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Experiments on Low-Energy Electron Scattering and Energy Losses

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INTRODUCTION

THE purpose of this review is to survey the status of experiments which can contribute to our knowledge of the interaction of slow, and moderately slow, free electrons with matter. In preparing this review it was felt that, beyond the presentation of the results achieved, there is a need to examine carefully the methods leading to these results. By "methods" I do not mean to go into details of instrumentation (this is carefully avoided). The time has come, however, to look with a critical eye at some of the steps performed while taking a series of measurements, or at the conditions under which the experiment proceeds. This review, therefore, is less a fact-gathering one, and more an attempt to call attention to some of the difficulties, sources of errors, and discrepancies in our work.

The definition of what constitutes "low-energy" electrons has changed so much in the past 10 to 20 years that a review on this subject is worthless unless the energy range covered by it is clearly outlined right at the beginning. For the purposes of this review let us assume, therefore, the definition that "low energy" comprises the energy range from 0 to 5×10^5 ev, anything below the rest energy of the electron. Most of the material included in this review is even more restricted; the practical range is from 10^2 to 5×10^4 ev, with a few exceptions below or above these limits.

A knowledge of the energy transfer is required to distinguish between "elastic" and "inelastic" events. In the early literature of electron scattering, the distinction between the two was not always clearly maintained. The following definitions will be used in this review:

(1) An *elastic* event is one in which the energy exchange between the incoming electron and the scattering system does not exceed the energy imparted for the recoil of an atom. This amount is usually a small fraction of the primary energy of the electron, not exceeding the ratio of the electron mass to the atomic mass m/M. In most experimental work, energy losses of this order can not be measured as the energy change is small compared with the energy resolution of existing measuring systems.

(2) An *inelastic* event will be defined as an interaction in which a fraction of the primary energy of the electron greater than m/M is transferred to the scatterer, resulting in some kind of an excitation. This review being limited to the experimental aspects of the scattering studies, the question of the nature of the excitation processes within the scatterer is partly outside of our scope. It is useful, however, to list briefly some results of excitation, as a short reference to one or the other may be necessary in discussing the experimental aspects of the scattering work. The most common are as follows: ionization, secondary emission, photon emission, and change in the translational or vibrational energy of the atoms, of the molecules, or of crystal lattices, etc. Which of these processes is taking place, cannot be decided in every case from a knowledge of the energy losses suffered by the primary electrons alone. Usually some other observation is required to supplement the energy distribution studies.

One such added quantity, which is within the scope of this review, is the measurement of the angular distribution of the scattered electrons. One particular aspect of angular studies is supposed to be quite well known, i.e., electron diffraction. Many substances, under varying conditions, have been studied using diffraction as an applied tool and the conclusion is almost inescapable. By now we ought to know in detail at least one aspect of small-angle scattering phenomena, to wit, the elastic part. One purpose of this review, however, is to show that the past studies were directed toward a very limited objective and that considerable amount of further work is required to elucidate both the small and large angle behavior of scattered electrons.

This may be the proper place to mention briefly the principles of instrumental requirements for studies of this kind. An ideal study of scattering phenomena has to give information on both the angular and energy distribution of the scattered electrons, as a function of primary energy, angle of incidence, properties of the scatterer, etc. Like any other physical measurement, the results have to be reproducible, which in some cases may be very difficult to achieve, as we shall see when discussing the properties of the scatterer. The utmost in information requires infinite resolution, both of energy and of angle. This means the subdividing of the measured range into the smallest possible intervals, which in turn offers the advantage of applying fewer corrections to the final result. The instruments used for these measurements have to be, however, by necessity some kind of spectrometers and suffer thus from the common ailment of these last, i.e., resolution and "transmission" are in an inverse relationship. Indefinite lowering of the energy intervals is prevented by a simultaneous lowering of the signal-to-noise ratio at the detector. In principle, there is a possibility of compensating for this effect by increasing the time of observation; unfortunately the interaction of the primary electron beam with the scatterer can produce irreversible changes in the latter, which being cumulative, make shortening of the time of observation rather imperative. This last remark applies more to solid scatterers than to gases, although even in gaseous compounds we have to remember that the energy losses suffered by the electrons are of the same order of magnitude and usually higher than the dissociation energy.

It is not the purpose of the present review to enter in a discussion of the spectrometers used for scattering investigations. A recent review[1] covered the description of the instruments used for the investigation of characteristic energy losses. Beyond these there are the instruments used for secondary emission work, which, more often than not, measure the energy distribution by means of the retarding potential method, integrating over all angles.[2] The latest improvement appears to be a combination of a high-grade velocity analyzer with a deceleration system, which, if properly executed, should improve considerably the "transmission-to-resolution" ratio of the earlier instruments.[3,4]

Whatever instrument may be used for the scattering measurements, the reliability of the results depends to a large degree on the nature of the scatterer. To make any measurement significant we need to know the chemical composition of the scatterer and its geometry. Neither of the two can be ascertained easily with the required accuracy. By chemical composition I do not mean the stoichiometric proportion of the elements in a compound, although in certain cases even this latter can give trouble. Much more difficult is a reasonably good control of the impurities contained in the substance.

In the case of solid scatterers, the meaning of "chemical composition" may be extended to include the role of surface impurities and of crystal structure. Surface impurities are of two kind. One may be present at the beginning of the investigation and may not or may slowly change under the action of the electron beam. The second is a beam-borne impurity, accumulating at the rate of bombardment of the surface and is practically unavoidable in dynamic, demountable vacuum systems.[5] There is indication in the literature[6] that the rate of accumulation can be slowed down or reversed by raising the temperature of the surface to 200°C. The relief thus gained is rather limited; not all specimens can be heated in a vacuum to 200°C without modification or even loss of the specimen. Thus, even though there is little indication in the present scattering literature about the possible role of these impurities in the scattering behavior, the fact alone that there is wide discrepancy between measurements carried out on (allegedly) the same substance, should warn us.

Crystal structure is another variable which may influence scattering behavior. Good measurements exist on a limited number of single crystals,[7–9] although in the last case the single crystal is essentially two-dimensional.[10] In examining the majority of papers published on this subject, one is obliged to conclude that a good study of the effects of crystal structure on scattering behavior remains one of the tasks of the future.

The reason for bunching together crystal structure and surface impurities with stoichiometric proportions under the common name of "chemical composition" now may be justified. All these properties are apt to change under electron bombardment and the changes have a tendency to be cumulative and irreversible. Thus the "chemical composition" causes one of the main limitations in the improvement of the scattering measurements. Irreversible changes make it impossible to regain by longer observation time the loss of intensity produced by the selection of smaller energy or angle intervals of the spectrometer.

The geometry of the scatterer is usually well enough defined in the multiple scattering region. The thickness of a solid is usually large enough to be measured with sufficient accuracy, and a gas volume can be confined by windows thin enough to be negligible as compared to the total volume. The effects of surface more or less disappear in the multiple scattering process. This is, however, far from being true in case of plural, and even less for single scattering. In the low-energy range covered by this review single scattering usually means that *less* than 100 atom layers of the scattering substance take part in the interaction. To measure the thickness of a solid of these dimensions is not always an easy task. The methods used, such as weighing,[11] multiple beam interferometry,[12] evaporation geometry,[13] electrochemical action,[14] etc., give answers, which, in extreme cases, may differ by as much as 100 to 200%. In appearance it is simpler to define the interaction path length in a gas, but if this gas is in dynamic equilibrium with the vacuum of the spectrometer,

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[1] Marton, Leder, and Mendlowitz, Advances in Electronics **7**, 183–238 (1955).

[2] See for instance E. J. Sternglass, Phys. Rev. **95**, 345–358 (1954); N. B. Gornyi, J. Exptl. Theoret. Phys. (U.S.S.R.) **27**, 649 (1954).

[3] Blackstock, Birkhoff, and Slater, Rev. Sci. Instr. **26**, 274–275 (1955).

[4] L. Marton, Bull. Am. Phys. Soc. Ser. II, **1**, 191 (1956).

[5] R. Castaing and J. Descamps, Compt. rend. **238**, 1506 (1954); H. Koenig, Z. Physik **129**, 483 (1951).

[6] A. E. Ennos, Brit. J. Appl. Phys. **4**, 101 (1953); **5**, 27 (1954).

[7] J. C. Turnbull and H. E. Farnsworth, Phys. Rev. **54**, 509 (1938).

[8] P. P. Reichertz and H. E. Farnsworth, Phys. Rev. **75**, 1902 (1949).

[9] Marton, Simpson, and McCraw, Phys. Rev. **99**, 495 (1955).

[10] The single crystals of reference 9 are only 100 to 200 A thick.

[11] P. L. Clegg and A. W. Crook, J. Sci. Instr. **29**, 201 (1952).

[12] S. Tolansky, *Multiple Beam Interferometry of Surfaces and Films* (Oxford University Press, New York, 1947).

[13] W. L. Bond, J. Opt. Soc. Am. **44**, 429 (1954).

[14] L. E. Preuss, J. Appl. Phys. **24**, 1401 (1953).

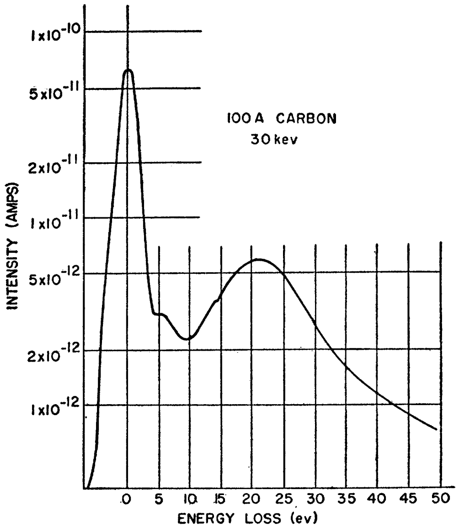

FIG. 1. Intensity *vs* energy loss for 30-kev electrons scattered in the forward direction on carbon.

the length becomes subject to very large corrections. Another important restriction is that, in the case of solids, surface effects are no more negligible as compared to volume effects. Surface effects are often conditioned by the method of preparation of the thin solid layer (e.g., evaporation of the substance onto a solid substrate with subsequent removal of the substrate).

The listing of all these difficulties is given as a warning to the experimental worker wishing to take up this subject, or to the theoretical one wishing to interpret the results. While it is not possible to explain all the discrepancies in results of different observers by the aforementioned effects alone, there is no doubt that in the past some of these factors have been neglected. Emphasizing them here may help to eliminate some of the excuses many of us (including ourselves) may have offered in the past for sloppy work. This may be the right place to point out how fruitful certain theories have been in stimulating new experiments, in particular the collective oscillation theory of Bohm and Pines.[15] An interplay of theoretical and experimental development helped greatly to advance our knowledge of low energy scattering phenomena. This has been especially true since the introduction of high resolution velocity analyzers which have enabled us to distinguish better between elastic and inelastic events. On the other hand the sharp distinction made in some theoretical studies between single, plural, and multiple scattering is less emphasized in the experimental work since the different regions tend to overlap.

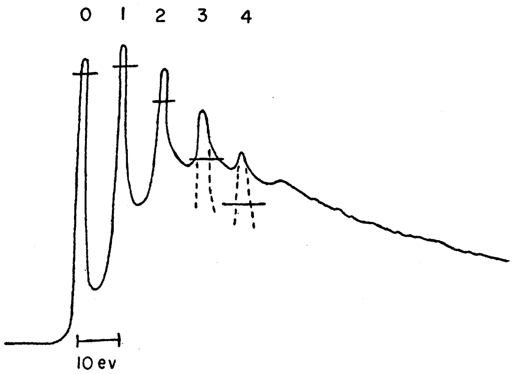

FIG. 2. Intensity (on an arbitrary scale) *vs* energy loss for electrons scattered in the forward direction on magnesium (courtesy Dr. H. Watanabe).

CHARACTERISTIC ENERGY LOSSES

An important aspect of modern scattering studies is the investigation of characteristic energy losses in solids. These losses, which at one time were called "discrete" losses and in some recent papers "eigenlosses," are best described as maxima in the energy distribution curve. They lie from 0 to 100 ev below the primary energy of the impinging electron. Figures 1–3 give typical examples of such losses, as observed in transmission of about 30 kev electrons thru thin films. A recent review[1] gives considerable detail on the methods of observation, on the experimental results, on the interpretation and on the historical background of these losses. Some of the material presented in that review may be briefly summarized here and new material added to it.

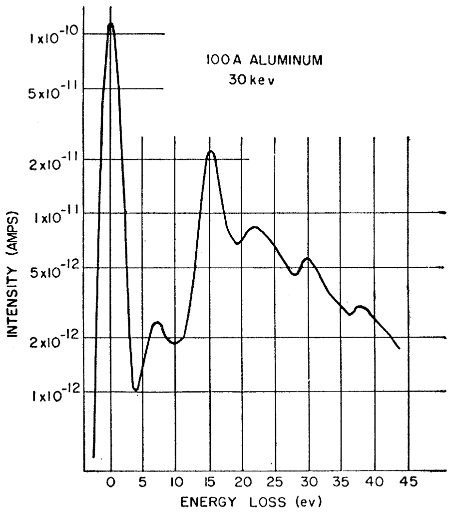

FIG. 3. Intensity *vs* energy loss for 30-kev electrons scattered in the forward direction on aluminum.

The most prevalent method of velocity analysis uses primary electrons in the 10- to 50-kev range. The thin scatterer is placed at right angles to the incident beam. The scattering is observed in the "forward" direction only, within a narrow solid angle in continuation of the primary beam. This solid angle is usually

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[15] D. Pines, *Advances in Solid State Physics* (Academic Press, Inc., 1955), Vol. I, pp. 368–449.

rather poorly defined or not defined at all. In first approximation these losses appear to be independent of angle, which may have justified poor definition of the observation angle in the early work. It is now known, however, that close observation shows marked changes of the energy, as well as of intensity with the angle. Lack of indication of the solid angle subtended by the entrance aperture of the analyzer is therefore no longer justifiable in modern work and papers, which do not contain this piece of information, should carry less weight than the ones listing it.

A wide variety of elements, throughout the periodic system, as well as a fair number of compounds, have been investigated in the "forward" direction. A complete tabulation of the results obtained prior to March, 1955 is given in reference 1. In recent work the emphasis is shifted to compounds rather than the elements; their discussion is delayed to a later chapter of this review.

Observation of the characteristic energy losses is not restricted to scattering measurements through *thin* solids. In fact, historically, the study of the energy distribution of electrons backscattered from the surfaces of thick solids precedes that of the transmission type.[16] Many of the papers devoted to reflection measurements (though not all) are extensions of secondary emission studies and as a consequence most of them are limited to relatively low primary energies (50 to 500 ev). For this reason the energy range studied comprises usually all energies between zero and those of the primaries. The solid angle of observation may vary anywhere between 2π and a relatively small angle of the order of 10^{-2} steradian defined by the entrance aperture of an analyzer. The angle at which the analyzer looks at the scatterer more often than not is quite arbitrarily chosen to provide an easy geometry of the instrument. In the case of 2π observation, energy analysis is usually of the retarding potential type, giving integral curves instead of the differential record of more common spectrometers.

Although a certain number of reflection-type measurements included a somewhat rudimentary analysis of the energy distribution as a function of angular distribution, only recently were instruments developed with high resolution for both the angular and the energy measurements. It is rather hard to satisfy the conditions of high resolution for both quantities at any arbitrary angle. Several modern instruments are limited to transmission type observation within a few degrees from the direction of the directly transmitted beam. A second limitation is that of energy range: the measurements usually do not cover more than 100 ev below and including the primary energy. The primary energy in these investigations is usually of the order of 20 to 40 kev. The number of substances investigated in this manner is smaller than both the preceding groups, but this is due rather to the newness of the instrument than any other cause. As far as this reviewer sees it, simultaneous information on energy and angular distribution is the most valuable of all, as it is more easily interpretated theoretically than information on the loss values alone.

The most important single result derived from these investigations is the existence of characteristic energy losses in *all* observed materials. Conductors, semiconductors, and insulators are very similar in their behavior, showing the same type of spectra. The spectral behavior can be classified as showing sharp lines, diffuse lines, and bands. Sharp lines may be defined as lines whose half-width does not exceed the half-width of the primary line. Diffuse lines may have two to three times the width of the primary lines, while bands, as the name implies, are much wider than the primary. Sharp lines may occur in integral multiples of a first, lowest energy line, although there may be a tendency toward broadening of the higher "harmonics." The spectrum of a single element or compound may show any of these lines or bands alone or in combinations. To a great extent our knowledge of characteristic loss spectroscopy is comparable to the early times in light spectroscopy when research workers, somewhat facetiously, were talking of the "zoology of terms."

There are indications that some of the observed losses may be due to energy transfer mechanisms which are reasonably well known. So, for instance, several lines in different elements have been tentatively identified with optical transitions, in particular in the soft x-ray region.[17] Sharp lines have been interpreted as due to the collective excitation, by means of the incident electron, of an electron plasma in the solid.[18] The excitation may appear as a base frequency and its higher harmonics, or repeated occurrences of the same first event.

A different type of identification of the transitions involved in the production of these spectra may be offered by a remarkable degree of coincidence of the numerical values of the energy loss lines with the differences between fine structure absorption maxima in the K or L edge in the x-ray spectra.[19] In this last case the fine structure has been interpreted by Kronig[20] and Hayasi[21] as due to transitions from the K or L level to unoccupied bands above the Fermi level. A numerical coincidence would imply that the characteristic energy losses are due to transitions from within the Fermi level to the same unoccupied bands. This kind of interpretation is consistent with an apparent dependence of some of the characteristic losses on the inverse square lattice constant.[19]

Isolated attempts exist to identify some of the charac-

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[16] For simplicity's sake the observation from bulk-type material will be henceforth called reflection method to distinguish it from scattering *through* thin layers, or the transmission method.

[17] L. Marton and L. B. Leder, Phys. Rev. **94**, 203 (1954).

[18] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953); D. Pines, Phys. Rev. **92**, 626 (1953).

[19] Leder, Mendlowitz, and Marton, Phys. Rev. **101**, 1460 (1954),

[20] R. L. Kronig, Z. Physik **70**, 317 (1931); **75**, 191 (1932); **75** 468 (1932).

[21] T. Hayasi, Sci. Repts. Tôhoku Univ. **33**, 123 (1949); **33**, 183 (1949); **34**, 185 (1950).

teristic losses with the fine structure observed in the isochromates taken at the short wavelength limit of x-ray spectra. The numerical coincidence is less good than in the previous case, which may be due to a lack of sufficiently precise data.[22] Last, but not least, it should be mentioned that a few peaks observed in the energy distribution studies of secondary electron emission have been identified with Auger-transitions.[23]

This rather confusing picture does not necessarily mean a very serious conflict in the interpretation of the same transition. A short while ago it appeared as if the plasma oscillation and the interband transition interpretations may be diametrically opposed; however, today there are indications that a more general collective oscillation theory can offer an explanation of a substantial number of the observed losses.[24] One factor which renders the comparison with theory rather difficult is our lack of precise data. By "lack of precise data" it is meant that ±5% is a common error in the determination of the energy loss values. That much discrepancy not only exists from one laboratory to another but, even worse: the same observer, operating the same equipment in the same laboratory may find inexplicable fluctuations in his own values. Such an experimental situation indicates that the art is still in its infancy and much work is needed to clear up all difficulties. The present disagreements about the precise numerical value of a given energy loss may be traced to a number of different factors, some of which may be more important than the others. A tentative listing of such factors includes the following: (a) limited energy resolution of the velocity analyzer, (b) limited angular resolution of the analyzer, (c) "line shape" of the primary electron beam, (d) energy calibration errors of the analyzer, (e) location of maxima on a continuous, sloping background, (f) variations in the angular acceptance of the analyzer, (g) impurities of the scatterer (both volume and surface), and (h) grain size variations of the scatterer.

This list is probably far from being complete and the relative importance of the individual factors may vary from place to place, from observer to observer, from time to time. So, for instance, only now we start to realize the important role "line shape" may play in the experiments. The average electron source, used for these investigations, produces a more or less collimated beam. The energy distribution of such a beam, as was shown by Boersch,[25] can be far from Maxwellian. The center of gravity of these energy distributions is shifted toward higher energies than expected, as manifested sometimes by a scarcity of low energy electrons and sometimes by an overabundance of the high energy electrons, or both. To make things more confusing, these distributions shift with varying bias applied to the guard electrode and with varying filament position. The worst feature is that the energy distribution is *not* constant across a beam and thus a slight displacement of the electron gun can alter the "line shape" radically.

In first approximation the energy losses appear to be independent of the temperature of the scatterer. Experimental evidence is somewhat limited: Rudberg[26] states that he kept his targets "incandescent," Kleinn[27] measured energy losses while the scatterer was heated to "about 200°C." Most of the material published is the result of investigations carried out at room temperature. Within these temperature limits there is no indication of a temperature dependence. This is in agreement with theoretical predictions: the plasma oscillation theory, for instance, does not predict a strong temperature variation. The influence of temperature on the plasma oscillation frequency is below present day measuring accuracy. This limitation may disappear, however, at extremely low temperatures. In the case of superconductors, in particular, when the bulk properties become quantum properties, a radical modification of the plasma oscillation frequency might occur.

The energy losses are also independent, in the first approximation, of the primary energy. This statement is correct as long as the primary energy is great as compared with the energy loss itself. For values of primary energies approaching the value of the loss the relative cross sections for different events change radically and some prominent losses may disappear while new losses may come to light. These last phenomena are also strongly dependent on scattering angle. For more extensive discussion of these effects we refer to the original papers of Farnsworth and Turnbull on Ag,[28] Farnsworth and Reichertz on Cu,[29] and Gornyi on CuO.[30]

Besides the determination of the numerical values of energy losses, it is important to measure the cross sections of these events. Thickness determination of the scatterer may present the major stumbling block in the measurement of absolute cross sections. In speaking of scatterer geometry some of the difficulties connected with thickness measurement were already mentioned. It is worthwhile to expand those remarks by adding here a specific case of ambiguity in thickness determination. A common procedure in preparing self-supporting thin films is to evaporate in vacuum the material in question onto the cleavage surface of a rock salt crystal and to transfer it to a metallic aperture. The transfer is effected by submerging the rock salt

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[22] C. Gerthsen and L. Albert, Z. angew. Phys. **6**, 196 (1954); L. Albert, Z. Physik **143**, 513 (1956).

[23] J. J. Lander, Phys. Rev. **91**, 1382 (1953).

[24] See D. Pines, Revs. Modern Phys. **28**, 184 (1956), this issue.

[25] H. Boersch, Z. Physik **139**, 115 (1954).

[26] E. Rudberg, Proc. Roy. Soc. (London) **A127**, 111 (1930).

[27] W. Kleinn, Optik **11**, 226 (1954).

[28] J. C. Turnbull and H. E. Farnsworth, Phys. Rev. **54**, 509 (1938).

[29] Reichertz and H. E. Farnsworth, Phys. Rev. **75**, 1902 (1949).

[30] N. B. Gornyi, J. Exptl. Theoret. Phys. (U.S.S.R.) **27**, 649 (1954).

crystal in water, whereby the thin film remains floating on the water surface, to fish it out by immersing a metallic aperture under the floating film and then lifting the two together. Using multiple beam interferometry for the thickness measurement, we can proceed in two ways: one is to evaporate, simultaneously with the scattering specimen and in its close neighborhood, onto a glass test plate. If proper precautions are taken the thickness deposited on the glass test plate should be identical with the one on the rock salt cleavage face and the test plate deposit thus should give the right value of the thickness of the scattering material. The other way of proceeding consists of floating over a simultaneously prepared scattering specimen onto a glass test plate and determine the thickness, as before, by multiple beam interferometry. In some rough tests of this kind on Be we have found as much as 100% discrepancy. While these tests were perhaps not too conclusive, it is worth emphasizing the limited reliability of thickness indications in the literature, together with their importance.

There are several instances where a more precise knowledge of the thickness would help greatly. One is the comparison of the characteristic loss values with the fine structure of x-ray absorption spectra. As long as we do not have reliable intensity measurements of the lines (and they will remain unreliable as long as we can't tie them down to a well-known specimen thickness and composition) a doubt will remain in their identification with the x-ray transitions. Another interesting observation, linked to thickness measurements, is the "critical thickness" reported by Gabor and Jull.[31] In their experiments "stratified" layers of metals were built up of thin layers, with some foreign material between. It was found that some characteristic lines barely were visible in the "sandwich" when they were easily observable in the equivalent thickness or less of the solid metal. In his latest paper Gabor[32] reports on difficulties in reconciling the interpretation of this last experiment with the results of Watanabe.[33]

Equally thickness dependent are the "mean free path" determinations. Blackstock, Ritchie, and Birkhoff[34] have reported a mean free path in the range of 930±370 A for the energy losses in Al in rather good agreement with the plasma oscillation theory. Attempts have been made by the same authors to determine the same quantity for Mg and Cu, but with less success. Surprisingly, the disagreement with theory in case of Mg was very marked where foil thicknesses were determined by direct weighing, while better agreement was obtained by applying the inverse square law to the evaporation process: a notoriously unreliable procedure.

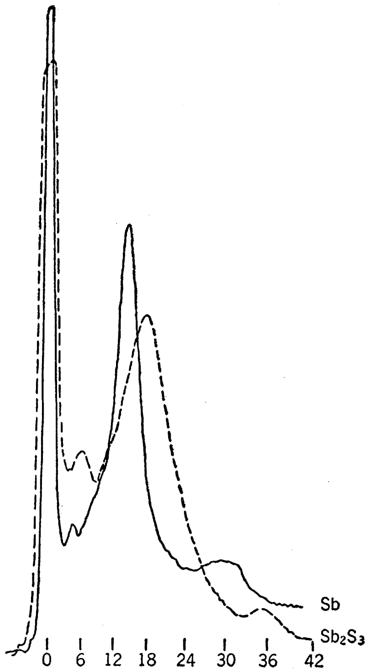

FIG. 4. Intensity (on an arbitrary scale) *vs* energy loss for electrons scattered in the forward direction on antimony and antimony trisulfide (courtesy Academic Press, Inc).

The understanding of another "strange" effect depends on a better knowledge of specimen thickness: the effect of crystal grain size. Marton, Simpson and McCraw[9] believe to have seen a variation of the ratio of elastically scattered electrons to those which have suffered a particular characteristic loss, as apparently equally thick layers of single crystal, coarse crystalline and fine crystalline gold were investigated. This observation would be worth repeating with closer control of the specimen thickness. In this same category belong some experiments on amorphous and crystalline selenium carried out by Friedmann.[35] The results of this investigation also appear to be inconclusive.

EFFECT OF CHEMICAL BINDING ON THE CHARACTERISTIC ENERGY LOSS

Leder and Marton[36] observed in 1954 that metallic elements and their simple compounds have a tendency to exhibit very similar spectra. Often a similar sequence of lines or bands is found, with the intensity ratios between adjoining lines barely changed, but exhibiting a small (positive or negative) shift of the lines from element to compound. A typical example is shown on Fig. 4. The order of magnitude of the observed shifts is quite comparable to that produced by the chemical binding in the values of the K, L, or M edges of the x-ray spectra. Das Gupta[37] attempted to calculate the heat of formation of the compounds from the observed x-ray shifts, which prompted Leder and Marton[36] to a similar attempt on the characteristic loss lines. The

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[31] D. Gabor and G. W. Jull, Nature **175**, 718 (1955).
[32] D. Gabor, Phil. Mag. **1**, 1 (1956).
[33] H. Watanabe, J. Phys. Soc. Japan **11**, 112 (1956).
[34] Blackstock, Ritchie, and Birkhoff, Phys. Rev. **100**, 1078 (1955).
[35] H. Friedmann, Naturwissenschaften **24**, 569 (1954).
[36] L. B. Leder and L. Marton, Phys. Rev. **95**, 1345 (1954).
[37] K. Das Gupta, Phys. Rev. **80**, 281 (1950).

TABLE I. Elements and compounds investigated.

Elements	Compounds	Reference
Be	BeO	W
Na	Na_2O, Na_2S, NaCl	NBS
Mg	MgO	R, W
Al	Al_2O_3	Ru, NBS, W
Si	SiO_2	NBS
Ca	CaO, $Ca(OH)_2$	R, W, NBS
Sn	SnO_2	W
Sb	Sb_2O_3, Sb_2S_3	NBS
Te	TeO_2	NBS
Ba	BaO	R
Pb	PbS, PbSe, PbTe, $Pb(OH)_2$	NBS

W = Watanabe, NBS = Marton and Leder, R = Rudberg, Ru = Ruthemann.

order of magnitude and the direction of the shift is consistent with the binding energy interpretation, but the available evidence is too meager to base any theory on it. It is worth mentioning, however, that since the publication of the Leder and Marton paper, considerably more elements and their compounds have been measured. Table I contains a listing of the combinations of the elements and their compounds which have been investigated with reasonably good accuracy.

Of all the materials investigated Al, and possibly Be and Mg, show decided difference between the spectra of the metals and their compounds. All other elements show a remarkable similarity between their spectra and that of the corresponding compounds. It is interesting to note that Al, Be, and Mg are the elements which fulfill best the requirements of the plasma oscillation theory, implying that there is no correlation between the two spectra in case of a loss arising from a plasma excitation in a metal. Conversely, in the case of interband transitions there may be a strong change in the density of states with a lesser change in the energy levels. It is to be hoped that further evolution of the theories[38] may eliminate some of the contradictions of the present day interpretations.

ANGULAR DISTRIBUTION OF ELECTRONS SCATTERED BY SOLIDS

Some of the early experimental work,[39] and even some more recent ones,[40] measure the angular distribution of *all* scattered electrons, without attempting to separate the elastic from the inelastic events. Figure 5 shows a typical example of this kind. One of the most important results of recent experimental studies is a demonstration that the angular dependence of elastically scattered electrons obeys different laws from those which were scattered inelastically. Furthermore, the angular distribution of the "continuous" inelastic background may be different than that of the characteristic losses.

Figure 6 shows a typical example of the results of more modern scattering measurements.[9] The presentation is "three-dimensional," with the abscissa representing the angle, the ordinate the energy loss and the third dimension, out of the plane of the paper, the intensity. This last variable is shown in the form of equal intensity contours. The sequence of these contours is quasi-logarithmic in order to encompass the enormous intensity range covered by the measurements. Three laboratories have been engaged in the past two years in investigations of this type.[9,41,42] All three have in common that the measurements extend to the angular range of a few times 10^{-2} radian, the energy range comprises about 100 ev including and below the primary energy, the primary itself varies from 20 to 50 kev and scattering is observed in transmission thru thin targets.

The most important results can be summarized as follows: (1) The variation of the intensity of elastically scattered electrons with angle is shown for a few typical cases in Fig. 7. They have in common a flat part close to 0 angle, a very rapid falloff up to a few milliradians, relatively flat portions from there on upon which are superposed diffraction maxima. The width of the flat center parts is undoubtedly due to the width of the primary beam.[43] The steep slope following this flat portion, however, is often much steeper than accounted for by current theories. The total intensity in the center

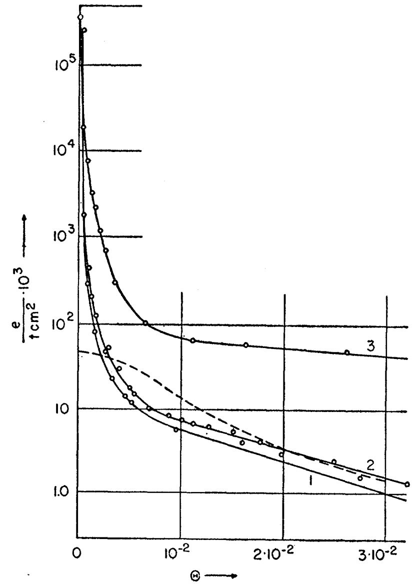

FIG. 5. Angular distribution of scattered electrons (elastic plus inelastic) measured by Biberman *et al.*, on a thin chromium foil. (1) 80 kev, (2) 60 kev, (3) 30 kev; dotted line—elastic distribution as calculated for 60 kev from the theory of Bullard and Massey (after Lenz).

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[38] U. Fano, Phys. Rev. (to be published).

[39] See for instance, Massey and Burhop, *Electronic and Ionic Impact Phenomena* (Cambridge University Press, New York, 1952).

[40] Biberman, Vtorov, Kovner, Sooshkin, and Yavorski, Proc. Acad. Sci. (U.S.S.R.) **69**, 519 (1949).

[41] F. Leonhard, Z. Naturforsch. **9a**, 727 (1954); **9a**, 1019 (1954).

[42] H. Watanabe, J. Phys. Soc. Japan **10**, 321 (1955).

[43] Figure 9(b) shows, besides other features, that a smaller limiting aperture at the specimen reduces the width of this central area.

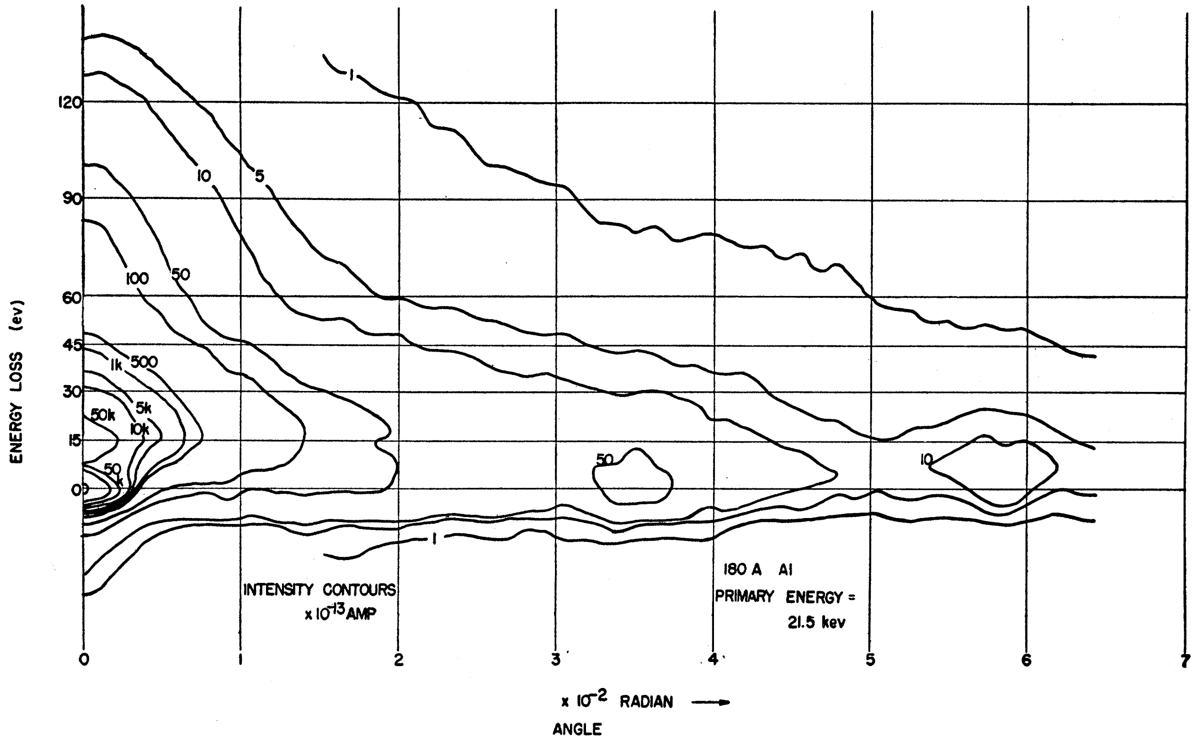

FIG. 6. Angular distribution of 21.5-kev electrons on 180 A thick aluminum. Angle is the abscissa, energy loss in ev the ordinate and intensity is represented by equal intensity contours in a quasi-logarithmic sequence.

portion also is too high as compared to the flat part to yield to an explanation by a scattering mechanism alone. Figure 8, taken from a paper by Lenz,[44] shows the calculated angular distribution of elastically scattered electrons based on different theoretical assumptions. If one omits the Rutherford distribution, he finds the peak intensity variation between the extreme theories is about 100. This variation, however, is small as compared to the calculated total (elastic plus inelastic) intensity. The observed values at zero angle show an excess of the elastically scattered ones as compared to the total. Or it may be better phrased by saying that the total number of elastically scattered electrons tends to be considerably less than calculated from modern theories with a sharp excess peak at zero angle. A special search has shown that experimental errors, such as the presence of holes in the scatterer, cannot account for this discrepancy. Figures 9(a) and 9(b) show three angular distributions from 550 A single crystal copper films. Copper was chosen for this experiment because very good single crystals can be grown and single crystals were used in order to make the diffraction as sharp as possible, as well to minimize the effects of grain boundary scattering. Two of the curves show the distribution with 0.3 and 0.1 mm limiting apertures, while the third was taken using a film which had a fine crack. The films were examined under an electron microscope where, at the highest magnification, no holes could be seen. It will be noted that improved aperturing of the beam, and the added incident beam intensity, while radically changing the elastic distribution, have only a minor effect on the characteristic loss distribution. Moreover, it appears

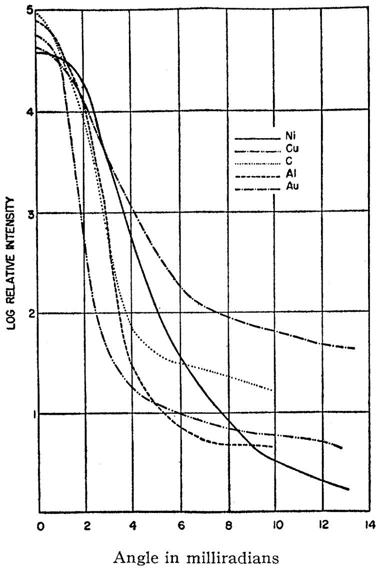

FIG. 7. Angular distribution of the elastically scattered electrons (roughly normalized at 0 angle) for different materials. Primary energy ~20 kev.

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[44] F. Lenz, Z. Naturforsch. 9a, 185 (1954).

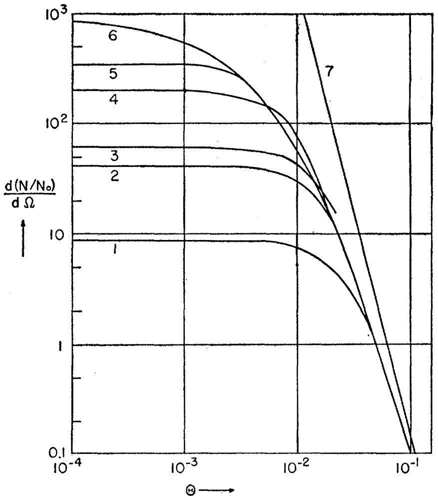
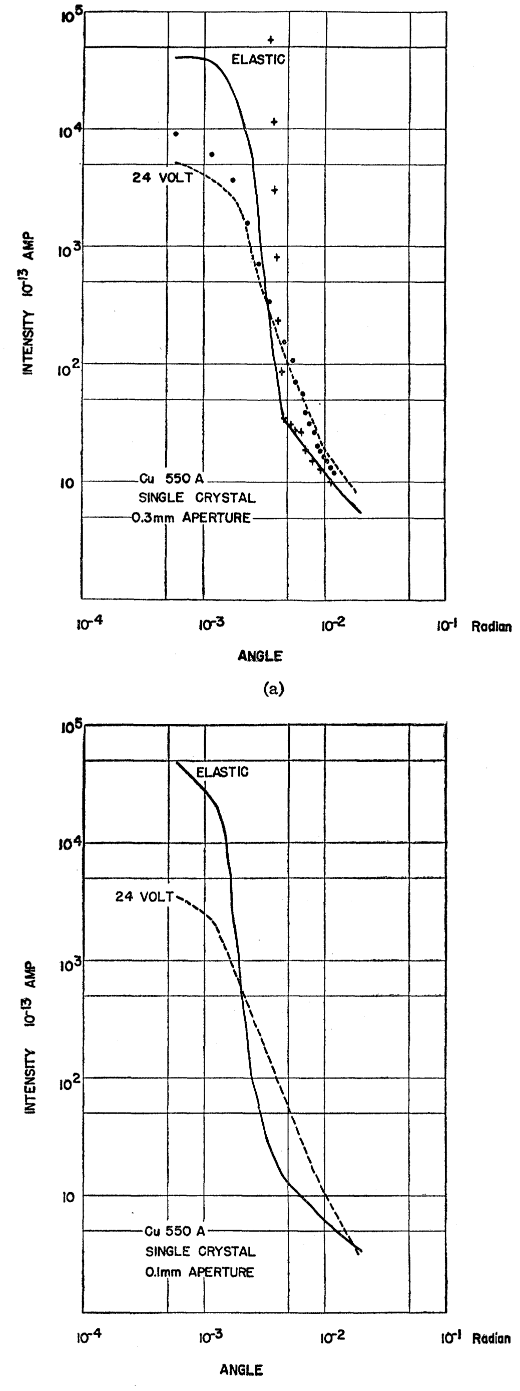


FIG. 8. Calculated distribution for 50 kev elastically scattered electrons using different theoretical approaches. Scatterer: carbon, 10^{-6} g/cm^2. (1) Using the diamagnetic susceptibility; (2) using the Hartree distribution; (3) Bethe's theory; (4) Moliere's theory; (5) Bullard and Massey's theory; (6) using the Thomas-Fermi distribution; (7) Rutherford scattering (after Lenz).

that at angles greater than 4 milliradians the angular dependence of the elastically scattered electrons is less rapid than that of the characteristically scattered ones. A tentative explanation may be that at zero angle, the zero order diffraction peak produces an excess intensity over the screened Coulomb interaction. The low amount of these last ones, however, as compared to theoretical predictions, at present remains a puzzle.[45]

(2) Watanabe[42] has shown in 1955 that the angular distribution of characteristic energy losses presents an arc-like curvature. Figure 10 is reproduced from Watanabe's original photograph on Al. Surprisingly, similar diagrams taken by Leonhard[41] show less evidence of this behavior, and neither could Marton, Simpson, and McCraw find any evidence for it in their earlier results. Recent measurements by Simpson, McCraw, and Marton,[46] however, contain some indication of the same behavior as may be seen upon inspection of Fig. 6. Similar arc-like features appear on cartographs of the following materials: C, Ni, Cu, and Au. The interest in these observations lies in Watanabe's identification with the dispersion relation derived from the plasma oscillation theory. Watanabe's observations give a close quantitative confirmation for Be and Al, whereas in the case of Mg and Ge the agreement is less good.

(3) Marton, Simpson and McCraw[9] published graphs representing the relative slopes of elastic and inelastic (characteristic loss) electrons with angle for Au. The characteristic loss part of these data were used by Ferrell[47] for a comparison with the plasma oscillation theory and apparent good agreement was found, although some questions were raised about the relative



(a)

(b)

FIG. 9. (a) Intensity *vs* angle for Cu single crystal of 550 A thickness. The solid line indicates the angular distribution for elastically scattered electrons, the dashed line shows the distribution of those having suffered a characteristic loss. The points indicate the corresponding distributions for an identical film with a microscopic crack. Entrance aperture of the velocity analyzer: 0.3 mm. (b) The analyzer entrance aperture is reduced to 0.1 mm.

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[45] See also in this respect F. Leonhard.[41]

[46] Simpson, McCraw, and Marton, Phys. Rev. (to be published).

[47] R. Ferrell, Phys. Rev. **101**, 554 (1956).

proportion of elastic and characteristic loss electrons. The earlier related experiments on 550 A thick single crystal copper were undertaken to answer partially these questions and the behavior of the inelastic part can be seen in Fig. 9. In the same spirit a certain number of other substances were investigated and presented on Fig. 11. It was found convenient to plot the ratio of elastically scattered electrons to those scattered with characteristic loss as a function of angle. It is interesting to notice that that ratio goes through a minimum which is slightly different for different substances, but remains unchanged for varying thicknesses of the same substance (Fig. 12).

(4) Diffraction maxima, which in the past were considered as a strictly elastic event, show a marked part of their total intensity consisting of electrons with characteristic losses. This was interpreted as a two-step process:[1,28,29] diffraction followed by energy loss, or energy loss followed by diffraction, with no indication at present about the sequence of the two events. A recent publication by Gabor,[32] however, calls the collective oscillations a "coherent but inelastic collision process," suggesting a possible third interpretation, namely, that some of the electrons may be diffracted and lose energy in a single step. At present no experiment is in sight to settle this question of interpretation.

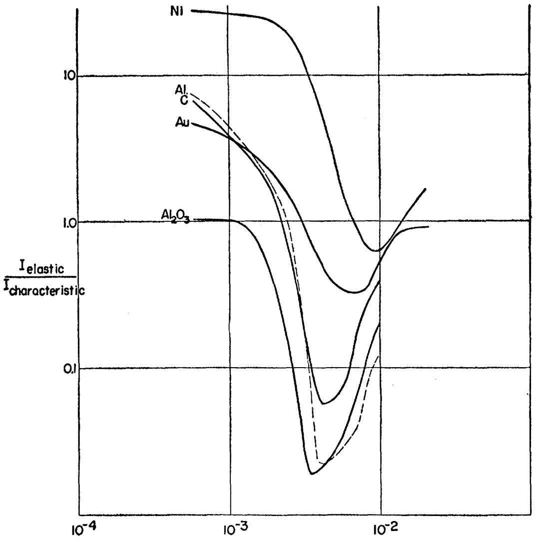

FIG. 11. Ratio of the number of elastically scattered electrons to the number of those having suffered a characteristic energy loss *vs* angle for different elements.

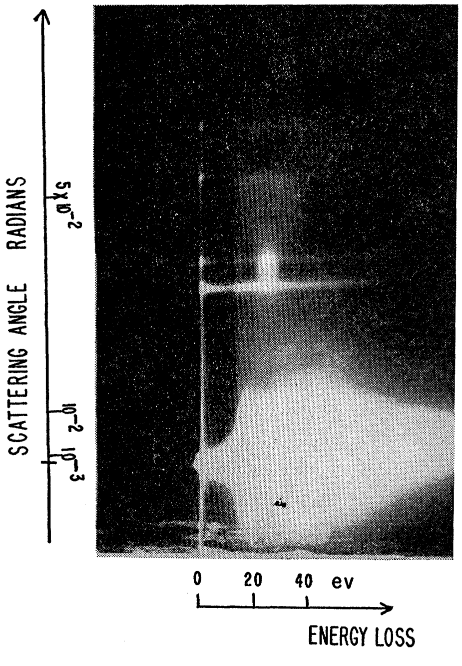

FIG. 10. Photographic record of energy loss *vs* angle as observed by Watanabe.[42] Angle is the ordinate and energy loss the abscissa. The characteristic loss at ~15 ev shows an arc-like variation of its energy value with angle (courtesy Dr. H. Watanabe).

SCATTERING AND ENERGY LOSSES IN GASES

Electron scattering in gases and vapors, in the energy range covered by this review, has been somewhat neglected in the last 10 to 20 years. The classical treatises of Mott and Massey[48] as well as Massey and Burhop[49] cover fully the ground up to about 1950. A few years ago Mollenstedt and Duker,[50] using the same equipment as for the transmission investigation of thin solids, measured energy losses in a few gases and vapors. This investigation did not reveal any startling new facts; it confirmed essentially the known optical transitions. In recent years two laboratories started investigations, using modern techniques, and both at the low end of the energy scale. Both series of investigations have in common the lack of publication, and the preliminary results presented here are given with the consent of the authors.

E. N. Lassettre and collaborators at The Ohio State University (in particular M. E. Krasnow and S. Silverman) have been engaged for several years in a program devoted to the study of collision cross sections of atmospheric constituents.[51] They measure the angular scattering of a beam of electrons of about 500-ev primary energy as function of energy loss. The angular range covered is from 3.5 to about 10 degrees (about 0.06 to 0.17 radian). Their most thorough investigations were carried out on helium, nitrogen, carbon monoxide and oxygen, with less thorough work on 25 other substances. The results can be summarized as follows: (1) At small scattering angles the observed excitation

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[48] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, New York, 1949).

[49] H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Oxford University Press, New York, 1952).

[50] G. Mollenstedt and H. Duker, Z. Naturforsch. **8a**, 79 (1953).

[51] E. N. Lassettre *et al.*, Scientific reports No. 2 (1953), No. 3 (1953), No. 4 (1953), No. 5 (1953), to Air Force Cambridge Research Center.

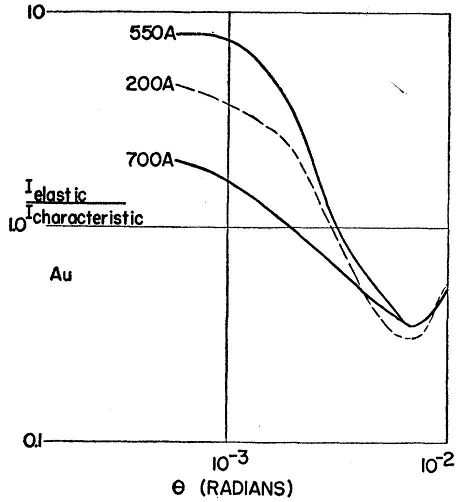

Fig. 12. Ratio of the number of elastically scattered electrons to the number of those having lost 24 ev for three different thicknesses of gold.

potentials correspond accurately to regions of strong ultraviolet absorption (where such data are available). The selection rules for the two types of excitation are the same (in the 29 substances studied only one forbidden transition was found which had sufficient intensity to be detected above the background). (2) A method has been developed for the determination of "absolute collision cross sections," by comparing the scattering in each gas to that for the 1^1S-2^1P transition in helium. This last is theoretically calculable and, after very careful measurements on helium, could be used for calibration purposes. The estimated error does not exceed 10%. (3) The first Born approximation applies to the small angle *inelastic* scattering of a variety of substances, when the energy loss is a small fraction of the primary energy. (4) Optical oscillator strengths can be determined from electron scattering experiments. (5) At large scattering angles one observes forbidden transitions excited by electron impact. The intensities of these forbidden transitions are comparable to the allowed ones. For instance, the 1^1S-2^1S transition in helium is undetectable at 0 angle, at 15° its intensity becomes comparable to that of the 1^1S-2^1P transition and, above that angle it becomes predominant. The fact that forbidden transitions can be detected at large angles is ascribed to a more rapid decrease with angle of the transition probability for the allowed transitions, thus permitting the observation of the forbidden ones above a greatly reduced background.

Observations at even lower energies are carried out by Rudolf Haas at the Technische Hochschule in Munich.[52] Electrons of about 1.5- to 3-ev energy are "allowed to diffuse" into nitrogen or nitrogen-argon mixtures in such a manner that 10 to 100 collisions may occur. The emerging electrons surprisingly have only 1.5-ev energy. The following interpretation, based on an old model of J. Franck, is offered by Haas and Maier-Leibnitz: the electron, passing near a nitrogen molecule, is captured for a short time to form N_2^-. The equilibrium distance of the atoms in N_2^- being different from that of N_2, the atoms start to oscillate toward their new positions. The lifetime of N_2^- is, however, quite short and, by the time the captured electron goes off, the atoms find themselves at a "wrong" distance. As it has been observed earlier in H_2, 1.5 ev corresponds therefore to the oscillatory energy of this process. What is new and surprising is the extraordinarily high cross section of this event in nitrogen. Practically all the energy appears to go into this process, while in hydrogen the probability of such an excitation is about 1%.

OUTLOOK FOR THE FUTURE

It has been pointed out at the beginning of this review that the emphasis is more on a critical viewpoint than the collection of data. Another review[1] often quoted here, contains most of the relevant data and forms together with this one a reasonably thorough compendium on the subject. This presentation may have exaggerated some of the difficulties germane to scattering measurements. Such exaggeration was done on purpose, to make everyone aware of the limited reliability of recent work and to induce him toward a very critical attitude when looking at older techniques.

This kind of presentation also brings us automatically toward this reviewer's estimate of what remains to be done. One of the first steps is to improve the measuring accuracy. Both the angular resolution and the energy resolution of our measurements should and can be enhanced. At the time of writing this review there are at least two efforts under way in the direction of improved energy resolution. Mollenstedt[53] reports achieving 0.25-ev resolution out of 45 kev and Marton[54] describes an attempt of the NBS group to push the new limit to 0.1 ev or even 0.05 ev instead of the previous best of 0.5 ev. This new limit does not exceed what was achieved previously in very low energy reflection type measurement. Its importance lies in opening up new possibilities in the transmission work, with the inherently greater angular resolution of this latter.

Much remains to be done about a better knowledge of the scatterer itself. In the case of gases modern methods of ultra-high vacuum techniques and of gas purification may help. In the case of solids we have to turn to the solid state physicist for help. For instance, the NBS group was plagued for a long time with difficulties in preparing single crystal specimens. These turned out to be due to screw dislocations in the substrates used for the preparation: a difficulty rather remote from the day-to-day thinking of the electron

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[52] Professor H. Maier-Leibnitz (private communication).

[53] Mollenstedt (private communication).

[54] Presented at the April 27, 1956 meeting of the American Physical Society in Washington, D. C. More extended publication is being prepared.

physicist. Here every effort should be made toward as good a knowledge of scatterer composition and geometry as possible. From the point of view of comparison with theory it is not only useful to have the impurity concentration under rigid control, but also to investigate alloys and intermetallic compounds. The studies on effects of crystal structure, or to be more specific, of crystal grain size, which were reported earlier in this review, gain new impetus from the theoretical investigations of Gabor[32] linking the probability of some characteristic losses to the geometrical coherence of the beam. This geometrical coherence is related to crystallite size and should make itself felt with "grains of the order of a few hundred angstroms."

Mentioned earlier was the desirability of investigating scattering behavior and energy losses in superconductors. While theoretically such an undertaking would offer interesting vistas, it should not be forgotten that the characteristic energy losses are large as compared to the transition energy from the superconducting state into the normal state. It may be safe to predict that, if such an experiment succeeds at all, it will have to be done at very low primary intensities in order not to destroy the superconducting state.

The cross section of certain characteristic energy losses should change with the energy spread of the incident beam according to Gabor's recent paper.[32] He suggests that with an oxide cathode, operating at 1000°K, the collective oscillations should be 2.5 times stronger than with a tungsten cathode, operating at 2500°K. The new analyzer of the NBS group,[54] when provided with a monochromator for the incident electron beam, should offer an easy means for testing this hypothesis.

The angular measurements need extension in several ways. One is a further study of the "dispersion relation." The only definite positive experimental evidence[41] is contradicted, at least partially, by others[44] and a clarification, using the best possible experimental setup, is necessary. The original experiments of Watanabe were executed in an instrument where the electron optics of the device can easily influence the intensity distribution and possibly the apparent energy distribution of the inelastic events.[1]

Quite apart from the arc-like behavior of the characteristic losses with angle, there is a marked discrepancy of the relative intensities of the losses as compared to the no-loss line between the data of Watanabe[42] and those of Simpson, McCraw, and Marton.[46]

Another aspect of the angular measurements is a refined study of the intensity "slopes" with angle for various energies. Every effort should be made to render such studies really quantitative, so that an absolute comparison of the scattering intensities with the theoretical ones becomes significant.

The reflection-type measurements, which normally yield a good energy resolution at very low incident energies, could be usefully extended to better angular resolution. This kind of work, at large angles, brings us really back to the classical investigations of Davisson and Germer,[55] which, in the light of more modern knowledge, would be very worthwhile repeating.

In the case of a few, well-identified, x-ray transitions we know, or at least we have good reasons to believe, that the corresponding characteristic energy losses are accompanied by radiation emitted from the solid. There was only one early and unsuccessful attempt[56] to detect the existence of radiation accompanying other characteristic losses. As there is a distinct possibility that some of the other lines may be due to radiative transitions, it would be a help to interpretation if it were known which are radiative and which are not. Although the expected efficiency of such transitions may be below even that of the x-ray transitions, modern photon counting methods offer a chance of detecting and analyzing them.

And, last but not least, a plea for better data in the related optical fields is in order. There are isolated attempts at comparison of characteristic losses with the fine structure of x-ray absorption edges,[19,57] with the fine structure in isochromates,[22] with ultraviolet spectra,[24] x-ray transitions,[17] etc. Most of these attempts remain qualitative as long as the corresponding optical information remains skimpy. The intensity relations in most of the optical material, relevant to these studies, is so poorly defined that a good part of any comparison can easily be doubted by many or called "numerology." At present the scattering measurements, with all their shortcomings, offer more reliable data, than their optical counterparts. Is it not time for better optical measurements?

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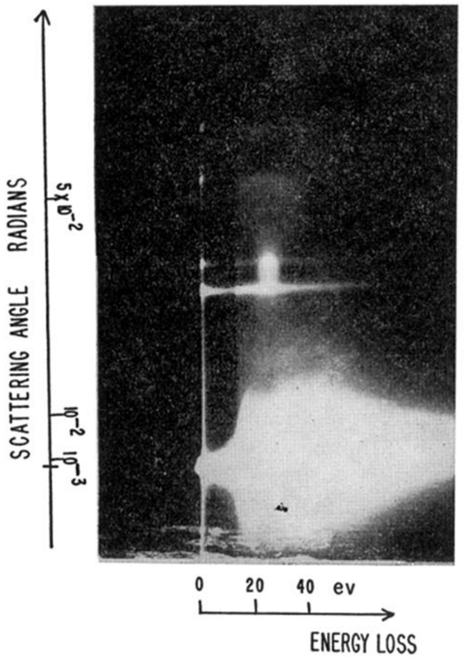
[55] C. J. Davisson and L. H. Germer, Phys. Rev. **30**, 705 (1927).

[56] E. Rudberg, Proc. Roy. Soc. (London) **A129**, 652 (1930).

[57] Y. Cauchois, Acta Cryst. **5**, 351 (1952).



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