Determination of Object Thickness in Electron Microscopy

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(Received June 9, 1941)

It is proposed that the thicknesses of electron microscope objects be determined by measuring the diminution in intensity of the electron beam caused by the object. Since this method would only be applied to specimens so thin that multiple scattering can be neglected, one need know only the total cross section for single scattering of electrons outside the aperture angle of the electron microscope objective. These cross sections are calculated for fast electrons (energies greater than 10,000 ev) by means of the Born approximation for several cases of practical interest, and the results are applied to some experimental observations.

I. INTRODUCTION

THE usual information one can gather about the size and shape of an object by means of an electron microscope concerns the dimensions perpendicular to the optical axis. The determination of the third dimension by means of differential focusing, used in light microscopy, cannot be applied because of the very great depth of focus of the electron microscope. For practical reasons, rotation of the specimen in front of the objective lens cannot generally be realized. In the absence of a specimen with a homogeneous size distribution and random orientation, indirect methods are used for the determination of the third dimension. Throughout this paper we shall call this third dimension parallel to the optical axis the thickness of the specimen. Our purpose is to review the existing methods for its determination and to propose a new one.

Some time ago one of us called attention to the use of accidental curling of a broken collodion film for the determination of particle thickness.[1] Figure 1 is a micrograph of such a curled film with some bacteria shown in profile on its edge. This most direct method is limited however to relatively thick specimens and—since such lucky accidents cannot always be reproduced—to specimens which can be easily placed at an orientation convenient for such observation.

A second method is the stereoscopic one. By taking stereomicrographs at known viewing angles, not only the relative distances of different parts of the specimen in the direction of the optical axis can be measured, but in some cases the thickness too (Fig. 2).[2] As with the first method, its application is limited to relatively thick specimens.

The third method which we propose is to compute the thickness from the measured in-

FIG. 1. Whooping cough bacteria on the edge of a curled-up collodium film.

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[1] See T. H. Osgood, J. App. Phys. **12**, 96 (1941).

[2] This micrograph was taken by keeping the object stationary and changing the angle of incidence of the condenser beam, instead of the usual method of tilting the specimen. This could be done because of the relatively large apertures of the electron microscope used for taking these pictures (see also L. Marton, Phys. Rev. **58**, 57 (1940)) and because the image quality is primarily defined by the solid angle of the incident (condenser) beam and not by the actual size of the objective aperture (due to the predominance of large angles in the scattered beam). (See also v. Borries and Ruska, Zeits. f. tech. Physik **19**, 404 (1938).) For stereophotogrammetric measurements see W. Eitel and E. Gotthardt, Naturwiss. **28**, 367 (1940); smallest measured thickness 200A, accuracy ±50A.

tensity distribution of the electronic image. For this purpose let us consider specimens of such thickness that the image formation is due to single scattering alone.[3] For a first approximation it may be assumed that the blackening of the photographic emulsion is proportional to the number of electrons reaching its surface. For a more complete determination, however, either a direct measure of the current in different portions of the image, or a quantitative study of the behavior of the emulsion (for instance, by methods similar to those developed for photographic photometry by Ornstein and his collaborators) may be necessary. Then, if t_0 is the transmission of the negative for a part of the image corresponding to the support, and t the transmission corresponding to object and support, the thickness x is given by

$$x=(1/SN)\ln(t_0/t), \tag{1}$$

where N is the number of scattering atoms per $\text{cm}^3=N_0\rho/M$, N_0 is Avogadro's number, ρ the density, M the atomic weight, and S is the total cross section for scattering outside the angle limited by the objective aperture. We shall always use ln to indicate the natural logarithm.

II. Theory

We wish to calculate the total cross section for scattering of an electron outside a small angle α, which is the half-angle of aperture of the objective lens of the electron microscope. There are three types of scattering that must be considered: elastic and inelastic scattering by the atom or ion, and scattering by the conduction (free) electrons in the case of a metal. The elastic scattering may be regarded as nuclear Rutherford scattering that is made finite at small angles by the screening effect of the atomic electrons. Since the inner electrons are far more effective in screening the nucleus than the outer electrons, the exact configuration of the valence electrons has little effect on the cross section and we can use results based on isolated neutral atoms even though the atoms are collected together in a solid and may be ionized.

[3] In contrast to a former paper where an estimation of "depth resolving power" was given by considering multiple scattering alone [L. Marton, Physica 9, 959 (1936)].

The inelastic scattering, on the other hand, is accompanied by excitation or ionization of the atom and so depends markedly on the wave functions of the atomic electrons. As we shall see, the loosely bound outer electrons contribute most to this, so that calculations based on free atoms cannot be regarded as precisely applicable to a solid. We do, however, perform the calculations for free ions instead of atoms where metals or salts of the alkalis or halogens are involved. For organic compounds of H, C, N, O, P, and S,[4] and for "metallic" Sb, in which cases definite ionic structures are not indicated, the best we can do is to calculate for free neutral atoms and assume that the scattering is additive. This is probably a fairly good assumption, since the energy and size of a valence electron state in a molecule are not very different from their values in a free atom.

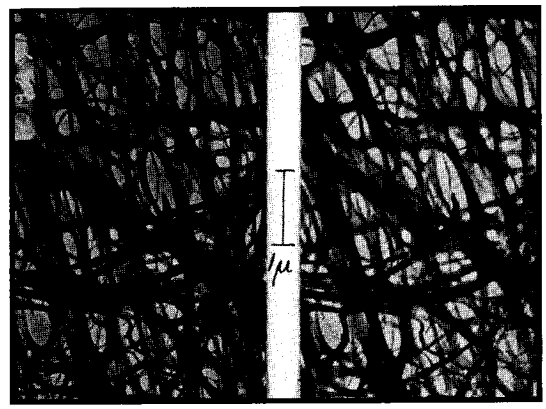

Fig. 2. Stereomicrograph of sodium laurate curd fibers.

The free electron scattering, which, of course, appears only for metals, resembles the elastic scattering in that it is also given by the Rutherford formula. For moderate angles it is $\sim\nu/Z^2$ times the elastic scattering, where ν is the number of free electrons per atom and Z is the atomic number, and is, therefore, negligible. It is, however, important at very small angles, since screening does not reduce it in the same way as the elastic scattering.

Elastic scattering

All calculations will be made for fast electrons with the help of the Born approximation (ener-

[4] F. Seitz, *Modern Theory of Solids* (McGraw-Hill, 1940), p. 72.

gies greater than 10,000 ev), and for small scattering angles θ. It is never necessary to consider large angle deflections, since these are relatively infrequent and contribute a negligible amount to the total cross section if α is small; we can always use the approximation: $\sin\theta \leqq \theta$, $\cos\theta \leqq 1$. The differential cross section for elastic scattering between θ and $\theta+d\theta$ is then given by the relativistic Rutherford formula:[5]

$$d\sigma_e = 8\pi(Ze^2/mv^2\gamma)^2 d\theta/\theta^3, \quad \gamma \equiv (1-v^2/c^2)^{-\frac{1}{2}}, \quad (2)$$

provided θ is larger than the "cut-off" angle θ_1 at which screening of the nucleus by the inner electrons plays an important role. Here, e, m, and v are the charge, rest mass and velocity of the incident electron. For $\theta < \theta_1$, the cross section is roughly constant and can be neglected. Using the Thomas-Fermi model and the Born approximation, one obtains to good approximation:

$$\theta_1 = Z^{\frac{1}{3}}c/180v\gamma. \quad (3)$$

For the lighter atoms, where the Thomas-Fermi model is not a good approximation, we use the numerical computations based on Hartree wave functions quoted by Mott and Massey;[6] because the Born approximation is used here, θ_1 is still proportional to $1/v\gamma$, that is, to the reciprocal of the momentum. We thus obtain on integration of (2):

$$\sigma_e = A(\hbar/mv)^2, \quad \alpha < \theta_1;$$
$$\sigma_e = 4\pi(Ze^2/mv^2\gamma\alpha^2)^2, \quad \alpha > \theta_1; \quad (4)$$

where $\hbar$ is Planck's constant divided by 2π. Here $A = 22Z^{4/3}$ for all except the lightest atoms, and is given in Table I for several cases of practical interest. For most microscopes, α is less than θ_1.

Inelastic scattering

The inelastic scattering cannot be calculated as accurately as can the elastic scattering. We give formulas here which are certainly of the correct order of magnitude, and are probably no less accurate than the assumption that the atomic cross sections are additive in the solid state. It is fortunate that the most doubtful parameter of this calculation appears only inside a logarithm, so that the computed result is insensitive to its choice.

[5] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford, 1933), p. 88.
[6] Reference 5, p. 124.

Mott and Massey[7] give for the differential cross section for excitation of an atom:

$$8\pi(e^2/\hbar v)^2 |\sum_{s=1}^{Z} (x_s)_{0n}|^2 d\theta/\theta, \quad (5)$$

where we have kept only the dipole term and have replaced their matrix element x_{0n} by $\sum_{s=1}^{Z} (x_s)_{0n}$ for a many-electron atom. Equation (5) is valid for angles in the range $\theta_2' < \theta < \theta_3'$, where:[7]

$$\theta_2' = (E_n - E_0)/mv^2\gamma^2, \quad \theta_3' = (2|E_0|/mv^2\gamma^2)^{\frac{1}{2}}; \quad (6)$$

E_n is the energy of the atom in the state n and E_0 is its energy in the ground state. Summing (5) over all excited states of the atom, we obtain:

$$d\sigma_i = 8\pi(e^2/\hbar v)^2 [(\sum_{s=1}^{Z} x_s)^2]_{00} d\theta/\theta, \quad (7)$$

where the limiting angles (6) can be expressed approximately in terms of a mean excitation energy I of the atom:

$$\theta_2 = I/mv^2\gamma^2, \quad \theta_3 = (2I/mv^2\gamma^2)^{\frac{1}{2}}. \quad (8)$$

Although the contribution to the scattering is negligible outside the limiting angles (8), the large angle deflections contribute a significant amount to the stopping power and have to be considered in calculating it.

TABLE I. *Parameters appearing in Eqs. (4), (8), and (10), A and B are dimensionless numbers, and I is given in ev.*

	A	B	I		A	B	I
1 H	7.3	13.3	13.5	17 Cl^-	930	76	77
2 He	10.6	8.8	38	18 A	875	55	110
3 Li^+	60	3.4	98	19 K^+	1110	43	140
6 C	246	35	44	20 Ca^{++}	1200	33	180
7 N	229	28	63	29 Cu^+	1950	91	130
8 O	209	23	83	35 Br^-	2520	120	130
9 F^-	274	26	91	37 Rb^+	2700	88	170
10 Ne	215	18	130	47 Ag^+	3720	200	170
11 Na^+	316	13	180	51 Sb	4150	220	180
13 Al^{+++}	547	7.5	300	53 I^-	4370	180	150
15 P	840	80	63	55 Cs^+	4600	120	230
16 S	846	70	74				

The matrix element in (7) is readily evaluated if one assumes that the ground state of the atom can be described by an antisymmetric product of

[7] Reference 5, Chapter XI, especially Eqs. (39), (38), (13), (7). The relativity modifications can be established by the method of impact parameters: E. J. Williams, Proc. Roy. Soc. **A139**, 163 (1933).

one-electron wave functions:

$$[(\sum_{s=1}^{Z} x_s)^2]_{00} = \sum_i (x^2)_{ii} - \sum_{i \neq j} |x_{ij}|^2 \equiv (B/4\pi)(\hbar^2/me^2)^2, \quad (9)$$

where i and j represent occupied one-electron states of the atom. On integrating (7), we finally obtain for the total inelastic scattering cross section:

$$\sigma_i = B(\hbar/mv)^2 \ln (2/\theta_2), \quad \alpha < \theta_2;$$
$$\sigma_i = B(\hbar/mv)^2 \ln (2\theta_2/\alpha^2), \quad \theta_2 < \alpha < \theta_3. \quad (10)$$

σ_i is negligible compared to σ_e for $\alpha > \theta_3$; in practical cases, α is less than θ_3. The quantity B has been calculated using Slater wave functions,[8] and I has been estimated as the average binding energy of the individual electrons, weighted according to their contribution to B. The results are collected in Table I for several cases of practical interest. The second part of (9), which subtracts out the contribution from forbidden transitions, is relatively unimportant, except within a shell of given total quantum number. The first part of (9) is just $Z/3$ times the mean square radius of the atom, and is thus a multiple of the diamagnetic susceptibility of the atom. Now it has been found that the experimental susceptibility is given much better by Slater wave functions than by Hartree wave functions or the Thomas-Fermi model.[9] This indicates that, although the latter solutions hold better for the inner electrons, which contribute little to B, the Slater functions are fitted semi-empirically to give good agreement with sizes and energies, especially for the outer electrons. The quantity I is much more difficult to estimate; this is not a serious source of error, however, because of the logarithmic dependence of σ_i on it.

It should be remarked that the velocity dependence of (4) and (10) is much more certain than the computed values of the parameters A, B, and I. Thus these parameters may eventually be determined experimentally with greater accuracy than given here.

Experimental evidence for inelastic scattering at small angles has been obtained by Kuper,[10] and the agreement with theory in the cases of helium is satisfactory.[11]

Free electron scattering

In a metal, the free conduction electrons also contribute to the scattering. This can be calculated using the Rutherford formula (2), with $Z=1$.[12] However, it must be remembered that because of the degeneracy of the electron gas (departure from degeneracy can be neglected at ordinary temperatures), only those electrons that would be knocked out of the occupied sphere in momentum space can cause scattering. The momentum transfer in a given collision is $p = mv\gamma\theta$, so that a fraction $(3p/4P - p^3/16P^3)$ of the electrons take part in a given collision, where $P = 2\pi\hbar(3\nu N/8\pi)^{\frac{1}{3}}$ is the maximum momentum of the Fermi distribution, ν is the number of free electrons per atom and N is the number of atoms per unit volume; for $p \geqq 2P$, all electrons can scatter. The differential cross section per atom is then:

$$d\sigma_f = 8\pi\nu(e^2/mv^2\gamma)^2(3\theta/4\theta_4 - \theta^3/16\theta_4^3)d\theta/\theta^3, \quad \theta < 2\theta_4; \quad (11)$$
$$d\sigma_f = 8\pi\nu(e^2/mv^2\gamma)^2 d\theta/\theta^3, \quad \theta > 2\theta_4;$$

here:

$$\theta_4 \equiv \theta P/p = (2\pi\hbar/mv\gamma)(3\nu N/8\pi)^{\frac{1}{3}}.$$

There seems to be no reason to expect screening due to distortion of the electron cloud except at very small angles. One should, therefore, integrate (11) from α as a lower limit:

$$\sigma_f = 8\pi\nu(e^2/mv^2\gamma)^2(3/4\theta_4\alpha - 3/8\theta_4^2 + \alpha/16\theta_4^3), \quad \alpha < 2\theta_4; \quad (12)$$
$$\sigma_f = 4\pi\nu(e^2/mv^2\gamma\alpha)^2, \quad \theta > 2\theta_4.$$

For the metals included in Table I, $\nu = 3$ for Al, and $\nu = 1$ for Cu and Ag.

Multiple scattering

It is of some interest to see at what value of the object thickness multiple scattering sets in and the single scattering cross sections derived

[8] J. C. Slater, Phys. Rev. **36**, 57 (1930).
[9] G. W. Brindley, Phil. Mag. **11**, 786 (1931); F. E. Hoare, Proc. Roy. Soc. **A147**, 88 (1934).
[10] J. B. H. Kuper, Phys. Rev. **53**, 993 (1938).
[11] J. B. H. Kuper and E. Teller, Phys. Rev. **58**, 602 (1940).
[12] See also reference 5, p. 270.

above can no longer be used. It can be shown[13] that the quantity that determines the amount of multiple scattering is $\int\theta^2 d\sigma$. From (7) and (11) it is then clear that the inelastic and free electron scattering contribute negligible amounts

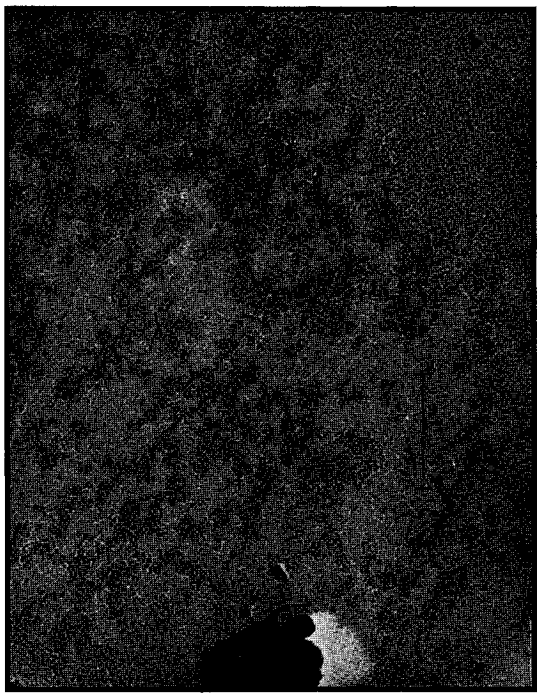

FIG. 3. Thin layer of antimony evaporated on collodion film.

to the multiple scattering. Thus the usual treatment of multiple scattering applies, and one need consider only single scattering so long as the remnant of the incident beam of unit intensity:

$$e^{-SNx}, \quad S\equiv\sigma_e+\sigma_i+\sigma_f, \tag{13}$$

is large compared to the fraction of the multiply scattered beam that enters the aperture:

$$\pi\alpha^2 f(0), \tag{14}$$

where Goudsmit and Saunderson[14] have found:

$$f(0)=(0.43\gamma^2/4\pi D)(v/c)^4 \times(5.60-\tfrac{1}{3}\ln Z+\tfrac{1}{2}\ln D)^{-1}, \tag{15}$$
$$D\equiv 24.8\times10^{-26}Z^2Nx.$$

[13] E. J. Williams, Proc. Roy. Soc. **A169**, 531 (1939).
[14] S. Goudsmit and J. L. Saunderson, Phys. Rev. **58**, 36 (1940).

Z should be taken as the root mean square average: $NZ^2=\sum_i N_iZ_i^2$. For small thicknesses, the transmitted intensity is given by (13) and for great thicknesses by (14). In between, where (13) and (14) are roughly equal, plural scattering will have to be considered. We omit a discussion of this case since, for applications to electron microscopes, (13) will be the dominant term.

III. APPLICATIONS

A first practical example is the calculation of the thickness of the granules of a thin Sb film on a collodion support as shown in Fig. 3. There have been many proposals to explain the anomalies in conductivity of thin metallic layers by a granular structure.[15] There have, however, been no direct proofs for such a structure. The electron microscope provides such evidence, showing, for instance, that a thin film of Sb is built up of individual granules of approximately 250A diameter. These granules are remarkably constant in their dimensions parallel to the support, and also show a discreteness in thickness. This indicates that the granules grow perpendicular to the support, and may do this in a step-wise manner. The best part of Fig. 3 for measuring the thickness of the particles in a single layer is close to the big dust particle which produced a cast shadow (due to sidewise evaporation). The t_0/t ratio is approximately 1.5. The number of atoms per cm^3 for Sb, assuming bulk density for the small particles, is 3.3×10^{22}. With $\alpha=2.4\times10^{-3}$, the total scattering cross section for 75-kv electrons is 3.4×10^{-17} cm^2. Thus the thickness is 36A. An attempt has been made to check this figure by observing the profile of such an Sb-film on a curled collodion film. The edge appears rippled with an apparent height of the particles of about $50A\pm20A$.

Our next example is in connection with the investigation of the structure of soap curd fibers.[16] Figure 4 represents such curd fibers of sodium laurate $NaC_{12}H_{23}O_2$. As indicated before, we can assume additivity of the atomic (or ionic) cross

[15] See, for instance, E. Perucca, Nuovo Cimento **15**, 365 (1938); J. Strong and B. Dibble, J. Opt Soc. Am. **30**, 431 (1940).
[16] L. Marton, J. W. McBain and R. D. Vold, J. Am. Chem. Soc. **63**, 1990 (1941).

sections and the thickness can be computed from

$$x=(\sum_i S_iN_i)^{-1}\ln(t_0/t). \qquad (16)$$

Here, $N_i = N_0p_in\rho/M$, where N_0 is again Avogadro's number, p_i the fraction of atoms of type i in the molecule, n the total number of

FIG. 4. Sodium laurate curd fibers.

atoms in one molecule (p_in is therefore the number of type i atoms in one molecule), ρ the density and M the molecular weight. The density of the dehydrated sodium laurate curd is 1. The measured value of the t_0/t ratio, from the fibers indicated by arrows on Fig. 4, is 1.20. Thus we obtain for 75-kv electrons with $\alpha=5\times10^{-4}$:

	N_i	S_i	N_iS_i
Na	2.7×10^{21}	2.6×10^{-18}	7000
C	32.4	3.2	104000
H	62.1	0.58	36000
O	5.4	2.5	13000
			160000

$x=115$A.

It may be pure coincidence that other sodium laurate micrographs show a mottled appearance (Fig. 5) with a periodicity of 120–130A.

Another interesting comparison is given by the thin films used as supports for a great number of electron microscope specimens. Different plastics have been used for this purpose, the most common being collodion (mixture of cellulose trinitrate and tetranitrate) and guncotton (cellulose hexanitrate). The thickness of an average good film has been computed by weighting and found to be about 100A. For collodion, t_0/t is observed to be between about 1.1 and 1.2; these give (assuming a mixture of equal parts of tri- and tetranitrate) $x=58$ and 110A, respectively, for $\alpha=2.4\times10^{-3}$, and $x=45$ and 87A for $\alpha=5\times10^{-4}$, at 75 kev.

Among many further interesting applications one more may be mentioned: the application to metallographic specimens. Such specimens cannot be directly observed by actual electron microscopes because there is no true reflection of electrons. On the other hand, a thermionic or a secondary electron microscope does not possess the same resolving power as a high voltage transmission microscope. The obvious way out of this difficulty is to prepare thin replicas of the surface to be investigated and to observe these replicas in transmission. Figure 6 shows an example: the structure of etched stellite reproduced by allowing a drop of diluted gelatin to dry on the surface.[17] The peeled-off gelatin film can either be observed directly or reproduced again by covering the side which was in contact with the metal with collodion solution and dissolving the gelatin after the collodion is dry. Except for shrinkage the replicas reproduce with great fidelity the structure of the surface, and by calculating the thickness of the "ridges" and

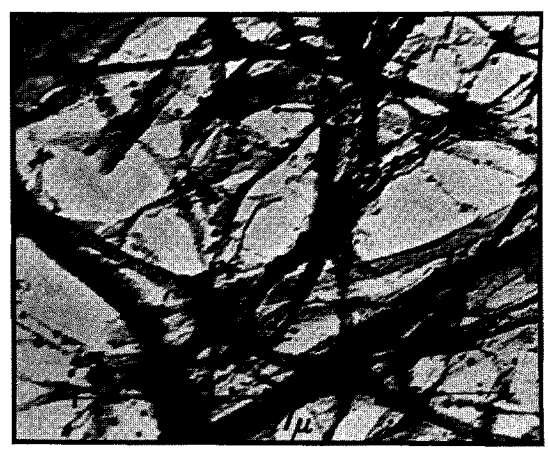

FIG. 5. Sodium laurate curd fibers.

[17] Prepared by Dr. E. G. Ramberg.

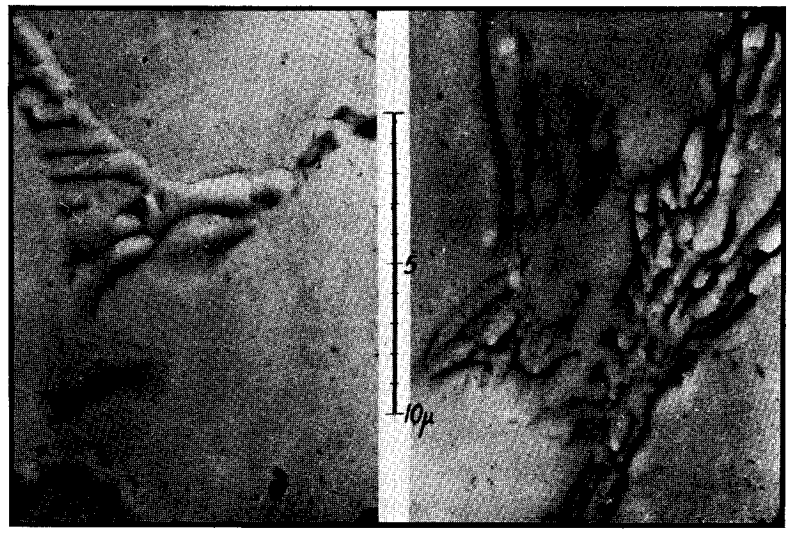

FIG. 6. Electron micrograph of stellite structure.

"valleys" of the replica one can get valuable information that is not made available by any other method.

It is worth noting that since α is less than θ_1 and θ_3 in cases of practical interest, the total cross section (except in the case of a metal) is rather insensitive to α, involving it only in the logarithm part of (10). This is illustrated by the computation for a collodion film given above, where a change in α by a factor 5 makes only about 30 percent change in the calculated thickness.

Calendar of Meetings

October

1– 4 Electrochemical Society, Chicago, Illinois
6–10 National Safety Council, Chicago, Illinois
12–15 American Society of Mechanical Engineers, Louisville, Kentucky
13–16 Society of Motion Picture Engineers, New York, New York
15–17 American Society of Civil Engineers, Chicago, Illinois
20–24 American Society for Metals, Philadelphia, Pennsylvania
20–24 American Welding Society, Philadelphia, Pennsylvania
24–25 Acoustical Society of America, New York, New York
24–25 Optical Society of America, New York, New York
24–25 Society of Rheology, New York, New York
30–Nov. 1 Society of Automotive Engineers, Los Angeles, California
30–Nov. 1 National Research Council Conference on Electrical Insulation, Williamsburg, Virginia

November

3– 5 American Institute of Chemical Engineers, Virginia Beach, Virginia
21–22 American Physical Society, Chicago, Illinois

December

1– 5 American Society of Mechanical Engineers, New York, New York
5– 8 National Research Council, Highway Research Board, Washington, D. C.
10 American Standards Association, New York, New York
29–31 American Physical Society, Princeton, New Jersey
29–31 Geological Society of America, Boston, Massachusetts
29–Jan. 3 American Association for the Advancement of Science, Dallas, Texas
29–Jan. 3 American Astronomical Society, Cleveland, Ohio