A Solid-State Interpretation of the Structure Near the Limit of the Continuous X-Ray Spectrum

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P. Ohlin has reported irregularities in his continuous x-ray spectrum isochromats taken at low voltage (3000 to 5000 volts) indicating that the continuous x-ray spectrum from thick targets may have, within 10 or 20 volts of the quantum limit, one or more indentations in which actual *reversals* of slope occur. Unpublished work of Bearden and Schwarz agrees with this. Much less pronounced irregularities about the same distance from the limit were observed at higher voltages (10,000 and 20,000 volts) by DuMond and Bollman much earlier. The present paper interprets these irregularities in terms of the permitted and excluded energy states for the electron in the crystal lattice in its final state after having radiated the x-ray photon. The paper explains (1) how negative slopes in the isochromats from a thick target are possible, (2) why the irregularities are much more pronounced for low than for high voltage isochromats, (3) how the observed isochromat curves may be corrected for the varying retardation of the cathode-ray electrons at varying depths beneath the surface of the target to obtain information regarding the transition probabilities and energy levels for the excluded and permitted empty energy bands for electrons in the target crystal lattice. Some of Ohlin's isochromats are reproduced giving their shapes before and after correction by this method. Confirming evidence from recent work of Davisson and Germer of entirely different nature regarding the position of the first excluded energy band above the Fermi conduction levels is cited.

THE IRREGULARITIES IN THE LOW VOLTAGE ISOCHROMATS EXHIBITING REVERSALS IN SLOPE

P. OHLIN at Uppsala, in a series of studies of the continuous x-ray spectrum for the purpose of determining the constant h/e, has observed curious irregularities[1] in his x-ray isochromats taken at long wave-lengths and low voltages. These occur within ten or fifteen volts of the short wave-length limit and appear in many cases as complete reversals of slope resulting in a sharply defined valley in which there may, in some cases, exist a saw-tooth structure. Schwarz and Bearden[2] have also observed just such structures in isochromats *taken at low voltages comparable with Ohlin's.*

The present author along with many others had long supposed that *a reversal in slope* in a thick target isochromat was an impossibility. The thick target spectrum is usually conceived as a superposition of thin target spectra coming from successively deeper and deeper elementary layers below the front surface of the target. Each successive thin target contribution has sensibly constant intensity per unit $d\nu$ extending from very low frequencies up to the quantum limit, but has lower and lower values of the high frequency quantum limit because the deeper layers are bombarded by electrons that have been retarded by greater penetration from the front surface.[3] On the basis of this somewhat idealized picture one cannot see how there can occur a reversal of slope in the profile of the spectrum or of the isochromat, for such a reversal seems at first to imply *negative intensity contributions* from some of the layers—an absurd impossibility. The spectrum from an ideal *thin target*, on the other hand, might well have such a structure near the short wave-length limit because of the permitted and excluded energy bands for the state of the final electron after the radiative transition. (Such a target must be "thin" in the sense of giving negligible cathode-ray retardation but not so thin as to destroy its crystal-lattice character and the resulting banded energy structure.) In a thick target the superposition of many such contributions progressively displaced in the manner suggested above would surely wash out such banded structural features. At the very best only plateaus could be expected *but no reversals of slope*. It was precisely this point which led the author to look more closely at the mechanism. Something must operate when isochromats are taken at low voltages to make

[1] P. Ohlin, Arkiv. f. Mat. Astr. Fysik **29A**, No. 3 (1942); **31A**, No. 9 (1944); **33A**, No. 23 (1946).
[2] Their complete work has never yet been published, at least to the author's knowledge. It was performed about six years ago.
[3] J. W. M. DuMond and V. Bollman, Phys. Rev. **51**, 409–410 (1937); *ibid.*, Figs. 8 and 9.

the observed spectra (or their images, the isochromats) *more nearly like thin target spectra*, and this must be less operative at higher voltages because such irregularities are much less marked there.[4]

SELF-ABSORPTION IN THE TARGET MATERIAL GIVES EFFECTIVELY THIN TARGETS AT LOWER VOLTAGES

The absorption of the radiation in the target material itself, as it emerges from layers beneath the front surface, limits the thickness of the total layer from which radiation is observable *to a far greater extent at low voltages than at high*. This is clearly demonstrated by the curves of Fig. 1 referring to copper and tungsten, two of the target materials used by Ohlin. Note that the curves giving the thickness of a target layer sufficient to retard electrons by 10 volts are convex *upward*, while the curves representing the order of depth from which the bulk of the observed radiation must come (limitation by fluorescent absorption in the target itself) *are convex downward*. The ratio of the x-ray path to the electron path in Ohlin's targets was estimated from the geometry shown in Fig. 10 of Ohlin's inaugural dissertation.[5] The curves marked "$1/e$ x-ray absorption layer" are therefore applicable as they stand only to this case of Ohlin's x-ray tube with direction of the observed x-ray approximately normal to the cathode-rays and with the target bevelled at approximately $\tan^{-1} 0.5$. Referring now to the abscissa scale, it is clear that, at Ohlin's voltages, absorption of the emerging radiation limits observations to layers in a tungsten target so thin that the electron retardation in those layers is of the order of 6 to 12 volts only, whereas even at the lower of DuMond and Bollman's two voltages (10 kv) the retardation in the observable layer would be of order 30 volts or more. Now it is also clear that such electron retardation exerts *a blurring effect*

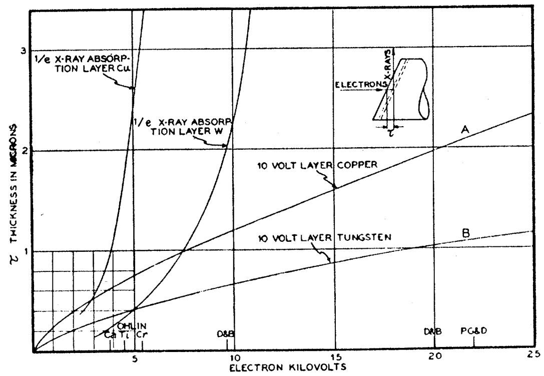

FIG. 1. The ordinates of the curves for copper and for tungsten, curves *A* and *B*, show the depth in microns that electrons of different initial energies (abscissae) must penetrate behind the face of a target of each material in order to be retarded by 10 volts. The curves marked $1/e$ absorption layer give on the same ordinate scale the depth, measured along the direction of the impinging electrons, from which the hardest continuous spectrum x-rays in Ohlin's targets must have come in order to be reduced in intensity by a factor $1/e$. This depth is assumed to be half the actual path of the x-rays in Ohlin's targets for the geometrical reasons illustrated in the small insert. For small retardations such as 10 volts in several kilovolts the electron retardation may be assumed to vary linearly with depth of penetration. These curves show that the layer from which the x-rays can be observed will produce much less electron retardation at low voltages, such as Ohlin's, than at higher voltages such as those of the observations of DuMond and co-workers. Ohlin's voltages, and also those of DuMond and Bollman, and Panofsky, Green, and DuMond are marked on the abscissa scale.

on the spectrum because the different parts of the total observed layer have been bombarded by electrons whose voltages vary over the entire range from that of the initially impinging electrons at the front surface to that of the most retarded electrons at the deepest observable depths. And the curves of Fig. 1 make it clear why this blurring effect will obliterate rugosities of profile such as those observed by Ohlin much more effectively at higher than at lower voltages. They also suggest that, even at Ohlin's low voltages and especially with his lower atomic number targets, such as copper, even *his* observed profiles have already suffered considerable blurring from the effect of electron retardation. It seems likely that if this effect could be completely removed Ohlin's corrected profiles might appear even more rugged. Fortunately this kind of blurring turns out to be rather readily amenable to analytical treatment so that we can pass beyond the qualitative considerations just presented above and actually effect a reasonably accurate quantitative cor-

[4] The reader is referred to the isochromats of the DuMond and Bollman paper (reference 3), Fig. 14, page 416, taken at 10 kv and 20 kv. He will find there in the observed points *slight vestiges of the Ohlin valley just above the knee* K_2. Although they are clearly evident and the author remembers distinctly that repeated observations in this region failed to remove these irregularities, they represented such small deviations from the smooth curve that at the time no important significance was attached to them.

[5] P. Ohlin, Dissertation (Uppsala, 1941).

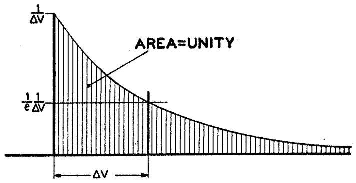

FIG. 2. The g curve which is folded into the ideal or thin target isochromat to give the observed thick target isochromat. The blurring effect of this g curve is the mathematical equivalent of the combined effects of (1) electron retardation and (2) absorption of the emerging continuous radiation. This g curve is normalized so as to have unit area.

rection of the observed curves when the initial blurring effect is not too extreme. (Let it be clearly understood that the blurring effect here referred to has nothing to do with "straggling" of electrons in speed or direction. For the thin layers and voltages here involved straggling is negligible.)

A METHOD OF CORRECTING ISOCHROMATS FOR THE EFFECTS OF ELECTRON RETARDATION AND SELF-ABSORPTION OF THE EMITTED CONTINUOUS RADIATION

Let us call $f(V)$ the ideal thin target isochromat that would be observed if the effects of electron retardation and absorption of the emerging continuous spectrum could be made

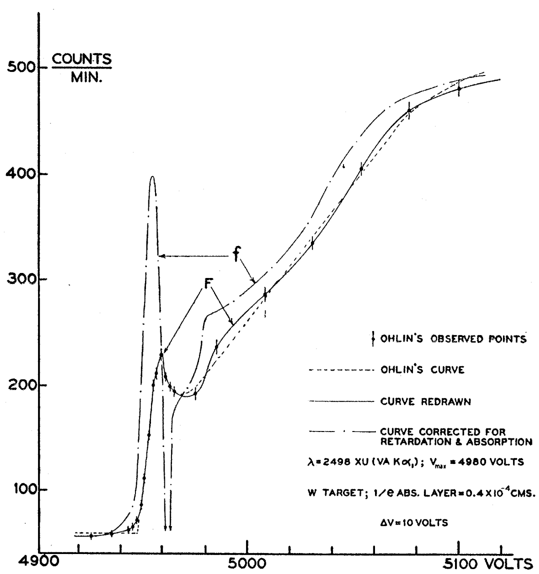

FIG. 3. One of Ohlin's isochromats taken with a tungsten target showing the profile both before and after correction for the blurring effects of electron retardation and absorption of the emerging continuous x-radiation.

completely negligible. Let $F(V)$ represent the actual observed isochromat which has undergone a certain amount of blurring from these two effects.

It is essential to realize that the combined effects of electron retardation and absorption of the emerging continuous spectrum transform the thin target isochromat $f(V)$ by "folding"[6] it with an exponential function $g(V)$ which is pictured in Fig. 2. The observed isochromat $F(V)$ is a weighted sum of many isochromats of the same shape as $f(V)$, which are successively displaced more and more to the right and at the same time weighted with exponentially diminishing weights according to the g curve of Fig. 2. Only one parameter is required to describe this weighting function g, namely, the displacement or retardation in volts ΔV at the point where the exponential curve has fallen to $1/e$ of its initial value. Clearly ΔV corresponds to the retardation suffered by electrons that have penetrated into the target to such a depth that the observed emerging radiation is reduced in intensity through fluorescent absorption by a factor $1/e$. For each target material and voltage, ΔV is a constant which depends on the ratio of the electron and x-ray paths in the target. ΔV will decrease with increasing x-ray absorption and increase with increasing electron retardation. The author has computed the value ΔV for each of the targets and voltages used by Ohlin in his studies of the isochromat structures. ΔV ranges from 6 volts to 25 volts in Ohlin's work.

The inverse operation of divesting a given folded function $F=f*g$ of the blurring effects of one of the folding factors g to obtain the other factor f is *in the present case fortunately both easy in theory and reasonably accurate in application.* From the physical situation we have that

$$F(V)=\frac{1}{\Delta V}\int_0^\infty f(V-u)e^{-u/\Delta V}du \qquad (1)$$

wherein the normalizing factor $(\Delta V)^{-1}$ has been

[6] The mathematical operation of "folding" one function into another usually comes under the theory of integral equations. The fold F of a function f by a function g is sometimes written symbolically as $F=f*g$. It may be defined as

$$F(t)=f*g=\int_A^B f(t-x)g(x)dx.$$

The limits A and B are defined to fit each particular case.

inserted to make the area under the exponential g curve unity so that ordinates and areas of the F and f curves will be comparable in magnitudes and as to physical dimensions. The variable u represents the retardation in volts of the cathode-ray electrons at any specified depth in the target. The significant depths over which the integral is extended are so small that straggling and changes in direction are negligible. The exponential factor in the integrand is the absorption factor for the emerging radiation generated at the depth for which the retardation is u. Now integrating (1) by parts

$$F(V)=-f(V-u)e^{-u/\Delta V}\Big]_0^\infty + \int_0^\infty\left\{\frac{\partial}{\partial u}[f(V-u)]\right\}e^{-u/\Delta V}du \quad (2)$$

$$=f(V)-\frac{\partial}{\partial V}\left\{\int_0^\infty f(V-u)e^{-u/\Delta V}du\right\} \quad (3)$$

$$=f(V)-\Delta V\frac{\partial F}{\partial V};\ \text{from Eq. (1).} \quad (4)$$

Solving for f we obtain

$$f(V)=F(V)+\Delta V\, dF/dV. \quad (5)$$

It is obviously very easy to apply formula (5) graphically to the profiles observed by Ohlin, without any numerical computations whatever, once ΔV has been computed for each curve. Ordinates are erected at intervals along the abscissa scale which are convenient submultiples of ΔV. A tangent fitted by means of a straight edge to the F curve at each of these ordinate points, is then projected to the right over an abscissa interval ΔV where its intersection with an ordinate gives the corrected value $f(V)$ which must then be replotted on the original ordinate where the tangent was constructed. The operation proceeds very rapidly on a drafting board using a T-square or a "universal" drafting machine.

The author has corrected a number of Ohlin's observed curves in this way, two of which are reproduced in Figs. 3 and 4. A slight uncertainty exists as to whether all of Ohlin's targets were such as to give just the same angle of grazing x-ray emergence as the one described in his dissertation. Small changes in this respect will chiefly change the heights of the peaks and depths of the valleys in the corrected curves but will not greatly affect the positions on the voltage scale at which these features occur.

The author has redrawn Ohlin's profile slightly in Figs. 3 and 4 so as to follow the observed points even a little more literally and with less smoothing out of apparent irregularities than did Ohlin. This is the curve represented with a full line and labelled F. The curve labelled f and represented with dots and dashes is the result of applying the correction of formula (5). This is then the profile that would be observed if the effects of electron retardation and absorption of the emerging radiation were completely removed.

The method of formula (5) obviously has its limitations. If ΔV is very large the term containing the derivative dF/dV dominates the expression and the corrected result becomes so sensitive to small local changes in slope of the observed isochromat that all accuracy is lost unless the precision of the original observations is much higher than can at present be attained.[7]

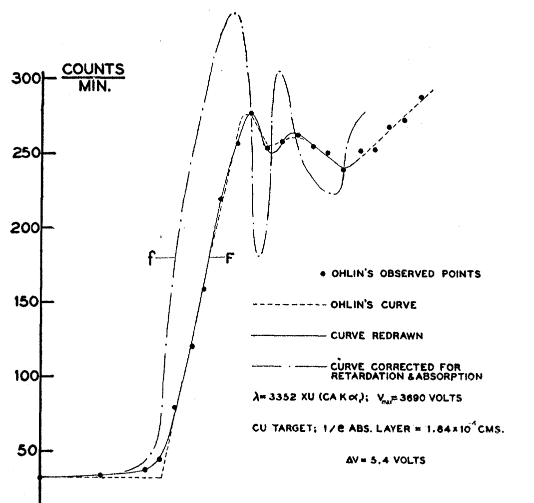

FIG. 4. Isochromat obtained by Ohlin with a copper target showing profiles before and after correction for electron retardation and x-ray absorption.

[7] When ΔV becomes so large that the cathode electrons, after a retardation ΔV, exhibit considerable straggling in speed and direction, formula (5) will cease to give a reliable correction. There may also be some error introduced even when ΔV is small by "rediffused" electrons returning from deeper layers of the target to the surface layer of "thick-

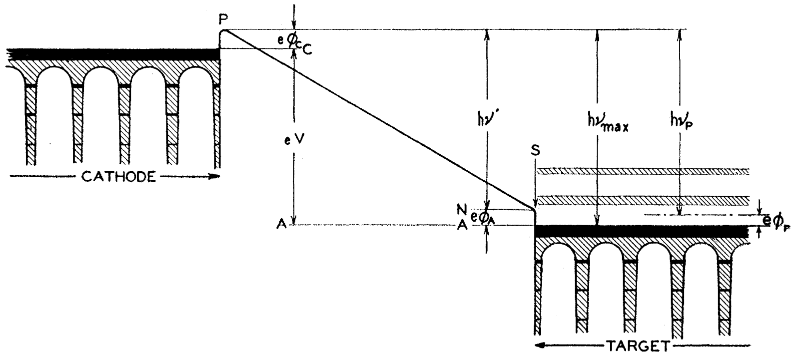

FIG. 5. Idealized energy diagram for transitions of electrons from the cathode to the anode of an x-ray tube. Energy is plotted vertically and a single space coordinate horizontally. The cathode is on the left, the target on the right. The arches and the line sloping downward from cathode to target represent the potential energy of an electron. The horizontal lines refer to the total energy and show the quantized energy levels or bands. Forbidden bands are cross-hatched. Permitted bands are white, save where they are occupied with electrons, in which case they are black. ϕ_C is the work function of the cathode, ϕ_A the work function of the target. The highest probability of transition corresponding to the first peak on the corrected isochromat is supposed to occur at some point ϕ_P volts above the uppermost Fermi levels in the target.

Even in the cases illustrated in Figs. 3 and 4 the derivative term introduces considerable uncertainty, especially in those regions of Ohlin's profile where his observed points are more widely spaced, since one cannot be quite certain of the true shape of the profile between the observations. In the light of the present interpretation it is hoped that Ohlin and others can repeat the isochromats very carefully with great attention to details and a still denser spacing of observed points. *The present evidence indicates pretty clearly near the short wave-length limit that there are one, or perhaps more, regions or bands in the corrected spectrum or isochromat in which the intensity falls nearly or even completely to zero.*

INTERPRETATION OF THE CORRECTED ISOCHROMATS IN TERMS OF ELECTRONIC ENERGY BANDS IN THE SOLID STATE

We believe these irregularities or dark bands, which are obviously much more pronounced after the correction has been made, reflect the fact that the final energy state of the cathode electron *after* the radiative transition has occurred *must be a permitted electronic energy state of the crystal lattice in which the transition occurs, and that there is here evidence for a banded structure of permitted and excluded energy states above the filled levels of the Fermi conduction electrons in the target.* We thus see in the profiles of the continuous spectrum a new means of studying the electronic energy bands of the solid state.

Figure 5 is a somewhat idealized energy diagram for the potential energy and also for the total energy of an electron in the cathode, the target, and in the electrical field between them in an x-ray tube. The excluded energy bands are shown in diagonal cross-hatching. The remaining regions are the permitted energy bands and where they are occupied by electrons, they are shown in black. In an electrical conductor there is always an unoccupied permitted energy region *above* the top of the densely filled Fermi levels. Above this in turn there may be an exluded or forbidden energy band followed again by a permitted band, etc. As one rises in this energy spectrum the excluded bands in all probability become narrower and narrower and eventually disappear altogether. One sees then that the initial sharp peak in the corrected isochromat of Figs. 3 and 4 in all probability corresponds to the transitions in Fig. 5, in which the final state of the electron is somewhere in the permitted band just above the top of the Fermi levels. The succeeding deep valley in the corrected isochromat probably corresponds to an excluded

ness" ΔV. Since such rediffused electrons would have suffered considerable retardation, errors of this type would probably affect the shape of the corrected isochromats chiefly in regions considerably distant from the short wave-length limit.

energy band immediately above this. A more accurate and detailed study of the isochromat profile may reveal, after correction, further successive bands of exclusion alternating with permitted bands.

It should be pointed out that the method of formula (5) corrects the isochromat only for the combined effects of electron retardation and absorption of the emerging radiation. After this correction has been made, there still remains the blurring effect of the "window curve" of the monochromator which is probably substantial. The author has made no attempt to correct Ohlin's isochromats for the effect of the monochromator window curve because (1) this is much more difficult, and (2) no data on the shape and width of the window are available to him. It is not inconceivable that some of the details of the corrected profile, now obscured by this further blurring effect, would later be revealed with improved resolving power.

Figure 4 shows that for the copper target the first deep dip or excluded energy band commences about ten or eleven volts above the short wave-length limit. Now the author has recently learned from Dr. C. J. Davisson[8] that in very recent work done with Dr. L. H. Germer at the Bell Telephone Laboratories (still unpublished) *there is clear evidence for just such an excluded energy band about ten volts above the topmost energy of the Fermi conduction electrons in copper.* Davisson and Germer bombarded a copper crystal with very slow electrons projected normally against the (111) planes. They found that when the cathode is six volts more negative than the copper target, the electrons refuse to enter the latter and are strongly reflected from the surface although they do enter at lower voltages. With increasing voltage, successive higher energies are found at which electrons are successively accepted and rejected according to a banded structure. To Davisson and Germer's measured voltage between their cathode and target (the difference in the energy levels A and C in Fig. 5) the present author believes there must be added the work function of their cathode (ϕ_C, Fig. 5, or 4.5 volts approximately) *to find the energy of their impinging electrons relative to the uppermost Fermi levels in their target.* The sum then (4.5 volts plus 6 volts or 10.5 volts) thus gives remarkable confirmation to the present observations regarding the first deep valley in the curve f of Fig. 4.

COMPARISON OF PRESENT THEORY WITH THAT OF NIJBOER

The author is indebted to Dr. P. Kirkpatrick of Stanford University who examined an advance copy of the present paper for calling his attention to B. R. A. Nijboer's recent paper[9] in which the idea is proposed that the Ohlin structures under discussion may be ascribed to the banded structure of the empty permitted energy levels for electrons in the target crystal lattice. J. A. Bearden also informs the author that the same idea occurred to him but that he rejected it because of the rather large energy jump indicated in his *uncorrected* isochromats measured from the short wave limit to the dip or valley. Thus the simple and primitive idea of associating these dips with banded energies in the solid state is not new. It has doubtless occurred to many. What *is* new and significant, however, in the present author's ideas is:

(1) The explanation of why these dips are so much more pronounced in low voltage isochromats than in high.

(2) The explanation of how *reversals in slope* in the isochromats from thick targets are possible at all.

(3) The development of formula (5) giving the quantitative method of correcting the observed isochromats so as to divest them of the blurring effects of electron retardation and absorption of emerging x-radiation. This correction makes possible the important interpretation of the corrected curves as reliable information on the banded structure of the electron energy levels in the target crystal lattice and, therefore, brings to bear a new tool for the study of the solid state.

Nijboer in his short paper admits his inability to explain the reversals in slope in the isochromats. This is because it did not occur to him to take into account the effects of target absorption and electron retardation in the way that we have explained here. Nijboer, on the other hand, tries to explain the Ohlin structures by calling into play the banded energy level structure of the target, not only in its effect on the x-ray transitions near the quantum limit *but once again*

[8] The author is much indebted to Dr. W. Shockley for first informing him of this most interesting confirmation. Dr. Davisson himself described the results to the author.

[9] B. R. A. Nijboer, Physica 12, No. 7, 461 (Oct. 1946).

in its effect on the retardation of the electrons entering the target. He points out that for small energy losses of the cathode-ray electrons these energy losses must also have a banded structure. *This is probably not the primary explanation of the Ohlin valleys, however, for if it were there would be no explanation for the fact that the valleys are far more pronounced in low voltage isochromats than in high voltage ones.* Furthermore, the banded structure of electron energy losses could hardly be observed *as a function of depth or thickness* of a layer of solid copper or tungsten of several microns and, therefore, many atom diameters thickness. This is because *multiple losses* in traversing such a solid layer are extremely likely. It must be recalled that energy losses communicated by the primary cathode electron to very distant electrons in the solid account for a good part of the retardation. For the Fermi (4*s*) electrons alone in solid copper these losses have zero volts as their lower limit and about 9.5 volts as their upper limit, and they can have all intermediate values with a very smooth probability distribution. The 3*d* electrons can accept energies which also have a fairly smooth distribution covering a range of energy losses from about 6 volts to 11 volts with only one very narrow excluded band at losses of about 10 volts.[10] One must also remember that if multiple collisions are likely to occur with a multiplicity n, then the probability distribution curve for multiple losses will be the result of *folding* the already rather smooth curve for single collision losses into itself n times. This should surely wash out its banded structural features almost completely even if n were only equal to 2. The author knows of no experimental evidence favorable to the idea that the retardation of a beam of fast electrons penetrating a thin layer of matter is not substantially *proportional to the thickness* of the layer for the first few volts or tens of volts retardation. On this assumption rests the validity of the author's theory of the Ohlin dips and his method of correcting the curves for electron retardation. Small deviations from a linear dependence of retardation on thickness will of course only introduce small corrections into the result. The g curve of Fig. 2 may not have the perfectly smooth idealized exponential profile there shown but the errors so introduced will probably be small.

Ohlin's published isochromats do not extend very far back from the short wave-length limit. If the present interpretation is correct, an application of the correction of formula (5) over a somewhat larger range of voltage should result in a corrected isochromat which eventually and rather rapidly levels off to a nearly flat plateau in the manner that theory[11] and experiment[12] lead us to expect for a thin target isochromat or spectrum. In order that this may occur the observed thick target spectrum at low voltages, such as Ohlin's, must itself bend over and level off rather rapidly. It would be interesting to know whether this actually occurs if Ohlin's low voltage isochromats are explored to greater distance. Reference 7, however, suggests that such a process must be interpreted with caution.

SUGGESTED TESTS AND APPLICATIONS OF THIS NEW INTERPRETATION

The present interpretation of the irregularities in Ohlin's isochromats lends itself to the following predictions which may afford a test of its correctness and a program for further investigation. (1) By varying the angle of the target face so as to change the obliquity of the angle of grazing emergence of the observed continuous x-radiation one can readily vary ΔV. A more grazing emergence gives a smaller ΔV, and it should thus be possible to exaggerate greatly and at will the ruggedness of the profile. (The target face must of course be smooth and free from pits.) (2) A *liquid* target would probably not manifest the same irregularities in the isochromat, nor to the same degree, if at all.[13] Little is known about the electronic energy states in liquid metallic conductors. (3) Comparison of the corrected isochromat profiles from targets of different conducting and even semiconducting materials with

[10] See Krutter's work described in Frederick Seitz, *Modern Theory of Solids, International Series in Physics* (McGraw-Hill Book Company, New York, 1940), p. 423.

[11] See W. Heitler *Quantum Theory of Radiation* (Clarendon Press, New York, 1936), pp. 161–171 and Fig. 14, taking into account corrections for Sommerfeld factor, etc. Also A. Sommerfeld, Ann. d. Physik **11**, 257 (1931), and P. Kirkpatrick and L. Wiedmann, Phys. Rev. **67**, 336 (1945).

[12] See W. W. Nicholas, J. Research Nat. Bur. Stand. **2**, 837 (1929).

[13] In the third of Ohlin's papers cited in reference 1 the curves for a lead target show much less pronounced dips. It is quite possible that the lead in the immediate vicinity of the focal spot was molten.

the already known facts from other sources[14] regarding the widths and patterns of the electronic energy bands of these same materials in the solid state, might reveal supporting evidence for the proposed interpretation. (4) Perhaps the easiest and most significant test of the proposed ideas might be made by exploring two isochromats at closely adjacent monochromatizing wave-lengths, λ_1 and λ_2, selected so that the critical K-absorption wave-length λ_K for the target material would lie between them. Under these circumstances ΔV would be much larger for the longer of the two wave-lengths because of the decreased absorption of the emerging radiation so that, of the two isochromat profiles, *the one for shorter wave-length should appear markedly more rugged.* The angle of grazing emergence of the radiation should obviously be selected so as to keep ΔV appropriately small in both cases. A corollary to this is that for best definition of the corrected profiles the isochromats should be taken at a wave-length just shorter than the K-absorption edge of the target material.

It is of some interest to discuss the bearing of the present conclusions on the original objective which motivated the investigations: the determination of h/e. The author's corrected isochromats obtained by applying formula (5) to Ohlin's curves show very little shift of the short wave-length limit after correction. These shifts, which are of the order of only one or two volts at most, *are all in a direction to lower the values of h/e obtained by Ohlin.* Since they are so small, however, relative to other uncertainties in his work and since, as already pointed out, even the present "corrected" isochromats have not been corrected for the monochromator window curve, it seems inappropriate at present to dwell in detail on this point.

It may be valuable, however, to recognize a new possibility that the present ideas suggest for improving precision in future h/e determinations. If the present interpretation is correct, that the first sharply defined peak or maximum in the corrected isochromat corresponds to transitions of the electron to final energy states in the band of permitted energies just above the top of the uppermost Fermi conduction electron energies, *then it may be possible to determine h/e with higher precision by determining the voltage where this corrected isochromat peak occurs* (instead of the voltage at the extreme limit of the isochromat). If we call this voltage at the first peak on the corrected isochromat V_P, and if the energy level where it occurs is ϕ_P volts higher than the top of the Fermi levels in the target, then

$$\frac{h}{e}=\frac{(V+\phi_C-\phi_P)\lambda}{c},$$

where ϕ_C is the work function of the cathode and λ is the wave-length for which the center of the monochromator window is set (see Fig. 5). One advantage in using the center of this permitted energy band as a reference point, rather than the top of the Fermi distribution, is that by so doing we are, so to speak, *matching a symmetrical exploring tool (the monochromator window curve) against a nearly symmetrical spectral feature (the permitted energy band)* as contrasted with the highly unsymmetrical feature (the lower limit of that permitted band) used at present. The advantage in interpretation of the results is that the center of the first peak of the isochromat can be ascertained much more accurately than the position of the limit itself, blurred as it is by the window curve.

It should be noted that, even if ϕ_P is not known, this new method for determining h/e can still be used *by running two isochromats at two different voltages and measuring the voltage difference between the peaks on the corrected curves* because ϕ_P (and also ϕ_C) will be substantially the same in both cases and will cancel out in taking the difference. Needless to say, both isochromats must be taken at sufficiently low voltage to permit effective correction of the curve without too great an uncertainty from the derivative term of Eq. (5).

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[14] See, for example, the interpretative studies of fine structures of absorption edges, such as those of R. de L. Kronig, Zeits. f. Physik **70**, 293 (1931), and experiments such as those of C. H. Shaw, Phys. Rev. **70**, 643 (1946) on gases.