law to the solid at the melting point. These data suggest that the assumptions underlying the evaluation of the Grüneisen parameter from the equation of state on the Debye model are met reasonably well by elementary solids, on the average.

V. CONCLUSION

The results obtained show that formal consideration of finite strain leaves the evaluation of the Grüneisen parameter from the equation of state unaltered, for either a Debye solid or a Druyvesteyn-Meyering solid. Hence, no reason exists on the basis of the theory of finite strain for the arbitrary modification in the evaluation of the parameter for a Debye solid, as proposed by Dugdale and MacDonald. This statement presupposes that the wave amplitudes of the lattice vibrations are infinitesimal. It is not denied that an intrinsically anharmonic theory, such as that of Born and Brody[21] or of Hooton,[22] may demand revision of the value of the Grüneisen parameter as determined from the equation of state, but such a model likewise requires revision of the value of the characteristic frequency, as fixed by Eq. (8) on the Debye theory. Underlying the definition of the Grüneisen parameter is the postulate that all lattice frequencies vary with volume in the same manner; it is not obvious, *a priori*, that this requirement can be met within the framework of an essentially anharmonic theory.

The development of I, II, and III is based on the Debye-Waller theory derived from the Debye model, in contrast to the original Lindemann theory based on an Einstein model. Since the form of Grüneisen parameter taken in the papers in question corresponds to the Debye theory, it is felt that in this respect the results have been justified fully.

ACKNOWLEDGMENTS

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Auger Electron Emission in the Energy Spectra of Secondary Electrons from Mo and W

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With the aim of determining to what extent the energy distribution of secondary electrons from targets of Mo and W may contain fine structure, measurements have been made using primary energies from 100 to 2000 electron volts. An electrostatic analyzer of the 127-degree type having an experimentally determined resolution of one percent was used. Observations of the pressure in the vacuum system, after heating the target above 2000°K and cooling to room temperature, showed that an energy spectrum could be recorded before formation of the first monolayer of contamination on the target surface.

Energy distribution measurements revealed: (1) Several subsidiary maxima at fixed differences in energy from the primary energy, these differences being characteristic of the target material and independent of the primary energy itself. (2) Several subsidiary maxima in the energy distribution at fixed positions along the energy scale lying between 10 and 500 electron volts, characteristic of the target material, and independent of the primary voltage. The maxima described in (1) are considered to be primary electrons reflected after suffering discrete losses of energy to the target. These discrete losses are believed to indicate the positions of the higher energy levels of the target material. The maxima described in (2) are interpreted as Auger electrons. Combining the energy level values determined from the discrete loss measurements with energy values for the deeper lying levels available from x-ray studies, it is possible to predict the energies with which Auger electrons might be expected to be emitted. Some of the predicted energies for Auger electrons agree reasonably well with with the energies observed experimentally both for Mo and for W.

I. INTRODUCTION

THE general shape of the energy distribution of secondary electrons from a metal target is that of a smooth curve whose two principal features are a large maximum of slow secondaries occurring near two or three volts and a sharper, usually smaller maximum, caused by elastically reflected primaries. Furthermore, several workers have observed some fine structure in the energy spectrum of secondaries from a number of different metals. Rudberg,[1] studying Cu, Ag, and Au, reported inelastic reflection of primary electrons that had suffered discrete losses of energy, these losses being independent of the primary energy and characteristic of the target material. Haworth[2,3] made similar observations for targets of Mo and Cb but observed further that

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[1] E. Rudberg, Phys. Rev. **50**, 138 (1936).
[2] L. J. Haworth, Phys. Rev. **48**, 88 (1935).
[3] L. J. Haworth, Phys. Rev. **50**, 216 (1936).

another type of fine structure occurred. This consisted of small subsidiary maxima or "humps" indicating that electrons were being preferentially emitted at certain fixed energies, these also being independent of the primary energy and characteristic of the target. The emission of secondary electrons at fixed energies was studied experimentally by Lander[4] and explained by him as the result of Auger processes. Lander was able to observe Auger electrons from twelve different types of targets.

This present work was undertaken to determine to what extent the energy spectra of secondary electrons from Mo and from W contained fine structure. These metals were chosen because they could be readily cleaned by heating to high temperatures. Previous measurements of secondary energy spectra from Mo and W include the work of Haworth already mentioned and also measurements by Kollath.[5] For Mo, Haworth found fixed energy "humps" of secondary electrons at 11, 24, and 35 electron volts and primary discrete losses of 10.6, 22, and 48 electron volts. Kollath observed the energy spectrum for Mo and W over the range from zero to 30 electron volts and found that both metals gave smooth curves, each having a single large maximum near two electron volts and exhibiting no apparent fine structure. The work reported here, carried out with the advantages of clean targets, good vacuum and sensitive and stable apparatus, reveals a very considerable amount of fine structure in the energy spectra of the secondary electrons from both Mo and W. This fine structure can be accounted for in terms of inelastic reflection of primary electrons and the resulting emission of electrons from the target by means of various Auger processes.

II. APPARATUS

The apparatus used in this work divides into two parts: the vacuum tube and the auxiliary circuits. The system is shown schematically in Fig. 1. The vacuum tube contains three principal components—the electron gun, the target under observation, and the energy analyzer. The electron gun employed a directly heated tantalum ribbon cathode, this being preferable to an oxide cathode because the tube had to be opened to change targets, and also preferable to a tungsten cathode because tantalum provides a higher emission current density. Since the gun had to operate through a range of voltages from 100 to 2000 volts, a positive grid was placed in front of the cathode to ensure adequate emission at the lower voltages. A simple lens system focused the primary electron beam, and deflecting plates served to center the beam on the target. The primary current density at a distance from the gun corresponding to the position of the target, was measured to be 140 ma per square inch for a gun voltage of 500; this value was an upper limit set by the spreading of the beam due to its own space charge.

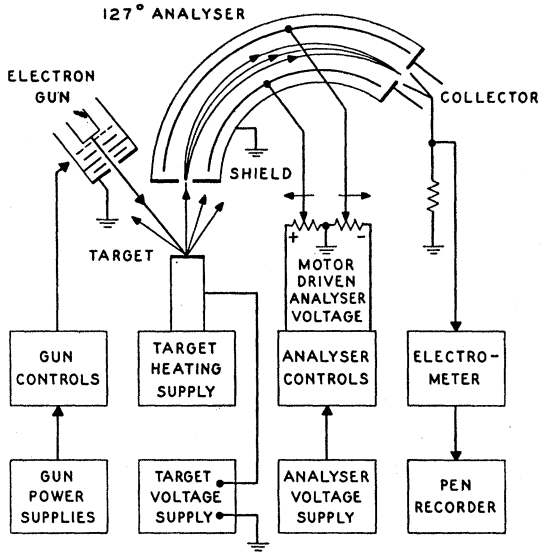

FIG. 1. Schematic diagram of the apparatus used showing the components of the experimental tube—electron gun, target, and analyzer, and the associated electric circuits.

The targets used were in ribbon form measuring in inches 1×0.125×0.0015 and were supported between two 0.1-inch Mo rods. The target ribbon could be heated to clean its surface by passage of a current of the order of 20 amperes for Mo and 30 amperes for W.

The analyzer was of the electrostatic 127-degree cylindrical condenser type previously used by many experimenters and described by Hughes and Rojansky.[6] This type of analyzer offers the advantages of simple construction, small size, absence of a magnetic field, and has the property of focusing electrons from entrance slit to exit slit. The voltage V_a applied between the deflecting plates is related to the energy V_0 in electron volts of an electron able to pass through both slits to the collector by

$$V_a = V_0 \ln(b/a), \tag{1}$$

where b and a are the radii of the outer and inner deflecting plates, respectively. Consequently, a measured spectrum of electron energies is linear against voltage applied to the analyzer. The range of energies ΔV of a group of electrons with mean energy V able to pass through the slits of the analyzer is given by

$$\Delta V = V(\Delta R/R_0), \tag{2}$$

where ΔR is the width of one slit and R_0 is the mean radius of the deflecting plates. Equation (2) expresses a troublesome effect present in all analyzers, electric or magnetic, which operate by producing a deflection of the electrons or ions being observed. Since both resolution and sensitivity are proportional to ΔV they are

[4] J. J. Lander, Phys. Rev. **91**, 1382 (1953).
[5] R. Kollath, Ann. Physik **1**, 357 (1947).
[6] A. L. Hughes and V. Rojansky, Rev. **34**, 284 (1929).

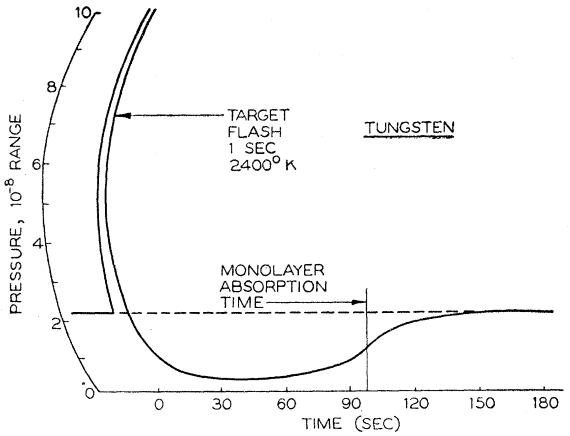

FIG. 2. Pressure in the vacuum system *versus* time following flashing the target. The interval of abnormally low pressure is used to determine the time required for a monolayer of contamination to accumulate on the target surface. This record was made for display purposes only; actual measurements were taken at much lower pressures and with much longer monolayer adsorption times.

both proportional to V, the mean energy of the particles being measured. The result is that the analyzer discriminates against low-energy particles, the effect being most severe at energies approaching zero. The effect might be described as a variation of the effective slit width. A measured energy spectrum can be corrected for the effect either by dividing all measured analyzer currents by a number proportional to the corresponding energy V or by applying this same correction automatically by means of a dividing resistance network synchronized with the sweep voltage. However, since the correction needed is greatest at energies near zero, a simpler and, in this work entirely adequate procedure, consists of applying a voltage between target and analyzer to increase the energy of electrons entering the analyzer by a constant fixed amount. As will be described later, this voltage was sometimes chosen with a different end in view. A certain amount of the distortion of the energy spectrum always remains owing both to some variation of the effective slit width still present, and to the preferential acceptance of slower electrons caused by the voltage applied between target and analyzer. Although this situation makes absolute measurements uncertain, the distortion remains constant and, therefore, does not interfere with the observation of changes occurring from one spectrum to another. The analyzer used in this work was equipped with collimating apertures at the first slit to restrict the angle of entry of electrons to plus and minus three degrees; the deflection path through the analyzer had a radius of 1.88 inches; the experimentally determined resolution of the device was one percent.

The circuits and auxiliary apparatus used with the experimental tube are shown schematically in Fig. 1. Power supplies and control circuits are required to operate the electron gun. A high current supply is used to heat the target while the target voltage supply permits keeping the target at other than ground potential. The voltages between cathode of the electron gun and target and between target and analyzer were measured and maintained with an accuracy of 2 parts in 10^4. The analyzer voltage supply and control circuits provide the voltages for the deflecting plates through a pair of potentiometers driven by a synchronous motor. The range of electron energies observed by the analyzer can be of any width within the limits zero to 2000 electron volts. The current reaching the collector flows through a resistor (usually about 10^{10} ohms) developing a voltage which is transferred through an electrometer to the pen recorder where the measured energy spectra are displayed. After gun and analyzer voltages have been set as desired, the energy spectrum is recorded automatically. A spectrum is recorded in four minutes, this being governed by the resolution of the analyzer and the time constant of the recording apparatus.

III. TARGET CLEANING PROCEDURE

In order that observations be representative of the target material itself it is of prime importance that the target surface be cleaned and remain clean during the course of each measurement. The cleaning procedure involved two operations—first, a prolonged high temperature treatment to drive out impurities within the target material (about 15 hours at temperatures of 2000°K for Mo and 2600°K for W), and secondly, a brief heat treatment immediately before each measurement (1 or 2 seconds at 1900°K for Mo and 2400°K for W). The results produced by this second brief heat treatment can be seen in Fig. 2 where pressure in the

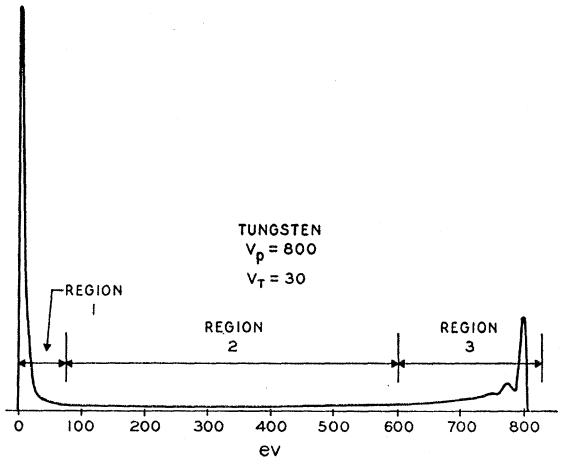

FIG. 3. The general shape of the energy spectrum of secondary electrons from a tungsten target with a primary voltage of $V_p=800$ and a voltage between target and analyzer of $V_T=30$. The ordinate is proportional to the number of electrons per unit energy interval and the abscissa is electron energy in electron volts. The spectrum is divided into three regions. Region 1 contains the large low-energy maximum located at two or three volts. Region 2 contains few electrons and is relatively flat. Region 3 includes elastically reflected primary electrons and also some fine structure just below the primary energy.

vacuum system is plotted as ordinate and time as abscissa. When the target is heated or "flashed," the pressure rises suddenly but begins to fall again as soon as the gas released from the target surface has been pumped away. When the target is cooled after the brief flash, the pressure falls below the preflash level. This is the result of the clean target surface adsorbing gas and acting as a rather fast vacuum pump. This process has been described by Becker and Hartman[7] and by Hagstrum.[8] When the target surface has become covered with a monolayer of gas, the probability of more gas being adsorbed is greatly reduced, the target ceases to act as a pump, and the pressure returns to its preflash level. The time during which the pressure remains below normal is a measure of the time required for the target surface to acquire a monolayer of contamination. This monolayer adsorption time is inversely proportional to the pressure, being about one second for a pressure of 1×10^{-6} mm of Hg. In this work, pressures below 1×10^{-10} mm of Hg could be maintained and monolayer adsorption times in excess of ten hours have been observed. By this procedure, then, the target could be cleaned before each energy spectrum was recorded and a record of the pressure in the vacuum system served to show that the measurement had been completed before a small fraction of a monolayer of contamination formed on the target surface.

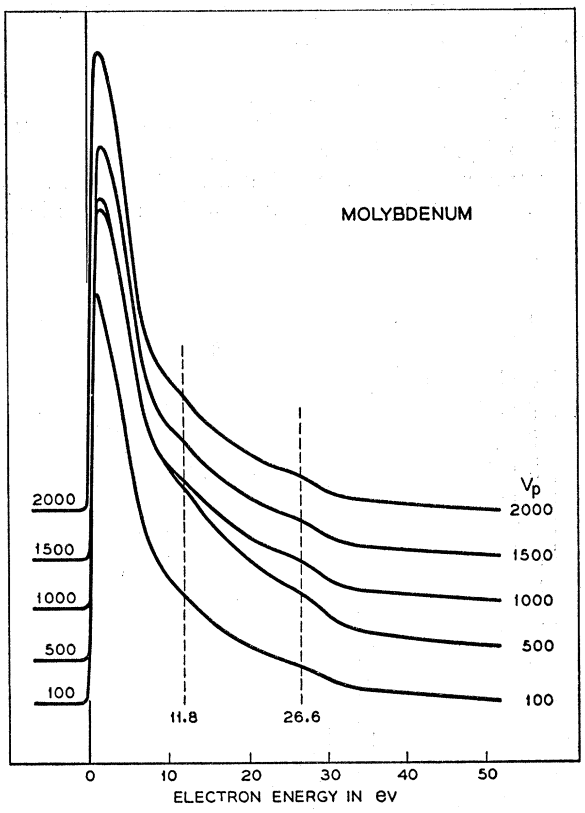

FIG. 4. Region 1 of the energy spectrum of Fig. 3 for a Mo target. The normally larger low-energy maximum has been attenuated by applying a retarding voltage between target and analyzer and the amplification has been increased to reveal subsidiary maxima as marked.

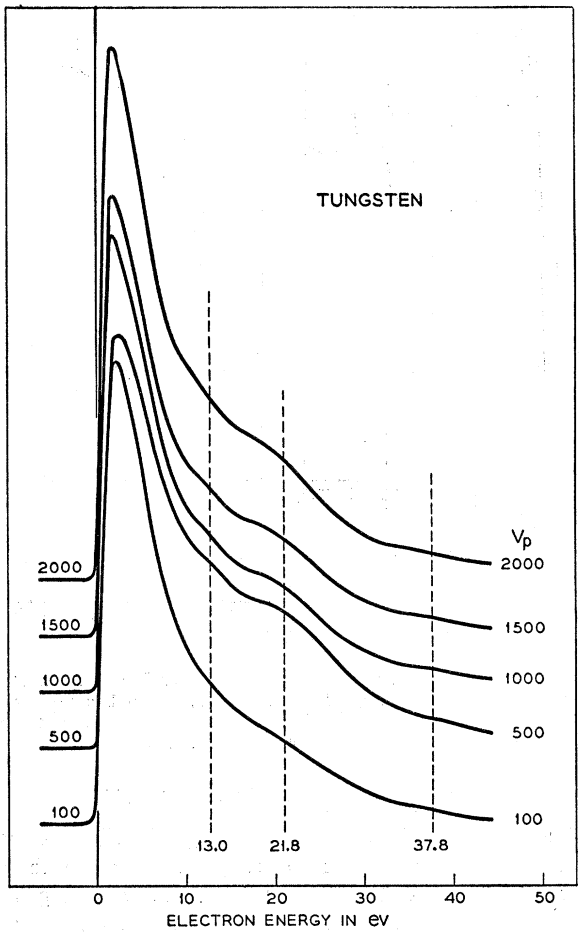

FIG. 5. Region 1 of the energy spectrum for a W target. See caption for Fig. 4.

IV. CONTACT POTENTIAL CORRECTIONS

Measurements must be corrected for two contact differences of potential. The first exists between the cathode of the electron gun and the target and its effect will be to make the primary electrons strike the target with an energy slightly different from that indicated on on the external voltmeter. The second exists between the target and the first slit of the analyzer. This necessitates a correction to the energy scale of all measured spectra. All numerical results quoted subsequently have been corrected for both of these effects using published values of work functions. Contact potential differences did not exist inside the analyzer since it was constructed entirely of copper.

[7] J. A. Becker and C. D. Hartman, J. Phys. Chem. **57**, 153 (1953).
[8] H. D. Hagstrum, Rev. Sci. Instr. **24**, 1122 (1953).

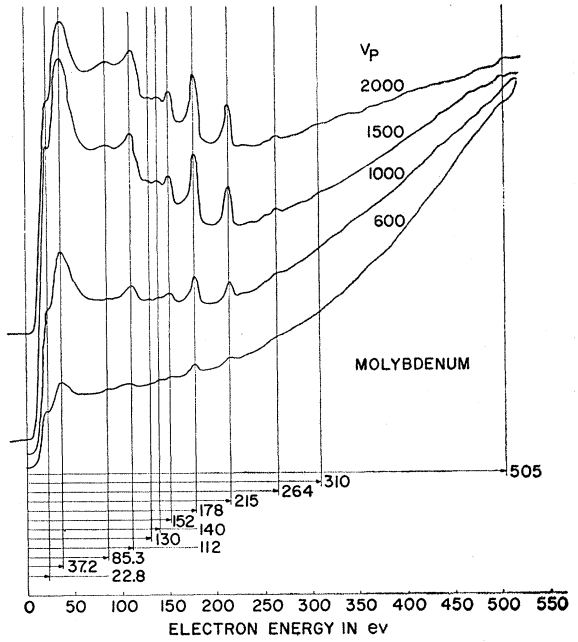

FIG. 6. Region 2 of the energy spectrum of Fig. 3 for a Mo target. The normally large low energy maximum has been attenuated and the amplification increased to reveal Auger electrons being emitted at certain fixed energies as marked.

V. EXPERIMENTAL MEASUREMENTS

The general shape of the energy distribution of secondary electrons from a tungsten target with a primary voltage of 800, is shown in Fig. 3. A voltage of 30 volts was placed between target and analyzer to increase the energies of all electrons by that amount and thus partially to correct for the variation of effective slit width of the analyzer. The energy distribution may be considered to consist of three parts. Region 1 includes the low-velocity or "true" secondaries. Region 2 is flat and contains relatively few electrons. Region 3 includes the elastically reflected primary electrons and some subsidiary maxima just below the primary energy. In this experimental work, these three regions were studied individually.

The search for fine structure in the energy distribution began in Region 1—the low-energy end of the spectrum. The results are shown in Fig. 4 for a Mo target and in Fig. 5 for W, with primary voltages between 100 and 2000 volts. Each curve is seen to contain small broad maxima characteristic of the target material and independent of primary voltage. In these measurements, as in those to follow, many more spectra were recorded than those shown in the figures and the energy values stated are the averages of a large number of observations; furthermore, these energy values refer to the true energy of the electrons as they left the target surface, the measurements having been corrected for contact differences of potential and for the voltage applied between target and analyzer.

Similar measurements were made for that part of the energy distribution called Region 2 in Fig. 3. These measurements are displayed in Fig. 6 for Mo and in Fig. 7 for a W target with primary voltages between 500 and 1000 volts. A fixed retarding voltage of 10 volts was used between target and analyzer to eliminate the low-energy secondaries. This permitted an increase in amplification of the currents being measured by a factor of approximately 1000. Figure 6 and Fig. 7 reveal the presence of a surprising amount of fine structure in the middle range of secondary energies. The details of this structure occur at fixed energies independent of the primary energy and characteristic of the target material. It can be seen that the fine structure tends to disappear for primary energies below 500 electron volts.

Finally, observations were made in Region 3 of Fig. 3. As was mentioned in the introduction, the detailed structure found in this region has been described and explained by previous workers. Figure 8 shows measurements made for Mo and Fig. 9 for W targets with primary energies from 100 to 2000 electron volts. These curves are superimposed so that the positions of the sharp peaks of elastically reflected primary electrons coincide. These primary peaks are drawn in for some of the curves. (The variation in their widths is indicative of the fact that the absolute resolution of the analyzer is dependent on energy.) The energy scales on the horizontal axes of Fig. 8 and Fig. 9 are arranged as "energy loss in electron volts" suffered by the primary electrons. This is in accordance with the hypothesis

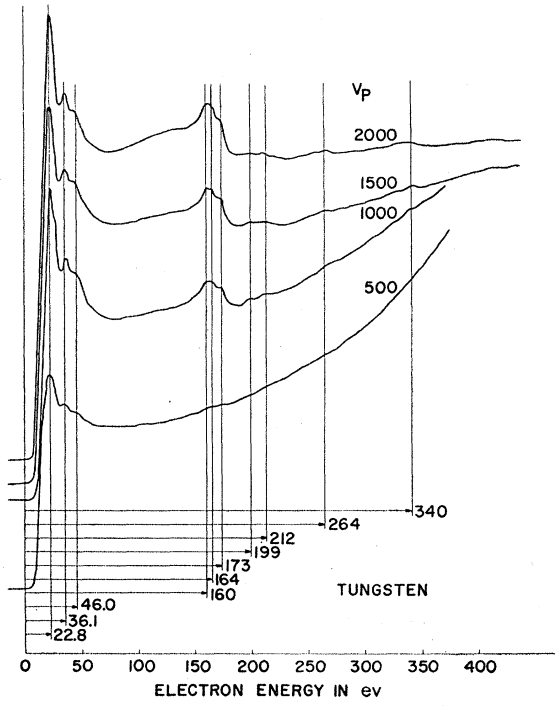

FIG. 7. Region 2 of the energy spectrum for a W target. See caption for Fig. 6.

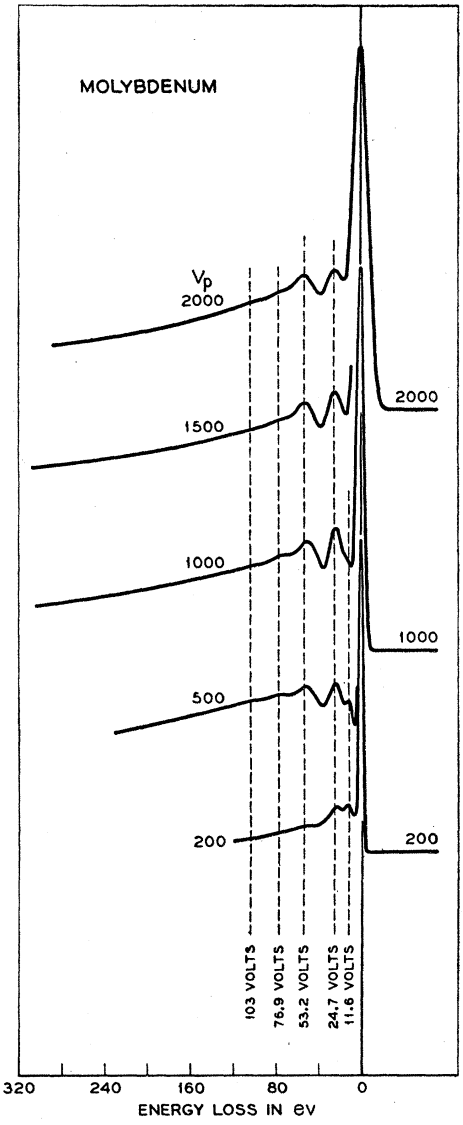

FIG. 8. The energy spectrum near the primary energy for a Mo target. Primary electrons are seen to be reflected both elastically without loss of energy and inelastically after suffering certain discrete energy losses which are independent of the primary energy and characteristic of the target material.

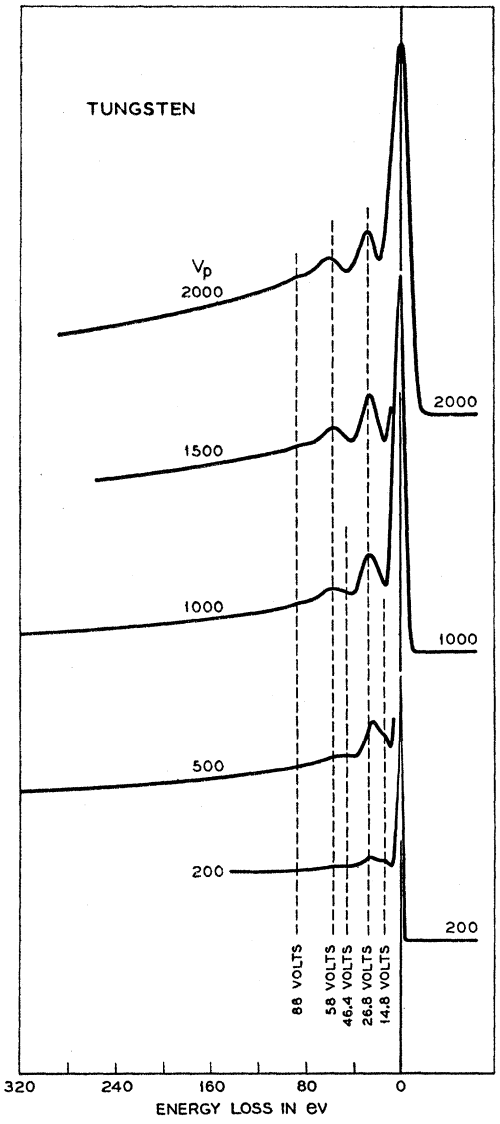

FIG. 9. The energy spectrum near the primary energy for a W target. See the caption for Fig. 8.

that the subsidiary maxima appearing below the primary energy are caused by primary electrons reflected from the target after having undergone discrete losses of energy. These discrete losses are indicated in Fig. 8 for Mo and Fig. 9 for W.

From the quantities of energy involved, it may be assumed that the discrete losses suffered by primary electrons are the result of interactions involving the outer electron shells of the target atoms. Since Mo and W occur in the same column of the periodic table, that is, their outer electron shells are assembled in a similar manner, it might be expected that primary electrons would show similar patterns of discrete losses for the two materials. The discrete loss patterns are compared in Fig. 10. The two spectra are much alike and lines are drawn in the figure to show the correspondence between certain of their small maxima. The energy loss of 46.4 electron volts seen in the case of W without a corresponding loss for Mo may be the result of the fourteen $4f$ electrons present in W and absent in Mo. The maximum at 46.4 electron volts has the proper location relative to the other maxima to agree with the position of the $4f$ band in W as determined from x-ray measurements.

VI. INTERPRETATION

Two features found as fine structure in these measurements must be discussed. The first is the discrete losses

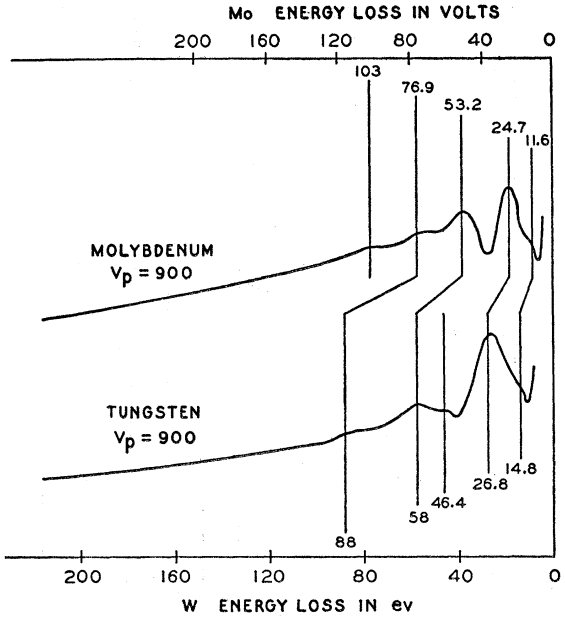

FIG. 10. A comparison of discrete energy losses suffered by primary electrons inelastically reflected from Mo and W targets. Vertical lines have been drawn to indicate the similarities which are attributable to the fact that Mo and W occur in the same column of the periodic table.

of energy suffered by primary electrons and shown in Fig. 8 and Fig. 9; as mentioned before, these losses have been observed and explained by others. The second feature is the emission of electrons at a series of fixed energies independent of the primary energy and characteristic of the target material as shown in Figs. 4 to 7. These two features can be explained and related with the aid of the energy-level diagram of Fig. 11 which is intended to be simply schematic. Shaded areas represent the filled portions of energy bands; the two uppermost bands are shown to be overlapping; the work function is indicated as ϕ.

Consider a primary electron which arrives at the target with energy V_p measured from the zero vacuum level, enters the lattice, and interacts with an electron in band D. Assume that energy is transferred from the primary to the D-band electron until the latter rises in energy to the uppermost filled level where it is free to behave as a conduction electron and the interaction ceases. We shall assume that this is the most probable transition. This process is shown on the left side of Fig. 11. The primary, having lost the energy V_0 because of its interaction with the D-band electron, leaves the target again and will be observed as an inelastically reflected primary having the energy V_p-V_0. This process, and others involving similar interactions with electrons in other bands, explains the observed discrete losses shown in Fig. 8 and Fig. 9. Furthermore, we shall use the measured values of discrete losses and shall add to each an amount of energy equal to the work function ϕ, in conformity with the assumption made above, to provide the locations of some of the upper energy bands of the target material, or more precisely, the location of the maxima of electron density within the various filled bands.

An explanation can now be given for the electrons observed to be emitted with certain fixed energies. These electrons will be considered to result from Auger processes.[9] The details of such processes are shown in the right side of Fig. 11. Two electrons take part in an Auger process. The first electron, originally in band C, drops to fill the vacancy in band D previously created by the action of a primary electron. In this way an amount of energy E_D-E_C is released. This energy, instead of appearing as a quantum of radiation, is given to a second electron, shown in Fig. 11 to have been originally in band A. This second electron is emitted from the metal thereby losing energy E_A and appearing outside the metal with a final energy $(E_D-E_C)-E_A$. In the special case in which the two electrons taking part in the Auger process were originally in the same band, say band B, the final energy of the emitted electron would be E_D-2E_B.

It will now be attempted to account in terms of Auger processes for the fixed electron energies observed in

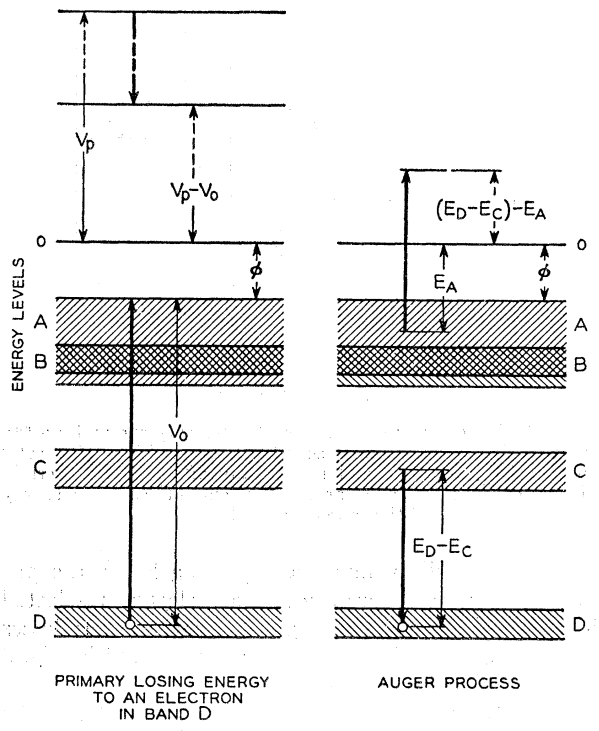

FIG. 11. A simple schematic representation of the energy band structure of a metal target material. The shaded areas represent the filled portions of the bands. On the left a primary electron suffers a discrete loss of energy by creating a vacancy in an energy band. On the right the vacancy is refilled and the energy so released causes the emission of an Auger electron.

[9] E. H. S. Burhop, *The Auger Effect and Other Radiationless Transitions* (University Press, Cambridge, 1952).

Figs. 4 to 7. For this, the positions of the energy bands of Mo and W must be known. The positions of the higher bands are available, as already mentioned, from the values of discrete losses suffered by primary electrons; the positions of the required lower levels are available from x-ray data.[10,11] These energy levels are tabulated in Table I for Mo and in Table II for W. By using these energy-level values, several Auger electron energies have been calculated and are shown in Table III for both Mo and W. The predicted Auger values given in these tables agree well with the experimentally observed energies. However, it must be emphasized that without knowing proper selection rules to apply, many Auger transitions other than those tabulated here can be proposed for which no experimental evidence has been observed. Consequently, it can be concluded that while the calculations made from the set of energy levels herein developed, are sufficient to account for the observed Auger electrons, they do not explain why electrons appear only at these particular energies and are not found at several other energies that can be predicted according to the same scheme. At least the extent of agreement achieved here may be sufficient to encourage further work of this sort.

TABLE I. Energy levels for Mo.

Level	Energy in ev	Source
$5s$	16	
$4d$	29	From primary loss
$4p$	57	measurements in
$4s$	81	the present work
?	107	
$3d$	233	
$3p$	399	From x-ray data
$3s$	510	
etc.		

TABLE II. Energy levels for W.

Level	Energy in ev	Source
$6s,p$	19	
$5d$	51	From primary loss
$5p$	63	measurements in
$5s$	93	the present work
$4f$	31	
$4d$	245	
$4p$	450	From x-ray data
$4s$	590	

TABLE III. Comparison of certain calculated Auger energies with those observed experimentally.

Auger transition	Calculated value (ev)	Observed value (ev)
Mo: Both electrons originally in the same band		
$4p-5s$	$57-2\times16=25$	26.6
$3d-4p$	$233-2\times57=119$	130
$3d-4d$	$233-2\times29=175$	178
Mo: Electrons originally in different bands		
$(3s-3d)-4p$	$(510-233)-57=220$	215
$(3s-3d)-5s$	$(510-233)-16=261$	264
$(3p-3d)-4s$	$(399-233)-81=85$	85.3
$(3p-3d)-4p$	$(399-233)-57=109$	112
$(3p-3d)-4d$	$(399-233)-29=137$	140
$(3p-3d)-5s$	$(399-233)-16=150$	152
$(3p-4s)-5s$	$(399-81)-16=302$	310
$(4s-4d)-5s$	$(81-29)-16=36$	37.2
W: Both electrons originally in same band		
$5d-6sp$	$51-2\times19=13$	13
$5p-6sp$	$63-2\times19=25$	23
$4d-6sp$	$245-2\times19=207$	212
$4p-4f$	$450-2\times51=348$	340
$4p-5s$	$450-2\times93=264$	264
W: Electrons originally in different bands		
$(4s-4p)-5s$	$(590-450)-93=47$	46
$(4p-4d)-5d$	$(450-245)-51=154$	160
$(4p-4d)-4f$	$(450-245)-31=174$	173
$(4d-4f)-5d$	$(245-31)-51=163$	164
$(4d-4f)-6sp$	$(245-31)-19=195$	199
$(5s-4f)-6sp$	$(93-31)-19=43$	38

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[10] J. C. Slater, *Quantum Theory of Matter* (McGraw-Hill Book Company, Inc., New York, 1951), p. 146.

[11] Landolt-Bornstein, *Atom and Molecular Physics* (Springer-Verlag, Berlin, 1952), Part VI.