departures for higher losses are attributed to the fact that the free-electron-like wave functions used are not a proper approximation to the actual functions in this region.

THE problem of inelastic scattering of electrons in matter, early discussed for relatively fast electrons by Thomson[1] and others as a problem of atomic scattering, was treated very completely by Bohr[2] on the basis of classical electron theory. More recently, quantum theory has been applied particularly to the scattering by free atoms. Fröhlich[3] has given a wave-mechanical treatment of the inelastic scattering from metals, using a special Bloch-Sommerfeld model for the metal. He was able to deduce from this the characteristic features exhibited by the distribution of the low energy secondary electrons. In the present paper we consider the transition probabilities for electronic excitation on the basis of the general electron theory of solids. In experiments on inelastic collisions, the target is usually bombarded by a nearly parallel, homogeneous beam of electrons and the energy distribution is measured for those electrons which are scattered into a small solid angle about a definite fixed direction with respect to the target and the incident beam. Tests with polycrystalline targets have shown the energy distribution to be essentially independent of both this latter direction and of the angle of incidence. For this reason we have calculated the total probability of all

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[1] J. J. Thomson, *Conduction of Electricity through Gases*, 343 (1903).

[2] N. Bohr, Phil. Mag. **25**, 10 (1913); **30**, 581 (1915).

[3] H. Fröhlich, Ann. d. Physik **13**, 229 (1932).