Soft X-Rays from (100) and (111) Faces of Copper Single Crystals

MORGAN L. WILLIAMS, *Brown University*

(Received July 13, 1933)

Between 90 and 220 volts 14 critical potentials were found for both the (111) and the (100) faces. Each break is the same within 1.5 volts for the two targets. Agreement with published results for polycrystalline copper is fair, although there are fewer discontinuities than for the ordinary metal, as in other experiments with single crystals. The critical potentials may be grouped to show level differences, attributed by Richardson to structure electrons in the crystal lattice. Comparison with other results for metals of similar structure casts doubt on this theory. Kronig's theoretical interpretation of fine structure in x-ray absorption presents a possible explanation of soft x-ray critical potentials. Assuming 4 to 7 volts inner potential, 10 of the 14 observed critical potentials agree with Kronig's calculated energy discontinuities and only one calculated discontinuity was not observed. A strong break at 104 volts, not predicted by this theory, is within 2 volts of Kurth's value for the N series convergence frequency. Similar good agreement exists between Thomas' critical potentials for polycrystalline iron and nickel and the energy discontinuities calculated from Kronig's theory. From these results it appears that the theory of forbidden energy zones may account for soft x-ray critical potentials.

INTRODUCTION

SOFT x-ray emission measurements by critical potential methods show many discontinuities not explained by the simple Bohr theory. Andrewes, Davies and Horton[1] suggested that some of these critical potentials might be due to the arrangement of atoms at the target surface, since the M electrons are not very deeply seated within the atoms of lighter elements. This suggestion was supported by Farnsworth's[2] observation that the position and shape of many of the discontinuities in secondary electron emission curves depend on the surface arrangement of atoms in the target or the orientation of single crystal targets. Using an imperfect natural graphite crystal, Richardson and Andrewes[3] found a decided reduction in the number of discontinuities, compared with those previously found for carbon targets. Richardson and Rao[4] reported similar results for the (100) face of a nickel single crystal. Using the same (100) face of nickel Rao[5] found the changes in slope of secondary electron curves to be in good agreement with the positions of the soft x-ray discontinuities. With a (111) face of a nickel crystal, Rupp[6] found electron diffraction maxima and soft x-ray breaks to agree as either the primary voltage or the angle of incidence was varied. He concluded that some, at least, of the soft x-ray critical potentials are connected with properties of the crystal grating.

The object of the present investigation was to determine whether there is a real difference in the soft x-ray critical potentials for different faces of the same metal crystal.

DESCRIPTION OF APPARATUS

Fig. 1 shows the electrical connections and a cross section of the experimental tube which is of Pyrex in the form of a cross consisting of a main tube G, 7 cm in diameter, with side arms A–A of 3 cm diameter placed near the top of the main tube. Targets T_1 and T_2, mounted on a pair of quartz rods R, may be moved by magnets acting on M–M. The targets were both cut from the same single crystal made in this laboratory.[7] The faces were prepared as described by Farnsworth.[8] Ammonium persulphate solution was used for final etching of the (100) target. The

[1] Andrewes, Davies and Horton, Proc. Roy. Soc. **A117**, 649 (1928).

[2] Farnsworth, Phys. Rev. **25**, 41 (1925); **31**, 419 (1928).

[3] Richardson and Andrewes, Proc. Roy. Soc. **A128**, 1 (1930).

[4] Richardson and Rao, Proc. Roy. Soc. **A128**, 57 (1930).

[5] Rao, Proc. Roy. Soc. **A128**, 57 (1930).

[6] Rupp, Naturwiss. **18**, 880 (1930).

[7] Farnsworth, Phys. Rev. **40**, 690 (1932).

[8] Farnsworth, Phys. Rev. **34**, 679 (1929).

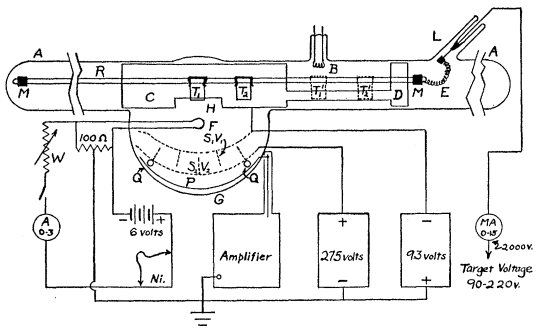

FIG. 1. Experimental tube and electrical connections.

(111) target was etched electrolytically in slightly acid copper sulphate solution. Low current density of about 3 m.a. per cm² produced best development of the (111) face. Final dimensions of the targets were about 8.0×7.5 mm face and 10.5 mm height. A cylindrical nickel shield C, 24 mm in diameter, surrounded the targets and with collar D supported the rods carrying them. An opening H, 18×19 mm, permitted exposure of only one target at a time to the filament F. Both targets were connected to the tungsten seal L by a tungsten spring E. A filament B of 8 mil tungsten was placed so that the targets could be withdrawn to position T_1' and heated by electron bombardment of their molybdenum supports which fitted into grooves cut in the targets. The x-ray filament F of oxide coated nickel, placed 7 mm below the target face, was usually operated at 2.2 amperes, so that the drop across the emitting portion was less than 0.5 volt. A large-capacity storage battery supplied the heating current, which was controlled by a tapped oil immersed chromel resistance W and clips sliding on nickel wires for fine adjustment. The ion trap consisted of two sets of screens and vanes S_1V_1 and S_2V_2, of 1/16-inch mesh nickel screening, insulated by Pyrex tubes. The potentials, −9.2 volts for the top screen S_1V_1 and cylinder C, and +275 volts for the lower screen S_2V_2, were supplied by dry cells shielded in sheet iron boxes. The photoelectric plate P of sheet nickel rested on the bottom of the main tube G and was insulated from the screens by 3 mm rods Q of clear fused quartz. The insulation resistance of P was higher than 10^{10} ohms. The photoelectric current was measured by a one-tube balanced amplifier of the type described by Soller,[9] slightly modified, having a sensitivity of 7.33 $\times 10^{-15}$ amp./mm with grid resistance 3.74×10^{9} ohms (pencil mark on amber). Part of the plate resistance R_1 (Soller's figure) was made variable, so the plate current could be balanced out for any grid input in the operating range. The effect was the same as in Compton and Thomas' method[10] of balancing out part of the electrometer current, allowing use of the full sensitivity to measure changes of photoelectric current over a small range of target voltages. The variable resistance used in this compensating circuit was a 400 ohm Centralab potentiometer. Large B batteries supplied the x-ray target voltage which could be adjusted to any value by taps and potentiometers. It was measured by a special high-resistance Weston voltmeter, which could be read accurately to less than 0.1 volt on the 300 volt range. The thermionic current I_t, of the order 0.5 m.a., was measured to 1 part in 5000 by a null circuit using a galvanometer to indicate balance of a standard cell against the potential drop in a resistance carrying I_t. Balance was secured and I_t held constant by changing the filament current. The experimental tube was shielded with Aquadag, and all wires entering the room were fully shielded.

The vacuum system, consisting of two mercury vapor pumps in series, backed by a Hyvac pump, was connected to the experimental tube through two traps immersed in carbon dioxide snow and acetone. Liquid air was used until experiments on contact potential difference in this laboratory had shown that results were the same with either carbon dioxide or liquid air. Pressure was measured by a General Electric FP62 ionization gauge placed near the x-ray chamber. The experimental tube and trap nearest to it were outgassed by baking for 3 periods totalling 50 hours at 430 to 480°C. Between bakings the filaments were flashed and the targets heated several hours at red heat. After this outgassing process, pressures while bombarding the targets did not rise above 10^{-6} mm of mercury. Pressures while taking readings, 2 to 5 hours after heating the targets, were 1 to 2×10^{-7} mm.

[9] Soller, Rev. Sci. Inst. **3**, 416 (1932).
[10] Compton and Thomas, Phys. Rev. **28**, 601 (1926).

Experimental Procedure

Before each run, the target was heated 2 to 10 hours. As outgassing progressed, the target temperature was gradually increased but evaporation was prevented until the last stages. At the conclusion of bombardment the target was immediately moved to the x-ray position and the target voltage adjusted at the highest value to be used in the run. As soon as the thermionic current I_t could be held at the desired value, the amplifier was adjusted by means of the variable resistance in the plate compensating circuit, so that its reading I_p' would be near the higher end of the scale. With the target voltage and I_t constant, readings of I_p' were taken at intervals until it ceased to change. During this time, 2 to 5 hours, I_p' decreased, rapidly at first, then more slowly. This is attributed to changing photoelectric characteristics of the nickel plate as it was outgassed by action of the soft x-rays. Nakaya[11] observed similar effects on outgassing a photoelectric plate by bombardment.

When I_p' had reached a steady state, readings were taken from which the soft x-ray critical potential curves were plotted. The amplifier sensitivity was adjusted by an Ayrton shunt on the galvanometer so that I_p' would cover nearly the whole scale for the range of voltages to be used in the run. While the target voltage was decreased by steps of 1.0 or 2.0 volts and I_t was kept constant, I_p' was read for each voltage. All runs were taken in the order of decreasing voltage, since I_t reached equilibrium more quickly than in the reverse order. Check runs taken with increasing target voltage showed breaks in the same positions. At the conclusion of each run the constancy of the amplifier was checked by repeating readings at certain voltages. A slight change in target voltage, too small to be observed on the voltmeter, could be detected by its effect on I_p'. Since I_t was held constant to 1 part in 5000, the limiting factor in the sensitivity of the apparatus was the accuracy of measuring the voltage, less than 0.1 volt. The oxide coated filament used at low temperature and the small potential drop along the emitting part of the filament make the speeds of the electrons more uniform than in most soft x-ray experiments to date.

Results

Fig. 2 shows a typical soft x-ray critical potential curve. Since I_t was held constant

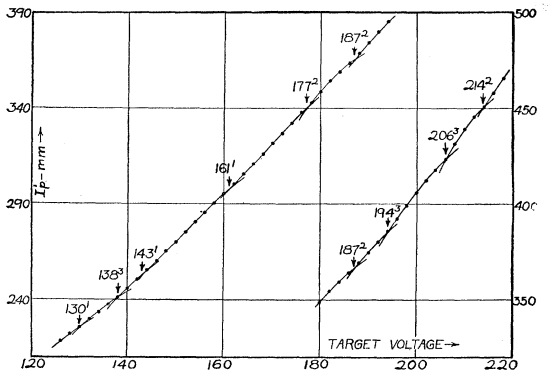

Fig. 2. Typical critical potential curve. Run No. 240, (100) target. The uncorrected voltage of each break is shown above the curve, followed by a superscript denoting the intensity or certainty of the break.

during each run, the amplifier reading I_p' is proportional to I_p/I_t minus a constant and is plotted directly against the voltage. The intensity or certainty of the break is estimated from the change in slope of the curves. Intensity (1) signifies the least change of slope which can be detected or a break dependent on the positions of only a few points and (3) indicates the most pronounced breaks.

The uncorrected voltages of all breaks found in 20 runs with the (111) target, in the range 90–220 volts, are tabulated in Table I. Table II shows the critical potentials found in 18 runs with the (100) target. Readings were started 1.5 to 8 hours after heating the targets. The pressure while taking readings varied from 1.1 to 2.2×10^{-7} mm in different runs, although it was nearly constant during each run. No significant changes in either intensity or position of the breaks can be attributed to these variations of pressure or to the amount of outgassing or time since outgassing the target. Runs taken during the earlier stages of outgassing were so irregular, from other causes, that no conclusions can be drawn from them. In an attempt to determine whether changed surface conditions on the target cause changes in the soft

[11] Nakaya, Proc. Roy. Soc. **A124**, 616 (1929).

TABLE I. *Critical potentials for (111) target (uncorrected).*

Groups including nearly all of the breaks are indicated at the heads of the columns. Breaks falling less than two volts outside of these groups are included in the column, *in italics*. They are included in the averages and the same weight is given to each value regardless of intensity. Breaks not obviously belonging to any group are written between the columns. A break missing in any run is indicated by an x where it should appear and is considered as zero intensity when computing the mean value. Superscripts denote intensity of the breaks. Numbers 243–257 are the final series of readings taken under most carefully controlled conditions. The remaining 6 runs which were taken before certain improvements in apparatus were made and were noted as exceptionally steady at time of reading, are seen to agree with the final series. Target was heated a total of 157.5 hours for run 243 and 243 hours for the last run 257. For the earlier runs given the total heating was from 20 to 74 hours.

Run No.	93–94	97–99	107–108	116–118	122–124	129–132	136–137	144–146	159–160	177–178	185–186	192–194	202–204	213–214
243							136^2	144^2	*158*^{2}	178	186^2	192	204^2	214^2
244	93^3	98^2	108^3	116^2	122^2	130^2								
246										177^2	*184*	193^2	204^2	214^2
247							136^2	146^3	159^2	178	186			
248						132	x	146^2	160^3	176^2				
249		98^2	108^3	118^2	124^2	132^1	136	145^2	159^2					
250	93^3	*100*	108^2	x	122^2									
251	93^2	97^2	108^3	{*115* *119*^{2}}	*125*	129^2	136^2							
252							137	144^2	160^2	178	186^2	194	203^2	214^2
									? 172					
253	94^2	99	108^2	x	122^2	129^2								
254									160^3	177	186^2	194^2	203^2	214
255	93^2	97^2	107^2	117^2	x	130^2	x	144^2	*162*^{2}					
256				118^3	122	130	137^2	146^2	160^2	178	186^2	192^2		
257										177	186^2	194^2		
									?					
189							137^3	144^2	159^2 168	x	186^2	194^2	204	x
196	93^2	99^2	108^3	116	x	130								
211	93^2	97^2	108^3	116^2	124	*133*	137							
212	93^2	*100*^{3}	108^3	116^2	123	129	136							
216										178^2	185	192^2	{*201*^{2} *207*}	213^2
217	*95*^{2}	99	107^2	117^2	x	131	137	145^2	160^2	x	185^2			
Mean voltage	93.3	98.4	107.8	116.8	123.0	130.5	136.5	144.9	159.7	177.4	185.6	193.1	203.7	213.8
Mean int.	2.2	1.8	2.6	1.5	1.1	1.5	1.3	2.1	2.3	1.1	1.5	1.5	1.9	1.5

x-ray characteristics, before runs 256 and 257 the (111) target was heated to a higher temperature than before, until a considerable amount of copper evaporated. No definite changes were observed in these runs.

The construction of the x-ray tube did not permit an experimental determination of the contact potential difference between target and filament. Farnsworth has found that for a copper target and an oxide coated filament the correction is negative and of the order 3 volts. Adding 1 volt for drop in the null resistances, we find 4 volts, to be subtracted from the voltmeter readings, as the most probable correction for the soft x-ray critical potentials.

DISCUSSION

The average critical potentials for the (111) and (100) faces of copper single crystals from Tables I and II are shown in the first two columns of Table III. Here the most probable correction of −4.0 volts is applied. It is evident that the same critical potentials appear for both targets. In the region 90–220 volts, 14 breaks are found and, in all cases, the voltage of the break agrees within 1.5 volts for the two targets.

Critical potentials for polycrystalline copper targets published by Compton and Thomas[10] and by Richardson and Rao[12] are shown, respectively, in columns 3 and 4. In both cases the corrected

[12] Richardson and Rao, Proc. Roy. Soc. **A128**, 16 (1930).

TABLE II. *Critical potentials for (100) target (uncorrected).*

Notation is the same as for Table I. Numbers 233–241 are the final series with total heating of target between 220 and 250 hours. Others were obtained in earlier runs under best conditions after 100 hours of heating.

Run No.	92–93	98–99	108–109	116–118	122–123	130–131	137–138	144–146	159–160	176–178	186–188	193–196	204–206	212–214
	Final series of readings													
233									160^3	176	187^2	194^2	206^2	214^2
234										178^2	188^3	*x*	206	212^2
235										178^3	187^2	195^2	206^2	212^2
236						130	138^3	145^2	159^2	176^2				
237		98^2	108^3	116	122^2	130^2	138	144^2	160^2	176^2				
238	93^2	98^2	109^3	118^2	123^2	131^3	138							
		? 104												
239	92^2	98^3	109^2	118	122^2	130^2								
240						130	138^3	*143*	*161*	177^2	187^2	194^3	206^3	214^2
241	93^2	$\left\{\begin{matrix}96^2\\100^2\end{matrix}\right\}$	109^3	*115*	*121*	$\left\{\begin{matrix}129^2\\133\end{matrix}\right\}$	138							
	Earlier runs													
203					*124*	130	137	144^3	160^2	178	187	*x*	204	212^2
206	92	$\left\{\begin{matrix}96^2\\100^2\end{matrix}\right\}$	108^2	118^2	123	131	*136*							
207								144^3	159	178^2	186^2	193^2	204	213
208							138^2	144^3	160^2	177^2	187^3	193^2	204^2	214^2
221							138^3	146^2	160^2	176^2	186^2	195^2	206^2	214^2
222		99^2	108^2	116	123^2	130^2	138^2	146^2	159^2					
223	93^2	99^2	108^3	116^2	123^3	130								
227	92^2	98^2	108^3	116	122^2	*132*	138^2	145^2	159	176				
228		98^2	*107^2*	116^2	122^2	130^3								
Mean voltage	92.5	98.2	108.2	116.6	122.5	130.4	137.7	144.6	159.7	176.9	186.9	194.0	205.2	213.1
Mean int.	1.8	2.3	2.6	1.4	1.9	1.7	1.8	2.2	1.9	1.8	2.1	2.2	1.7	1.9

voltages are given. Both groups of experimenters found more breaks for polycrystalline copper than were found by the author with single crystal targets. This is in agreement with the results of others[3, 4] using single crystals. Agreement between the author's results and published results for polycrystalline copper is only fair since, on considering the small separation of the breaks found for the ordinary metal in this voltage range, it is evident that a considerable number of points might accidentally agree within two volts. However, it may be said that agreement of the critical potentials found for the single crystals with certain of the critical potentials for the polycrystalline metal is as good as is usually found in soft x-ray measurements of different experimenters.

All of the 14 breaks observed in this experiment may be separated into 3 groups and arranged in a table showing horizontal and vertical differences of the order of magnitude predicted by an approximate calculation based on Richardson's theory of structure electrons.[13] Some doubt is cast upon this apparent correlation by comparison of results of other observers for metals of similar crystal structure. For example, nickel has the same crystal structure as copper and the atomic numbers and lattice constants of these metals differ only slightly, hence correction terms neglected in the approximate calculation should be of the same order of magnitude. If we use the true lattice constants in the development of Richardson's formula and substitute the atomic number for z (neglecting screening effects) the calculated level spacings for copper and nickel are very nearly the same; but Richardson's[13] tabulation of Rao's[5] critical potentials of secondary electron emission from a nickel single crystal shows level spacing considerably larger than that found for the soft x-ray

[13] Richardson, Proc. Roy. Soc. **A128**, 63 (1930).

TABLE III. *Comparison of critical potentials for copper.*

1 (111) Face Corrected Author		2 (100) Face Corrected Author		3 P.C.Cu C. & T.[9]		4 P.C.Cu R. & R.[12]		5 Absorption Kronig[14]	
Volts	Int.	Volts	Int.	Volts	Int.	Volts	Int.	Volts	r
89.3	2.2	88.5	1.8	86.7	1.2			93	6
				92.2	1.6				
94.4	1.8	94.2	2.3	94.5	0.9			101	24
				98.8	1.6			104	15
103.8	2.6	104.2	2.6	104.5	2.0			—	—
				108.2	1.8	107.3	1.0		
112.8	1.5	112.6	1.4	111.0	1.4	111.0	0.7	116	12
				115.2	1.8				
119.0	1.1	118.5	1.9	117.8	1.5	117.8	0.6	124	12
								127	12
126.5	1.5	126.4	1.7	127.1	1.4	128.0	1.5	—	—
132.5	1.3	133.7	1.8	132.9	0.9	133.5	1.8	139	4
140.9	2.1	140.6	2.2	140.6	1.5	139.5	0.8	148	24
				148.4	1.4	148.3	0.9	150	12
155.7	2.3	155.7	1.9	157.1	1.4	157.4	0.9	162	24
				164.6	1.6				
				168.3	1.1	166.3	1.1	170*	36
173.4	1.1	172.9	1.8					—	—
				178.6	1.5	178.4	0.7		
181.6	1.5	182.9	2.1					—	—
189.1	1.5	190.0	2.2	188.8	1.7	188.0	0.6	194	12
								197	24
199.7	1.9	201.2	1.7	—	—	197.1	1.3	208	18
				204.8	1.4	205.3	0.6		
209.8	1.5	209.1	1.9					217	28
				216.8	1.4	217.1	0.5		

critical potentials of copper in the present experiment.

It thus seems necessary to seek other possible explanations of the soft x-ray discontinuities. One such possibility, suggested to the author by Dr. Farnsworth, is presented by Kronig's[14] recent interpretation of fine structure of x-ray absorption spectra by means of the quantum mechanics of electrons in crystal lattices. This theory is based on the idea introduced by Bloch that influence of the crystal lattice can be replaced by a periodic potential field having the same period as the lattice. The theory shows that not every value of velocity is possible for electrons moving through a crystal lattice but rather that an energy spectrum exists, consisting of alternating zones of permitted and forbidden energies. Kronig has calculated, from the wave equation, the perturbed energy of an electron travelling in a crystal lattice. It is shown that there are discontinuities in the energy of the perturbed electron when its momentum parameters are related in a certain way to parameters α, β, γ, which may be considered as defining planes in the crystal lattice. Although these discontinuities or forbidden energy zones depend on direction of propagation of the electron, Kronig has shown that there are still finite variations in the absorption coefficient corresponding to each discontinuity, after integration over all directions of propagation. In terms of the parameters, the energies of these discontinuities are $W_{\min}=(\alpha^2+\beta^2+\gamma^2)h^2/8ma^2$, where h is Planck's constant, m the electron mass, and a the distance between potential barriers equal to the lattice constant of the absorbing substance. Using values of α, β, γ determined by the sequence of planes in the metal lattice, Kronig calculated the energies, in electron volts, of these discontinuities for copper. Results of these calculations are shown in the fifth column of Table III. Here r represents the abundance of the

[14] Kronig, Zeits. f. Physik **75**, 191 (1932).

discontinuity planes considering permutations and changes of sign of the parameters.

In 4 cases, pairs of Kronig's calculated values are separated by 3 volts or less. If we group these pairs as indicated by the brackets in Table III, it can be seen that 10 of the 14 critical potentials found by the author fall 4 to 7 volts below a calculated value or group. This uses all but one of the calculated values—the one at 170 volts marked with a star. This calculated discontinuity is due to the (553) and (731) planes of the crystal, planes in which atomic density is very small. The four observed critical potentials which do not correspond to a calculated value are 104, 126.4, 173.2, and 182.2 volts. All of these were found by other observers with polycrystalline copper targets, so it is improbable that they might be due to impurities. The break at 104 volts is very strong, in fact, for both targets the intensity is the highest of all the breaks observed. Kurth,[15] gives 116A, or 106 volts, as the convergence frequency of the N series for copper, which checks closely with this observed strong break.

Similar correlation can be shown between Kronig's table of energy values for iron, which has different crystal structure, and soft x-ray breaks observed by Thomas[9] for the polycrystalline metal. Strikingly good agreement is found on comparing Thomas' critical potentials for nickel with the energy discontinuities, which may be calculated from Kronig's table for copper by correcting for the difference in lattice constants. Thomas found one break not predicted by the theory and the calculations show two discontinuities close together which were not reported by Thomas. All except 2 of the 12 breaks reported by Thomas fall within 4 volts below a calculated value. It was noted above that critical potentials for copper found in the present experiment also fall below the calculated values by 4 to 7 volts. This might be explained by an inner potential of the metal which causes acceleration of electrons on entering the target. Farnsworth[7] found that the experimental voltage for electron diffraction beams from a copper crystal falls below the theoretical voltage, so that an inner potential ϕ of the order 25 volts is required. Since it appears that the full value of ϕ is not effective unless the velocity of incident electrons exceeds a certain value, Farnsworth suggests that ϕ depends on depth of penetration of the surface layer. The fact that a smaller inner potential is required to correlate soft x-ray data is in accord with this suggestion, since the high absorption coefficient for soft x-rays requires that they be generated near the surface of the target.

The observed agreement between soft x-ray critical potentials and Kronig's calculated absorption discontinuities may be explained as follows: The absorption discontinuities are calculated for forbidden zones of energy of electrons moving through the crystal lattice. Electrons having energies falling within these forbidden zones cannot enter the target so they are reflected, either diffusely or as diffraction beams. Consequently, electrons having these energies are not available for production of x-rays and a minimum in the soft x-ray curves results. These minima in the continuous radiation, superimposed on the general upward trend as voltage is increased, appear as discontinuities in the critical potential curves and account for the breaks not predicted by the Bohr theory. Thus many of the observed soft x-ray critical potentials are not due to true characteristic radiation of the atoms, but are characteristic rather of the lattice structure of the target.

The observed agreement between the breaks found for the two different crystal faces remains to be considered. Since Kronig's values are obtained by integrating over all directions of motion of electrons in the lattice, it appears at first sight that some of the discontinuities might not appear when bombarding electrons fall within 15 to 20° of normal incidence on a single crystal target, as in the present experiment. Obviously one would expect different breaks to be missing for different orientations of the targets. Failure to observe this difference may be accounted for by random changes of direction of the incident electrons on first striking the targets. In Kikuchi's[16] experiments on diffraction of high-speed electrons from mica, certain lines in the photographs are explained as due to electrons scattered on first entering the crystal and

[15] Kurth, Phys. Rev. **18**, 461 (1921).

[16] Kikuchi, Japanese J. Phys. **5**, 83 (1928).

subsequently reflected from crystal planes at the Bragg angle. This requires an amount of scattering, on first striking the target, sufficient to account for the agreement of the soft x-ray breaks for the two targets. It is known from diffraction experiments with low-speed electrons that only a small fraction of incident electrons is returned as diffraction beams and consequently a considerable number must also be scattered diffusely.

In conclusion, the author wishes to express his sincere thanks to Dr. H. E. Farnsworth, for his many helpful suggestions and criticisms during the course of this research.