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Electron Energy Losses in Solids and Their Influence on the Electron Diffraction Diagram

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In the classical interpretation of electron diffraction diagrams, diffraction is a purely coherent phenomenon and therefore crystallographic data can be obtained from the diffraction diagram by assuming a wave length derived from the accelerating potential of the electrons. This picture has been subsequently modified with the recognition that inelastic processes are taking place in the specimen. My talk today deals essentially with these inelastic processes and describes, in the outline at least, part of our present knowledge. I say part, because obviously in such a short talk I cannot cover all aspects of it. I trust, however, that in several of the papers given at this symposium the missing parts will be covered by the eminent scientists present who carried out a very good portion of that work themselves.

It has been recognized in the past ten or twenty years that electrons of any velocity, interacting with solids, suffer energy losses which are characteristic for that solid. They are characteristic in the sense that in some substances the energy losses have rather sharp, well-defined values. An example of such a behavior is shown in Fig. 1. Fig. 1 illustrates aluminum as a sample, and the primary electrons have 20 kev energy. A certain number of these electrons pass through the sample without any visible inelastic interaction. These constitute the truly coherent, elastic part of the radiation which is considered in the classical interpretation of diffraction. A certain proportion of the primary electrons, however, interact with the charges distributed in the solid and produce a well-defined electron loss at 15 ev. To understand the scale of Fig. 1, this means that the second peak corresponds to electrons having an energy of 19,985 ev. This effect can be accurately described as a single inelastic collision with simple energy and momentum transfer; because of the nature of such processes, repeated collisions may occur and indeed we find that all the peaks of the graph correspond to 30 ev, 45 ev, and higher multiples of a single energy loss.

Fig. 1 shows these energy losses in the

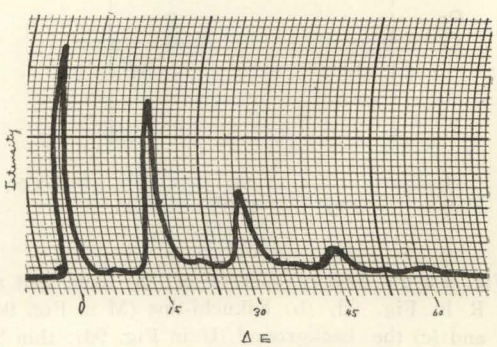

Fig. 1. Aluminum spectrum.

direction of the central spot of the diffraction diagram in direct transmission through the thin film. The angular range is very much restricted, sometimes around a fraction of a milliradian.

Now obviously those engaged in electron diffraction work are not interested in the center spot alone. They are interested in the behavior at relatively large angles when looking at the conventional Debye-Scherrer diagram Fig. 2. We may now tilt the diffraction diagram by almost 90 degrees and then decompose the energy components in different planes. The result may be something like in Fig. 3, where the top of the figure shows the two innermost rings together with the center spot greatly inclined and the different energy components represented by the various rings and their shadings downward from the topmost ring. Therefore, the second ring system from the top corresponds to electrons having lost 15 ev of their initial energy. The next corresponds to electrons having lost 30, and so on. The prominent features of this figure, besides the rings, are the gradually expanding center spot, expanding and diminishing in intensity, and a continuous background which connects the space between the first and all consecutive planes. Although until now I mentioned only the characteristic losses which occur in multiples of a primary loss, I have shown in Fig. 3 a little bit of continuous loss which I ask you to disregard for the time being. This is due to a different mechanism. We may come back later to this point in our discussion. If we take a slice out of this model, from the axis outward, we obtain the contour plot represented in Fig. 4 where energy loss is the ordinate, angle is the abcissa, intensity is represented by constant intensity contours, the scale of these constant intensity contours being logarithmic.

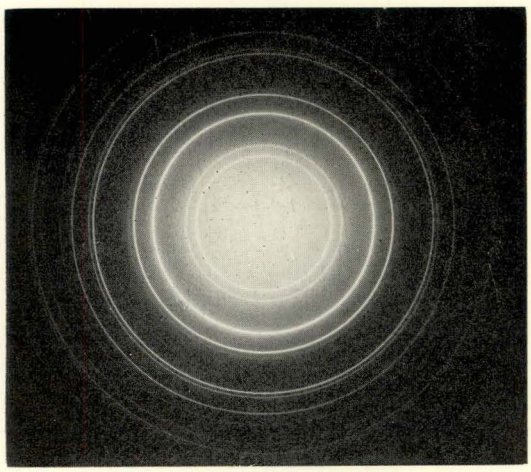

Fig. 2. Aluminum diffraction diagram.

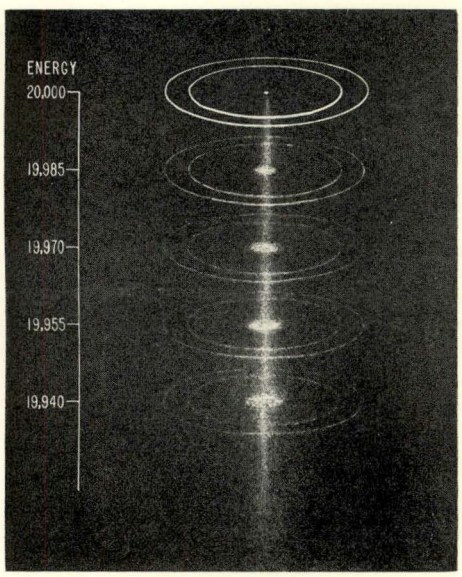

Fig. 3. Aluminum; decomposition of diffraction diagram.

Aluminum and a certain number of other materials are characterized by the sharpness of the loss and by relatively high cross section for the inelastic event. This is not true for all solids, however. In many materials, while the characteristic loss may be sharp, the cross section is considerably lower than

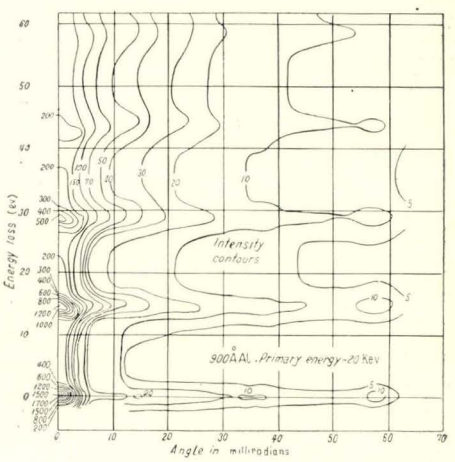

Fig. 4. Cartograph.

in aluminum and magnesium. Many other materials do not have a sharp characteristic energy loss. In these materials the characteristic loss is a somewhat washed out broad band, as for instance shown in Fig. 5. The washed out broad characteristic peak may be described as another type of contributing phenomenon. It must be emphasized, however, that all materials investigated until now show characteristic losses. There is no exception until now to that rule.

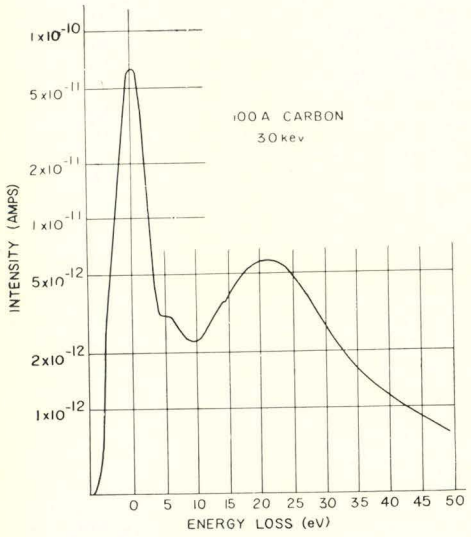

Fig. 5. Carbon spectrum.

A few words about interpretation of these characteristic energy losses. If we assume that the charges distributed throughout the solids constitute a kind of solid state plasma, which can be excited to collective oscillation by the incoming electron, the theory of Bohm and Pines gives for the frequency of this oscillation*.

$$\omega_p = \sqrt{\frac{4\pi e^2}{m} N} ,$$

where e is the charge, m the mass of the electron and N is the density of electrons participating in this collective oscillation. These plasma oscillations are longitudinal oscillations and one may expect a possible coupling with transverse oscillations to take place. The frequency of such transverse oscillations can be calculated to be

* We will show later that the same equation can be obtained starting from different considerations.

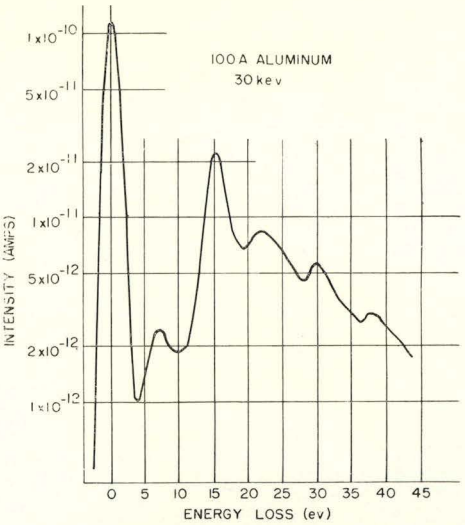

Fig. 6. Aluminum spectrum showing low-lying loss.

$$\omega_t = \frac{\omega_p}{\sqrt{2}} ,$$

assuming that the solid has a plane face, which is bounded by a vacuum. The frequency being lower than the mean plasma oscillation, it is customary to call these transverse oscillations "low-lying losses". Fig. 6 shows that these low-lying losses can be observed, but that their cross section is much smaller at the relatively high energies of diffraction investigations than the main plasma oscillation and for all that ensues in our discussion, they can be neglected.

The continuous study of the characteristic energy losses is pursued in different laboratories all over the world including some excellent works done in Japan.

Now we turn our attention to somewhat more quantitative aspects of these characteristic energy losses. The contemplation of Fig. 1 has already shown that there must be

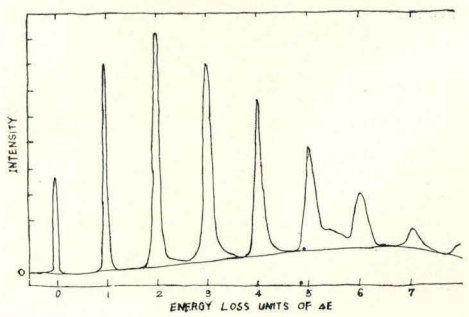

Fig. 7. Aluminum spectrum illustrating Poisson distribution.

some relation of the intensities of the successive multiple losses and these are brought out more clearly in Fig. 7. If the successive losses are independent collisions, Poisson's law should apply and we should be able to describe the successive intensities of higher peaks by the well-known Poisson distribution:

$$p\left(\frac{t}{\lambda}\right)=\frac{1}{N!}\left(\frac{t}{\lambda}\right)^{N}e^{-t/\lambda},$$

where t is the thickness of the specimen, λ is the mean free path of the electron in the material at the selected primary energy, and N is the number of inelastic collisions which can be 0, 1, 2, 3, all the way to infinity. Different laboratories have followed this up. In our laboratory, Dr. Fowler, in particular, has done extensive determinations jointly with Mr. Swanson. Fig. 8 shows the agreement between the theoretical curve and the observed points for a relatively thick specimen

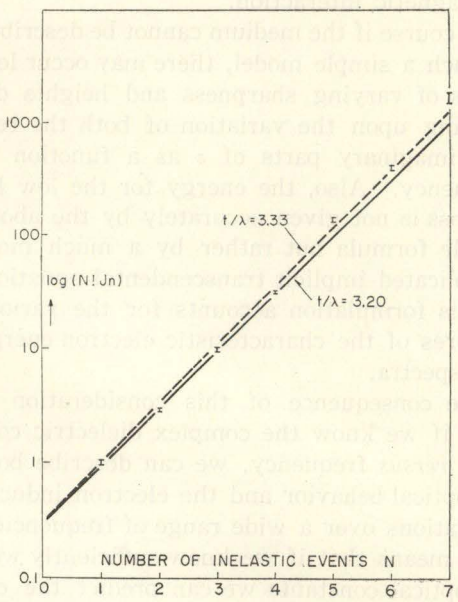

Fig. 8. Comparison between observed distribution and calculated Possion distribution.

of aluminum. A series of such determinations give a mean free path for 20 kev electrons in aluminum to be 810±60 angstroms. For the same material, Birkhoff and collaborators find about 590±185 angstroms at 30 kev. In considering the difficulties of this type of measurement, the agreement is remarkably good.

Careful investigation of the angular distribution of these multiple losses has been carried out, by Watanabe in Tokyo, Arai in Sendai, Fowler, Swanson, Simpson, and myself at the National Bureau of Standards, and Fig. 9 illustrates the type of behavior in the central diffraction spot. The innermost solid line represents the angular distribution of the purely elastic part of the electron beam. The first curve surrounding the elastic distribution is the normalized angular distribution of the first loss line; this is surrounded then by the second loss line, the third loss line, and so on. The solid curves are calculated distributions on the assumption that the elastic peaks represent zeroth order diffraction, from which one can obtain the first, second, third loss distributions by a simple folding process,

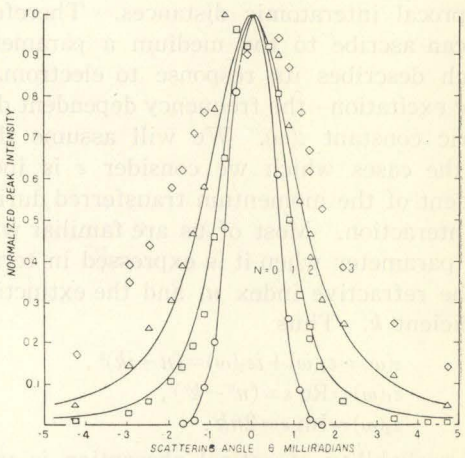

Fig. 9. Normalized angular distributions. $N=0$, elastic peak distribution. $N=1$, first characteristic loss. $N=2$, second characteristic loss. $N=3$, third characteristic loss.

assuming a Coulomb interaction with the usual energy and momentum conservation laws. The cross section for the inelastic process may be expressed as

$$f(\Theta)\propto\frac{\Theta_E}{\Theta_E^2+\Theta^2},$$

where

$$\Theta_E=\frac{\Delta E}{2E}.$$

An important point in all this is that if we examine similar normalized curves for angular distributions, we find that both the elastic and the inelastic angular distributions are independent of thickness and vary only with the angular spread of the incident beam as pre-

dicted by Wentzel's plural scattering theory. All this leads to the following model for the plural scattering process: the elastic intensity results from a coherent diffraction into the zero order central spot with zero momentum transfer, whereas inelastic intensity is obtained from random incoherent plural scattering, where the angular distribution is described by folding with the differential cross section for single inelastic scattering. It could be mentioned that this interpretation is consistent with the interpretation of Kikuchi line patterns employed by Shinohara.

We next consider these energy losses from a broader point of view. We are dealing with a class of phenomena which we may ascribe to "long range interactions"—that is the momentum changes are small as compared with reciprocal interatomic distances. Therefore we can ascribe to the medium a parameter which describes its response to electromagnetic excitation—the frequency dependent dielectric constant $\varepsilon(\omega)$. We will assume that for the cases which we consider ε is independent of the momentum transferred during an interaction. Most of us are familiar with this parameter when it is expressed in terms of the refractive index n, and the extinction coefficient k. Thus

$$\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega)=(n+ik)^2\,,$$
$$\varepsilon_1(\omega)=\mathrm{Re}\;\varepsilon=(n^2-k^2)\,,$$
$$\varepsilon_2(\omega)=\mathrm{Im}\;\varepsilon=2nk\,.$$

The probability of optical absorption is proportional to $\omega\mathrm{Im}\;\varepsilon$, where ω is the circular frequency of the photon with energy $\hbar\omega$. The probability of energy absorption from the electron beam is proportional to

$$\mathrm{Im}\frac{1}{\varepsilon}=-\frac{\mathrm{Im}\;\varepsilon}{|\varepsilon|^2}\,.$$

The reason for the dielectric constant appearing in the denominator is that the force exerted by the incident electron upon the charges within the scatterer is attenuated by the surrounding medium. Of course this is restricted to long range interactions. If one now considers an infinite plasma of electrons neutralized by a background of positive charges as a model for the medium, then it is found that the frequency-dependent dielectric constant tends to vanish at

$$\omega=\omega_p=\sqrt{\frac{4\pi Ne^2}{m}}\,,$$

where N is the density of electrons, e the electronic charge, and m the mass of the electron. At this frequency, we have a peak of the plasma frequency $\mathrm{Im}(1/\varepsilon)$ and an absorption maximum in the electron absorption spectrum. This is the "bulk" type of plasma oscillation. If the plasma is bounded by an infinite plane by a dielectric medium with dielectric constant ε_b, there may occur a different discrete loss at a lower energy

$$E_{ll}=\frac{\hbar\omega_p}{\sqrt{1+\varepsilon_b}}\,.$$

If the bounding medium is the vacuum $\varepsilon_b=1$, then

$$E_{ll}\rightarrow\frac{\hbar\omega_p}{\sqrt{2}}\,.$$

This lower lying loss is due to a coupling with the transverse components of the electromagnetic interaction whereas the main loss arises from the longitudinal modes of the electromagnetic interaction.

Of course if the medium cannot be described by such a simple model, there may occur loss peaks of varying sharpness and heights depending upon the variation of both the real and imaginary parts of ε as a function of frequency. Also, the energy for the low lying loss is not given accurately by the above simple formula but rather by a much more complicated implicit transcendental equation.

This formulation accounts for the various features of the characteristic electron energy loss spectra.

The consequence of this consideration is that, if we know the complex dielectric constant *versus* frequency, we can describe both the optical behavior and the electron induced oscillations over a wide range of frequencies. This means that if we know sufficiently well the optical constants we can predict the energy losses and *vice versa*. Work is under way for extensive comparison of these two properties, although it is considerably hampered by the fact that no two measurements have been carried out on the identical sample. Under such conditions the comparisons are often meaningless. For instance, extensive measurements are available in the literature on the optical constants of germanium. A careful comparison with the electron energy loss behavior seems to indicate that practically all optical measurements published so

far are for germanium contaminated with germanium oxide. Many more examples of this kind could be cited. Under these conditions the only thing to do is to repeat the measurements under very well-controlled conditions on the identical sample and that is what we are in the process of doing.

In all the preceding treatment, I have limited myself essentially to the treatment of the central spot or very close to the intense distribution in the central spot, and only in the introductory part of my talk did I extend to the treatment of the diffraction rings. This I did for the simple reason that most of our information is available at angles close to the central spot and the total amount of information at diffraction angles limited because of the great reduction in intensity. One can however state, even now, that the spots or rings in the diffraction pattern will show a similar broadening due to the same random inelastic scattering; that the dominant broadening is due to a transverse momentum acquired in the inelastic collision, rather than to a change in wave length in the elastic diffraction process. These are all logical developments of the theory used to interpret the angular dependence of the aluminum spectra.

In preparing this presentation the author had many discussions with his colleagues Drs. H. A. Fowler and H. Mendlowitz. Their contributions to this paper have been very great and I take pleasure in acknowledging the important part played by them.

DISCUSSION

H. RAETHER: (1) For the comparison of your results with ours, I may add that we have used a beam of angular width of 1.5×10^{-4}, so that we can derive immediately the $\vartheta_{1/2}$ value without folding the secondary distribution with the primary distribution. Which value of $\vartheta_{1/2}$ have you obtained and do they agree with the theoretical value $\vartheta_{1/2}=\Delta E/2E_0$?

(2) If one applies Poisson distribution to derive the mean free path of inelastic scattering Ω_{inel}, one has to integrate the inelastic intensity from 0 to 180°. The contribution of the large angles is not to be neglected. Thus, the high value of your observed value compared with theoretical value of Ω_{inel} is understandable.

L. MARTON: (1) I compared the angular distributions given in your paper, and found that our 10% values of normalized intensities are rather close to yours. Furthermore, I firmly believe that a folding process as described in our paper is a proper way to describe the multiple process as it is in close agreement with Wentzel's theory of plural scattering.

(2) We are integrating over ±5 milliradians so as to include almost completely the tails of the inelastic distributions.

M. BLACKMAN: Have you measured the elastic mean free path for aluminium and how does this agree with theory?

L. MARTON: We have not measured any cross-section, but limited ourselves to inelastic mean free path determination.