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SOFT X-RAYS: IMPROVEMENTS IN TECHNIQUE AND NEW RESULTS FOR C, Cu, AND W

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Abstract

Improved technique in soft x-ray measurements.—A new tube designed for high sensitivity in detecting soft x-rays by their photoelectric action and using a system of gauzes to exclude ions from the detecting plate was found to give results identical with the previous tube in which a vane system was employed. In either type of tube the range of voltage applied to exclude ions from the detecting plate must be determined. Failure to observe this seems to account for some results which have appeared in the literature of this subject. Greatly increased precision was secured by measuring both the thermionic and the photoelectric currents, I and E, by balanced methods in which the full scale of the instruments was used to measure current increments, instead of total currents, as the voltage was increased in small steps. The applied voltage V was measured by a similar balanced method in which residuals only were read on the voltmeter. By these devices the observations were so precise that critical potentials could be determined from curves in which were plotted the second differences of the ratio E/I against V, which rendered discontinuities much more marked than in previous methods. The method is illustrated by application to tungsten in a small voltage range.

Critical Potentials of C and Cu. 62 critical potentials were found for carbon in the range 0–160 volts. 31 new critical potentials of copper were found in the range 65–280 volts, which had not previously been investigated for fine structure. These critical potentials are given in tables.

RECENT work by one of us,[1] by Rollefson[2] and by Richardson and Chalklin[3] has shown that the soft x-ray spectrum of solids, as found by the critical potential method, is much more complicated than had previously been assumed and raises serious questions regarding the significance of much of the work which has been done in this field. It is significant that the best agreement between experimenters in this field is in those cases in which the greatest pains have been taken to make measurements in very small voltage intervals, with unusual precautions

[1] C. H. Thomas, Phys. Rev., **25**, 322 (1925).
[2] G. K. Rollefson, Phys. Rev. **23**, 35 (1924).
[3] O. W. Richardson and F. C. Chalklin, Proc. Roy. Soc. A **110**, 247 (1926).

to secure steady circuit conditions and with high precision of measurements (*e.g.*, Richardson and Chalklin[3] and Thomas[1] in the case of iron).

The present work was undertaken wth four principal objects in view: (1) to find out conclusively whether this "fine structure" of soft x-rays is real; (2) to develop apparatus and method to reach the limit of reliability and accuracy; (3) to investigate sources of spurious "breaks," or apparent critical potentials which are due to experimental defects; (4) to use the improved method in further investigation of the soft x-ray spectrum.

Briefly stated, the investigation shows: (1) that the fine structure is real; (2) that it cannot be observed unless accuracy of readings far exceeds, for instance, the accuracy attainable in measurement of electrometer currents by the rate of deflection method; (3) that a type of very pronounced "break" frequently found by previous observers is *not* a critical potential of soft x-rays.

Apparatus

Two principal types of tube have heretofore been used in soft x-ray work, differing in the method employed for keeping ions away from the metal plate which serves photoelectrically to detect the radiation. One method consists in interposing, between the source of radiation and the detecting plate, two or more vanes between which the radiation may pass and between which there is an electric field acting to draw to the vanes any ions which might otherwise reach the detecting plate. The second method, introduced by Horton and Davies,[4] employs a system of wire gauzes through whose openings the radiation may pass and between which fields are applied to prevent ions of either sign from reaching the detecting plate. Since the recent work in this laboratory has been done with an apparatus of the first type, we constructed a new apparatus (Fig. 1) of the second type in order to see whether the type of tube affected in any way the determination of critical potentials.

In a G 702 P glass tube of 3 inch diameter were mounted the Pt foil detecting plate P and the set of four Ni wire gauzes of fine mesh. These gauze cylinders were separated from each other by short glass cylinders at their ends, and held in a rigid group by the clamp C. In order to facilitate changing and cleaning the target T, this was mounted, together with the filament source of electrons F, on a stem introduced through a very long and well ground joint, which was hermetically sealed by De Khotinsky cement at its open end. Since this cement was kept cool during operation, since the rate of diffusion of its vapor through the long ground

[4] F. Horton, U. Andrewes and A. C. Davies, Phil. Mag. **46**, 721 (1923).

joint was very slow, and since the rate of exhaustion of residual gas through the short 1 inch connecting tube to the evacuating system was very rapid, the ill effects of residual cement vapor were reduced to a minimum. The filament was of 10 mil (0.25 mm) tungsten and was heated by a current of from 5 to 7 amps. with a voltage drop of 1.8 to 2.4 volts. The voltage drop over the central, hot, electron-emitting portion of the filament was not more than one volt and was generally about 0.5 volt. The target was a flat rectangular plate of dimensions 10×14 mm.

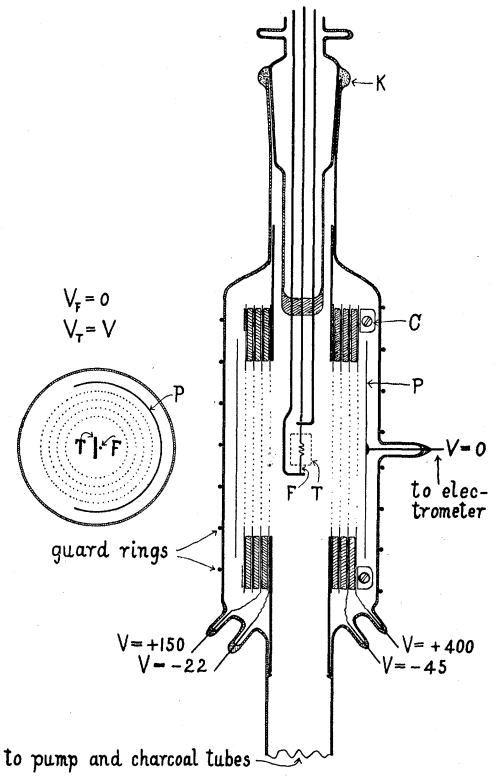

Fig. 1. Diagram of tube.

Before assembling the apparatus all metal parts were heated to incandescence *in vacuo* by induced currents until the evolution of gas ceased. Before any series of runs the apparatus and traps were heated at 450–500°C for three hours, the filament glowed and the target heated to incandescence by bombardment by electrons from the filament. The carbon (graphite) target was initially well degassed by heating *in vacuo* for 170 hours at a white heat. In every case the target was taken out and repolished after about 20 hours of service, since experience showed

that within this time there were no indications of tungsten or other material deposited on the target. A two stage mercury condensation pump was operated continuously during the experiments and three traps were interposed between the pump and the tube. The trap nearest the pump was continuously immersed in liquid air and the other two, which contained a little cocoanut charcoal, were immersed in liquid air while measurements were being made.

All important parts of the apparatus and circuits were electrically shielded and protected by guard ring devices from leakage. The photoelectric currents E were measured by a very steady Dolezalek electrometer of sensitivity 2300 mm per volt and shunted with convenient India ink resistances.* The thermionic current of bombarding electrons I was measured by a Paul Universal Test Set and the bombarding voltage V by a Weston Laboratory Standard voltmeter with multiple ranges.

Preliminary tests were made to examine the effectiveness of the gauze system for protecting the plate P from ions. The general scheme of voltages shown in Fig. 1 was found suitable. However, it was discovered that *the safe range of voltages between filament and target is a function of the potentials of these gauzes, particularly of the outer gauze.* For instance, with the outer gauze 400 volts positive with respect to the filament and the detecting plate, this plate detected only radiation falling on it provided the bombarding voltage on the target did not exceed about 280 volts, but with larger bombarding voltages the electrometer current increased rapidly and in a manner suggesting that the gauzes were failing to exclude positive ions at the high bombarding voltages. If the potential on the outer gauze were less than 400 volts, the safe working range was proportionally diminished and if greater than 400 volts it was increased. The criterion of safety (meaning certainty that electrometer currents were due only to radiation falling on the plate) was that the electrometer current be independent of the voltage on the gauzes.

* Some experiments were made to find the most satisfactory type of India ink resistance for use as an electrometer shunt. Of several types of ink tried, Higgin's waterproof black ink alone proved satisfactory. In making resistances of more than 10^9 ohms it was not found satisfactory to attempt to secure high resistance by ruling a very fine line, since such resistances were generally variable and did not follow Ohm's law. (This is probably due to the location of most of the resistance in breaks or near-discontinuities in the line so that the voltage gradient at such points was very high). Very satisfactory high resistances were secured by ruling a great many coarse parallel lines and joining these lines alternately at the two ends so as to give a very long path. As many as 100 such lines can advantageously be used, drawn on good quality smooth drawing paper, giving an aggregate length of about 25 m. The conductivity of the paper was negligible.

The setting-in of ion currents at high voltages introduces a spurious "break" in the curve showing E/I as a function of V, which is very sharp and of characteristic shape in that the curve shows approach to saturation some distance above the break. We know these breaks to be of no significance, for their position depends on the voltages on the gauzes. We are inclined to think that some critical potentials previously reported in the literature are of this spurious type. For instance, that one reported by Miss Levi[5] for Co and shown in her Fig. 12 is of the shape of those which we found to be spurious and is one which we were quite unable to find in Co unless the gauze voltage was so low as to let through positive ions. It is important, therefore, to make tests to determine the voltage range within which the gauze or vane system is effective in excluding positive ions, and to work only within this range. This point has received consideration in the work of Richardson and Chalklin.[3] Our tests indicate that this positive ion effect varies somewhat with the degree of evacuation and with the nature of the target, and it is probably associated with the ionization of an adsorbed gas layer whose elimination is practically impossible in an apparatus of this kind, as recently shown by Kistiakowski.[6]

Having thus found the safe working range for this apparatus, we then proceeded to determine the critical potentials within this range (about 280 volts) for the same iron target which had been used with the vane type of tube in the experiments previously reported, and using the technique there described. *Our curves showed every critical potential previously reported and no others, which we take as proof that these critical potentials are actually characteristic of the metal target and are not accidental or dependent on the particular type of apparatus used to determine them.*

After thus checking the operation of the new tube, we proceeded to determine the critical potentials of Cu in a range 70–280 volts, which had not been covered in the work previously reported.[1] The results are given in Table I, in which all voltage corrections have been included.

Improvement in Method

We next made the following improvements in technique which lead to greatly increased precision and certainty in the determination of critical potentials.

The bombarding voltages were obtained from Edison storage batteries. To increase the accuracy of measuring the voltage increments between successive readings, especially at the higher voltage ranges, the voltage was applied in two parts: first a storage battery of e.m.f. about equal to

[5] M. Levi, Trans. Roy. Soc. Canada **18,** 159 (1924).
[6] Kistiakowski, Jour. Phys. Chem. **30** (Sept. 1926).

the lowest voltage desired in the run was measured accurately; then a potential divider system across a second storage battery, of e.m.f. a little greater than the range of voltage desired for the run, was connected in series with the first battery. The voltage settings were read off the standard voltmeter in this potential divider circuit and added to the constant voltage of the first battery. In this way the voltages were given accurately to 1/10 percent while the voltage increments between successive readings were accurate to 1/30 percent or better.

TABLE I

Critical potentials for copper (additional to those given by Thomas, Phys. Rev. 26, 739 1925).

Volts	Intensity	Volts	Intensity	Volts	Intensity
66.9	1.6 R	117.8	1.5 R	216.8	1.4 R
73.5	1.8 R	127.1	1.4 R	221.6 ?	1.5 R
82.5	1.2 R	132.9 ?	0.9 R	228.7	1.3 R
86.7	1.2 R	140.6	1.5 R	235.6	1.9 R
92.2	1.6 R	148.4	1.4 R	244.6 ?	1.3 R
94.5 ?	0.9 R	157.1	1.4 R	250.3	1.6 R
98.8	1.6 R	164.6	1.6 R	254.8	1.3 R
104.5	2.0 R	168.3	1.1 R	268.6 ?	1.3 R
108.2	1.8 R	178.6	1.5 R	276.7	1.9 R
111.0	1.4 R	188.8	1.7 I		
115.2	1.8 R	204.8	1.4 R		

To increase the precision of measurement of the thermionic current I, a balanced method was used as shown in the upper part of Fig. 2. The terminals marked + and − are the external terminals of the Universal Test Set for small current measurement and the resistances S are self-contained shunt resistances for altering the range of the instrument whose galvanometer is shown at G. The improvement consisted in opening the instrument to attach leads as shown to the right, which included a storage cell, a key and a high resistance in series. By this attachment the effect of the thermionic current on the galvanometer could be balanced by an opposing current from the storage cell and the instrument used in its high sensitivity range to measure relatively large currents. The method of operation can be explained by considering an example. Suppose the run was to be made over a range of bombarding voltage from 175 to 200 volts. The balancing circuit was set to give zero galvanometer reading at 175 volts, and the sensitivity adjusted to give full scale deflection at 200 volts. Thus the galvanometer measured current increments as the voltage was raised in small steps. The method of calibration is obvious. By using the reversing switch on the Test Set, the range during a run could be doubled, *i.e.*, taken from minus to plus full scale deflection. In this way the thermionic current increments as the

voltage was raised were easily measurable with an error less than 1/100 percent, and could have been bettered if necessary.

A somewhat similar method was employed to increase the accuracy of measurement of the photoelectric current E. This current passed to earth through some combination of India ink shunts s and was measured by the electrometer E. The effect of this current on the electrometer was practically balanced by the reverse current from a storage cell, a potential

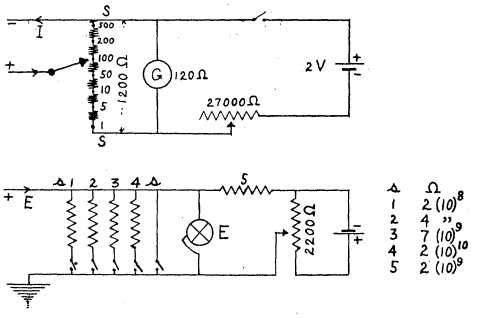

Fig. 2. Electrical connections.

divider and an India ink resistance 5. As in the case of the thermionic current, the electrometer deflection was thus reduced to zero at the lowest voltage in the run, so that the full scale of the electrometer was available for measuring the increments in photoelectric current as the voltage was raised in small steps. This method, combined with use of a reading lens to observe the unusually sharply defined spot on the electrometer scale, enabled the increments in photoelectric current to be measured to at least 1/100 percent which is, we believe, a new record for electrometer measurements.

As in the earlier work, the heating current through the filament was rendered sufficiently steady by the use of a high capacity storage battery, an oil immersed regulation rheostat with no sliding contacts and by allowing two hours of heating to elapse before beginning readings in order to allow the storage battery to reach equilibrium.

With these improvements in technique, a new method of plotting results was advantageous, since the precision of measurements far exceeded the possible accuracy of plotting. The most convenient of several methods was to plot second differences of E/I as a function of V thus: We measured ΔE and I as V was increased. We then calculated the increment ratios $\Delta(E/I)$ using a six place computing machine. We then subtracted a conveniently chosen constant K from each value of $\Delta(E/I)$. Finally we added these residuals, from the lowest voltage in the run up

to any given value V and plotted the sum as ordinate against V as abscissa. This is equivalent to plotting an exaggerated derivative of the ordinary E/I against V curve. In this way no spurious discontinuities are introduced into the curve, but all discontinuities really present are greatly exaggerated.

As an illustration of what can be done with the aid of these refinements we show, in Fig. 3, the soft x-radiation curve of tungsten for which measurements were made at 4 volt intervals over a large voltage range and the values of E/I were plotted directly. This is the usual type of curve and shows evidence of radiation at 14, 40 and in the region of 170 volts. By the new method we then made several runs over the limited range of voltage indicated by the heavy arrow in Fig. 3, and the results appear in Fig. 4.

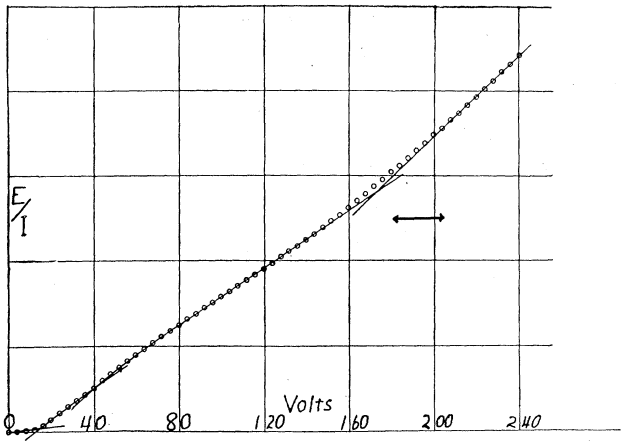

Fig. 3.

In Fig. 4, curve (a) shows a direct plot of values of E/I against V, and the ordinates on the left suggest the precision of the measurements. This curve shows some suggestions of critical potentials near 190, 197 and 201 volts. But the real story is told by the difference curves, of which (b), (c) and (d) are samples. The ordinates on the right are for curve (d), while curves (b) and (c) are slightly different because of the use of different values of the constant K and because of vertical displacement to avoid confusion in plotting. In all essential details these curves agree and show at least eight distinct critical potentials.

Such results prove that this critical potential method is really capable of use as a precision method of investigating soft x-rays. The method described above should render the further investigation of heavy metals

rather easy, since Richardson and Chalklin[3] have pointed out that the x-radiation is relatively intense from elements of high atomic number.

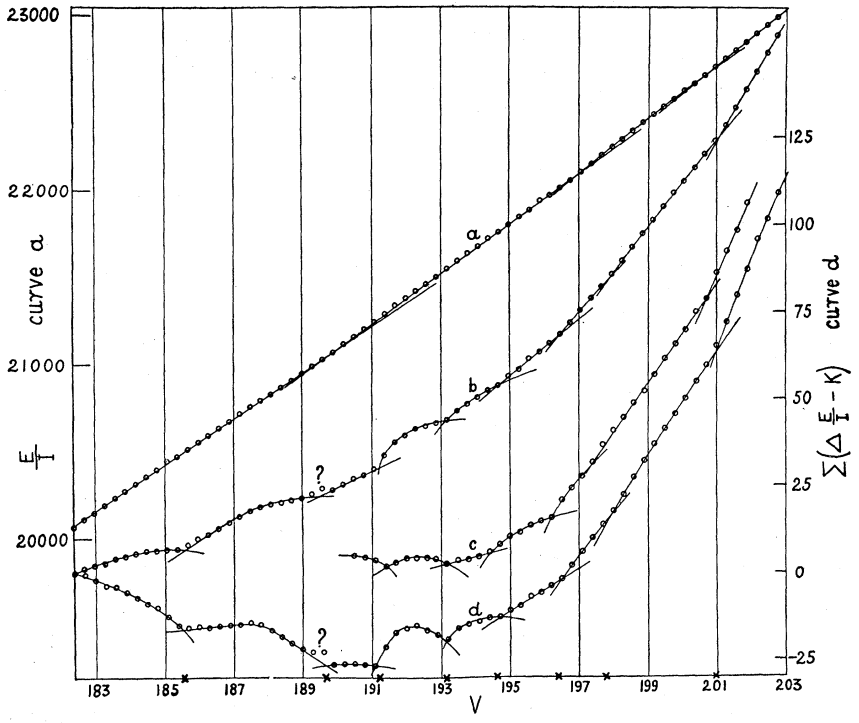

Fig. 4.

SOFT X-RAY SPECTRUM OF CARBON

Because of its low atomic number, carbon is both interesting and difficult. We therefore made a study of its spectrum in the range 0–160 volts. Fig. 5 shows two typical difference curves in the range 24–40 volts, which is especially interesting because it includes the critical potential, ascribed to the L series, which has been found by many observers. (Kurth[7] 32.9 volts, Hughes[8] 34.5 volts, McLennan and Clark[9] 33.0 volts, Levi[5] 35.0 volts, Richardson and Chalklin[3] 34.6 volts, all uncorrected for work function.) It is seen that, superimposed on the large change in slope to which these values refer, there is a finer structure.

Table II gives the critical potentials found for carbon, with the voltage corrections included. The "intensity" is taken as proportional to the

[7] E. H. Kurth, Phys. Rev. **18,** 461 (1921).
[8] A. L. Hughes. Phil. Mag. **43,** 145 (1922).
[9] J. C. McLennan and M. Clark, Proc. Roy. Soc. A **102,** 389 (1923).

change in slope of the curve at the "break." The "certainty" is expressed as a fraction whose denominator shows the number of independent runs, or curves, over the range of voltage in which the break might be found and whose numerator shows the number of curves in which the break was evident. Certainties marked thus: 8/9 (9/9) mean that the break was definitely and independently located on 8 of the 9 curves, while the remaining curve shows evidence of the break which is not decisive enough to justify its being taken as an independent determination.

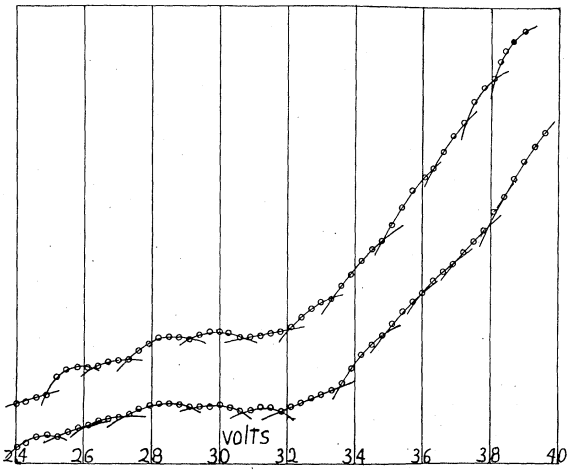

Fig. 5.

TABLE II

Critical potentials for carbon.

Volts	Intensity	Certainty	Volts	Intensity	Certainty	Volts	Intensity	Certainty
8.95	1	2/2	33.17	2.8	6/6	65.52	2	4/6
10.26	3	2/2	34.70	2.6	7/7	67.55	3	6/7
11.70	3.5	2/2	35.95	3	7/7	70.03	2	4/8 (7/8)
13.15	3	3/3	37.38	4.8	7/7	73.54	3.1	7/7
13.90	3	2/3	38.70	2.5	6/8	78.70	4	1/6
14.80	5	7/7	39.76	2.4	7/8	85.05	2	4/4
15.62	5	7/7	40.89	2.9	9/10 (10/10)	92.84	1.3	5/5
16.68	7	7/7	41.83	4	7/7	98.99	2.1	6/6**
17.95	5.5	8/8	43.19	2	4/4	102.7	1.5	6/7 (7/7)
18.85	3	4/5	44.37	2.2	3/3	109.0	1.1	4/4
19.54	3	4/5	46.32	2.9	6/6	114.6	1.3	4/4**
20.90	3	4/4	47.99	2.1	4/7 (7/7)	120.3	1.2	2/3
21.81	2	4/7	49.20	4	7/7	124.4	1	4/5
22.96	3.4	6/6	51.20	3	7/8	128.3	1.8	2/4
24.18	1.4	6/8	52.50	1.2	4/8 (7/8)	130.6	1	2/4
25.10	3	8/9	53.85	3	7/8	133.5	1.5	3/4
26.15	2	6/7	54.85	1	4/8	137.4	1	3/4
27.24	3.5	8/9 (9/9)	56.37	2.5	9/9	141.9	0.9	4/5
28.88	3	10/11	59.69	3.5	7/9**	148.5	1.0	5/5
29.99	2	7/8	62.56	3.6	8/8	155.1	0.6	5/5
31.10	3.9	6/7 (7/7)	64.55	2	4/7			

** Probably double.

Discussion

Voltage corrections. As pointed out in the two previous papers,[1] the voltage correction should include the mean initial energy of emission of electrons from the filament, the voltage drop to the middle of the filament, the contact difference between the filament and the target and the work function of the target. Richardson and Chalklin[3] have pointed out that the last two elements in this correction combine into simply the work function of the filament, in virtue of the relation between work functions and contact difference of potential given by Richardson.[10] We have taken the additive corrections in the present experiments to be 3.7 volts for carbon and 4.0 volts for copper.

Interpretation. The discovery of this complex structure of critical potentials introduces difficulties in their interpretation. There are too many of them to fit into the Moseley diagram as obtained from the x-ray spectrum by application of the combination principle and many of them have values which fall outside the range of values to be expected from consideration of the Moseley diagram. This applies particularly to the critical potentials of presumably the types M, N, O, etc., for the critical potential data appear to fit the K and L series in the Moseley diagram very well. Whence come the complications in the region of the lower critical potentials?

It may well be that some of the observed critical potentials represent the sum of two lower critical potentials and are due to the ability of a bombarding electron to excite two atoms in succession. It may be that, for the outer energy states of the atoms, the quantization is complicated by the neighboring atoms in the lattice structure so as to superimpose a fine structure on the otherwise relatively simple atomic spectrum, somewhat along the lines suggested by Frenkel,[11] although it is difficult to account for large energy changes on such a basis. It may be that the "coarse" structure of critical potentials, found without the refinements shown in the present paper, is more fundamental and easier of interpretation than the fine structure here described. Nevertheless this fine structure appears to be real, and must be capable of interpretation.

The obvious need is for direct spectroscopic work on the spectrum from solid targets in this low voltage region. Dr. J. C. Boyce and one of the writers have been engaged in an attempt to photograph such spectra, but thus far without success. With a 4 inch concave speculum metal grating, exposures up to 170 hours have failed to record anything

[10] O. W. Richardson, Phil. Mag. **23,** 263 (1912).
[11] J. Frenkel, Zeits. f. Physik **29,** 214 (1924).

except the zero order image of the slit. Experiments with a glass reflection grating, which we owe to Professor R. W. Wood, have shown its superiority in this spectral region, as tested by the spectra of gases, and we are now using it in a further attempt to photograph the soft x-ray spectrum from solids.

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