

iron diffusing in the formation of FeO and mainly oxygen diffusing in the formation of Fe_3O_4 and Fe_2O_3 ,¹⁰ the order of formation being as indicated. It is assumed therefore that aggregates of iron oxide form in the film, with FeO forming first and, in those regions of highest oxygen concentration, the relatively unstable FeO oxidizing further to Fe_3O_4 . Theories describing the coercive force in magnetic materials relative to nonmagnetic inclusions are discussed by Kittel⁴ and predict the rise in coercive force found experimentally. Since Fe_3O_4 is magnetic, one would expect that the reversing field (coercive force by Kittel's definition) required to move the domain wall through these regions would be less than that required to move the walls through the nonmagnetic FeO inclusions. This then could explain the outside-to-inside domain wall movement noted. With

further diffusion of oxygen the Fe_3O_4 would oxidize to Fe_2O_3 , while those regions with FeO inclusions would also oxidize further to Fe_3O_4 . The inner regions of the film might then contain the largest amounts of magnetic Fe_3O_4 inclusions and therefore nucleate first during the magnetization reversal. This could explain the reversals of nucleation and wall movement direction noted experimentally.

The presence of these inclusions is believed to retard the motion of the domain walls through the film, thus causing the time delays mentioned previously.

The total percentage of impurity inclusions in shape-sensitive films are minute and it appears that slight variations in the concentration of these impurities contribute to the observed properties of the films. Since measurement techniques of sufficient sophistication to determine these impurity variations were not available, further validation of the above proposed theory will have to await the development of such techniques.

¹⁰ O. Kubaschewski and B. E. Hopkins, *Oxidation of Metals and Alloys* (Academic Press Inc., New York, 1953).

Numerical Evaluation of X-Ray Absorption Factors for Cylindrical Samples and Annular Sample Cells*

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An analysis is presented for the absorption corrections necessary for the x-ray analysis of diffraction data from a liquid sample confined within a cylindrical sample cell. The evaluation of necessary absorption integrals has been formulated in a numerical calculus procedure appropriate for a digital computer. The procedure has been verified against previous graphical computations.

INTRODUCTION

THEORETICAL expressions which describe the scattering of x rays from a liquid or an amorphous solid are usually derived without consideration for x-ray absorption. In practice, both the incident and the scattered beams are subject to self-absorption, not only within the sample itself, but to further absorption within the walls of any material used as a sample cell. To the extent that this absorption is a function of scattering angle, corrections must be made for its effects before experimental data are treated on an absolute basis.

Blake¹ presented formulas and tables for the self-absorption of x rays within a cylindrical sample. Ritter² extended the analysis by considering the effect of an annular cell surrounding a diffraction sample, presenting a graphical method for estimating the pertinent absorption constants. The computations are lengthy and involved, especially if carried out by the graphical techniques employed by Ritter. With the availability of high-speed electronic computers, it was felt that Ritter's computation should be reformulated in terms of numerical calculus. In his analysis, Ritter assumed that an experimentally observed intensity was a linear combination of an independent component from the confined sample and a component from the sample cell. He thus implicitly assumed that there were

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¹ F. C. Blake, *Revs. Modern Phys.* **54**, 169 (1933).

² H. L. Ritter, R. L. Harris, and R. E. Wood, *J. Appl. Phys.* **22**, 169 (1951).

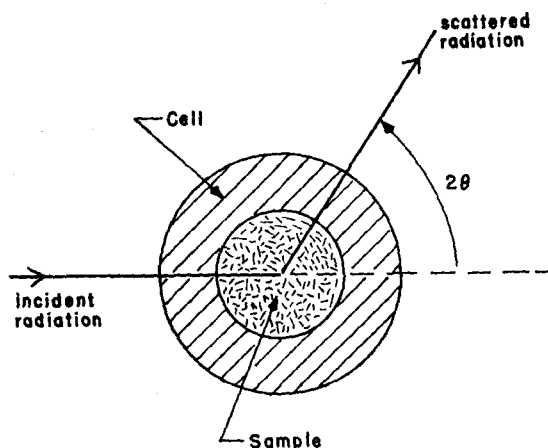


FIG. 1. Scattering geometry.

no significant coupling effects between the materials composing the sample and the sample cell. It will be shown in the present paper that this latter assumption is valid under most circumstances, but it merits examination to establish the limits of its validity.

NOTATION

$a, b, c, d, a_0, a_1, b_0, b_1$	Denote zones in scattering cross section; see Fig. 2
$A_{c,c}$	Cylindrical absorption factor for scattering and self-absorption in cell, Eq. (5)
$A_{c,sc}$	Cylindrical absorption factor for scattering in cell and absorption in both sample and cell, Eq. (10)
$A_{s,sc}$	Cylindrical absorption factor for scattering in sample and absorption in both sample and cell, Eq. (11)
$A_{s,s}$	Cylindrical absorption factor for scattering and self-absorption in sample, Eq. (16)
$A_{sc,sc}$	Cylindrical absorption factor for scattering in both sample and cell and absorption in both sample and cell, Eq. (12)
$I(s)$	Theoretical intensity of diffracted coherent radiation
$I_c(s)$	Theoretical intensity from evacuated cell, Eq. (6)
$I_c^E(s)$	Experimental intensity from evacuated cell, Eq. (1)
$I_{c+s}^E(s)$	Experimental intensity from cell and sample, Eq. (7)
$I_s(s)$	Theoretical intensity from isolated sample, Eq. (8)
$I_{sc}(s)$	Theoretical intensity from scattering arising from the correlation of densities in the sample with those in the cell, Eq. (9)
K	Ratio of outside to inside diameter of cell
l_c	Optical path length in cell
l_s	Optical path length in sample
m, n	Integers
m_R	Integer related to the radial cell dimension

N_c	Number of electrons in cell
N_s	Number of electrons in sample
\mathbf{r}, \mathbf{r}'	Radius vectors
r, r'	Magnitudes of \mathbf{r} and \mathbf{r}'
R	Inside radius of cell
s	Scattering angle parameter
s	Magnitude of s , $(4\pi/\lambda)\sin\theta$
V	Volume
V_c, V_c'	Volume of cell
V_s	Volume of sample
V_{corr}	Volume within which there exist significant correlations in structure between sample and sample cell
α	Defined in Table I.
β	Defined in Table I.
η	Defined in Table I.
θ	Half angle of diffraction
λ	Wavelength of radiation
μ_c	Linear absorption coefficient of cell material
μ_s	Linear absorption coefficient of sample
ν	Defined in Table I
ρ_c	Electron density in sample cell
$\rho(r)$	Electron density
ρ_s	Electron density in sample
σ	Defined in Table I
ω	Angular coordinate
Subscripts:	
c	Refers to cell
s	Refers to sample

SCATTERING AND ABSORPTION

The scattering geometry under consideration here is illustrated in Fig. 1. For monochromatic radiation of fixed intensity, we are interested in analysis of the origin of the intensity observed at any particular scattering angle. The scattered intensity will originate from the interaction of the secondary radiation of the electrons composing material in the sample area and separately from electrons composing material of the sample cell. Any incident beam or radiation will be absorbed in both the sample and the sample cell; furthermore, secondary radiation originating within the sample or within the sample cell may be absorbed in either the sample, or the sample cell, or both. The item of usual experimental interest is the scattering from the sample itself, fully corrected for absorption both within the sample and the sample cell.

We consider the results of two separate experiments. The first will be the observation of x-ray intensity as a function of angle for the sample cell alone. This will be denoted by $I_c^E(s)$, where we use s in the conventional sense of the angular scattering parameter, $s = (4\pi/\lambda) \times \sin\theta$. Secondly, we consider the experiment of observing scattered intensity as a function of s for the assemblage consisting of the sample plus sample cell, denoted by $I_{c+s}^E(s)$. These two intensities, and all subsequent intensities, are taken as coherent and normalized by

the intensity which would be scattered by an isolated classical electron under identical conditions. Given these two observed experimental intensities, the problem is to find an appropriately weighted difference which will provide the scattering that would originate from an isolated sample.

Considering first the experiment with the empty sample cell, $I_c^E(s)$ may be expressed by the following formulation which includes the effect of absorption in both the incident and scattered beams:

$$I_c^E(s) = \int_{V_c} \int_{V_c} \langle \rho_c(\mathbf{r}') \rho_c(\mathbf{r}'+\mathbf{r}) \rangle_{av} e^{is \cdot \mathbf{r}} e^{-\mu_c l_c(\mathbf{r}'; s)} \times dV_c' dV_c. \quad (1)$$

In this equation $\rho_c(\mathbf{r}')$ is the density of electrons at a point located at \mathbf{r}' with respect to an arbitrary origin of coordinates; $\rho_c(\mathbf{r}'+\mathbf{r})$ is the electron density at a point \mathbf{r} from \mathbf{r}' . In this expression, as well as in those which follow, the path length, $l_c(\mathbf{r}'; s)$, is the total distance traversed by a ray incident on the point \mathbf{r}' , plus the distance traversed by the ray scattered from the point \mathbf{r}' in the direction s .

Validity of Eq. (1) is dependent on the very reasonable physical assumption that the correlations in structure are significant only over distances very small compared to the characteristic dimensions of the macroscopic sample cell. The time average of the product $\langle \rho_c(\mathbf{r}') \rho_c(\mathbf{r}'+\mathbf{r}) \rangle_{av}$ may be replaced by $N_c \rho_c(\mathbf{r})/V_c$, where the position dependent density $\rho_c(\mathbf{r})$ reflects the correlations in density between the points \mathbf{r}' and $\mathbf{r}'+\mathbf{r}$. As a simplification we will restrict the present analysis to macroscopically homogeneous isotropic systems for which $\rho(\mathbf{r})$ is independent of \mathbf{r}' . Equation (1) then simplifies to

$$I_c^E(s) = \left\{ \frac{1}{V_c} \int_{V_c} e^{-\mu_c l_c(\mathbf{r}'; s)} dV_c' \right\} \times \left\{ N_c \int_{V_c} \rho_c(\mathbf{r}) e^{is \cdot \mathbf{r}} dV_c \right\}. \quad (2)$$

For symmetry about an axis normal to the scattering plane

$$I_c^E(s) = \left\{ \frac{1}{A_c} \int_{A_c} e^{-\mu_c l_c(\mathbf{r}'; s)} dA \right\} \times \left\{ N_c \int_{V_c} \rho_c(\mathbf{r}) e^{is \cdot \mathbf{r}} dV_c \right\}, \quad (3)$$

where A represents the cross-sectional area. This results then in the formal representation of the experimentally observed intensity as the product of a geometric absorption correction and an intrinsic scattering:

$$I_c^E(s) = A_{c,e}(s) I_c(s), \quad (4)$$

where

$$A_{c,e}(s) = \frac{1}{\pi R^2 (K^2 - 1)} \int_R^{KR} \int_0^{2\pi} e^{-\mu_c l_c(\mathbf{r}'; s)} r' dr' d\omega \quad (5)$$

and

$$I_c(s) = N_c \int_{V_c} \rho_c(\mathbf{r}) e^{is \cdot \mathbf{r}} dV_c. \quad (6)$$

In the case of the experiment involving both the sample and the sample cell, by making a similar assumption of the essential independence of the intrinsic scattering power of the material and the x-ray absorption attenuation integral, an expansion of a rigorous scattering formula results in the following expression:

$$I_{c+s}^E(s) = A_{c,sc}(s) I_c(s) + A_{s,sc}(s) I_s(s) + A_{sc,sc}(s) I_{sc}(s), \quad (7)$$

where

$$I_s(s) = N_s \int_{V_s} \rho_s(\mathbf{r}) e^{is \cdot \mathbf{r}} dV_s, \quad (8)$$

$$I_{sc}(s) = 2 \int_{V_s} \int_{V_c} \rho_c(\mathbf{r}_c) \rho_s(\mathbf{r}_s) e^{is \cdot \mathbf{r}_c - \mathbf{r}_s} dV_c dV_s, \quad (9)$$

$$A_{c,sc}(s) = \frac{1}{\pi R^2 (K^2 - 1)} \int_R^{KR} \int_0^{2\pi} e^{-\mu_s l_s(\mathbf{r}, \omega; s) - \mu_c l_c(\mathbf{r}, \omega; s)} \times r dr d\omega, \quad (10)$$

$$A_{s,sc}(s) = \frac{1}{\pi R^2} \int_0^R \int_0^{2\pi} e^{-\mu_s l_s(\mathbf{r}, \omega; s) - \mu_c l_c(\mathbf{r}, \omega; s)} r dr d\omega, \quad (11)$$

$$A_{sc,sc}(s) = \frac{1}{V_{corr}} \int_{V_{corr}} e^{-\mu_s l_s(\mathbf{r}, \omega; s) - \mu_c l_c(\mathbf{r}, \omega; s)} r dr d\omega. \quad (12)$$

It is necessary to consider briefly the significance and magnitude of the $I_{sc}(s)$, which involves scattering arising from the correlation of densities in the sample with those in the sample cell. This was a term that Ritter implicitly omitted from his analysis. In general, correlation effects between cell and sample atoms will exist only within a few angstroms of the mechanical boundary of the cell. On both sides of this region the structure of either material is completely independent from that of the other. Therefore, it is quite plausible that over the limits of the multiple integral the positive and negative values of the integrand will approximately nullify one another. Except for a negligible contribution from this latter integral, the gross intensity from the cell and sample system can thus be written as contributions from an evacuated cell and from a sample enclosed in a nonabsorbing container, completely neglecting the interaction of the cell and sample materials. It should be pointed out, however, that this approximation would break down in the event that there were significant correlation between the ordering in the sample and that in the cell. This could well occur if the sample cell were

crystalline, or single crystal, and if the sample itself were crystalline or an aggregate of small polycrystallites.

If this interaction between the sample and the sample cell is thus neglected, the following expression results for the experimentally accessible intensity from the sample plus cell, with absorption in both media.

$$I_{s+c}^E(s) = I_c(s)A_{c,sc}(s) + I_s(s)A_{s,sc}(s). \quad (13)$$

Or using the result of Eq. (2),

$$I_{s+c}^E(s) = I_c^E(s) \frac{A_{c,sc}}{A_{c,c}} + I_s(s)A_{s,sc}. \quad (14)$$

Through algebraic manipulation of this equation, the desired value of the scattering from the sample corrected for absorption is given in terms of experimental intensities and the geometric factors, $A_{i,j}$.

$$I_s(s) = I_{c+s}^E(s) \frac{1}{A_{s,sc}(s)} - I_c^E(s) \frac{A_{c,sc}(s)}{A_{s,sc}(s)A_{c,c}(s)}. \quad (15)$$

Although in the present case the geometry will be discussed as though the sample were at the center of the region with the sample cell forming the annulus, it might happen, as suggested by Ritter, that occasionally a sample would be formed in the annular region around a central supporting rod. In the latter case all results of the present analysis will be applicable by simple inversion of the role of the sample and the sample cell. In such an analysis it would be helpful to have available values of the absorption coefficient for the experiment involving scattering from a simple cylinder:

$$A_{s,s}(s) = \frac{1}{\pi R^2} \int_0^R \int_0^{2\pi} e^{-\mu s l(s; r, \omega; \theta)} r d\omega dr. \quad (16)$$

Actually this is essentially the self-absorption factor for cylinders reported by Blake.¹ We include it here for completeness.

EVALUATION OF ABSORPTION INTEGRALS

The numerical evaluation of the integral in Eqs. (5), (10), (11), and (16) involves first an appropriate choice for the area increments over which the absorption factor is summed and, secondly, the computation of optical path lengths within sample and cell as a function of radial and angular coordinates and as a function of the scattering angle parameter, $s = (4\pi/\lambda)\sin\theta$.

The integrations are approximated by summations of finite elements over a grid determined by increments in the radial and angular variables. Within the central sample region, $r \leq R$, the area may be divided into m_R finite rings, the successive boundaries of which are located by

$$r = (m/m_R)R, \quad m = 1, 2, \dots, m_R. \quad (17)$$

In the annular region a slight complication exists since

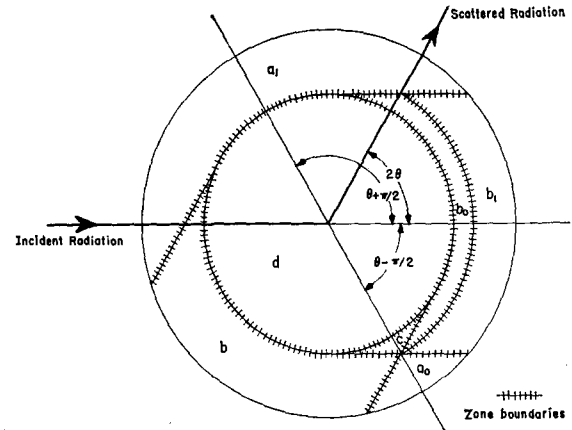


FIG. 2. The three zones for cell scatter.

the continuation of the sequence of rings given by Eq. (17) may not uniformly cover the region $R \leq r \leq KR$. However, since the selection of m_R is to some extent arbitrary, it will be possible to pick an m_R such that an integer multiple of R/m_R will closely approximate KR . This is equivalent to requiring that

$$m/m_R \simeq K, \quad m, m_R \text{ integer}; m > m_R \quad (18)$$

or

$$Km_R = \text{integer}. \quad (19)$$

In the approximation of the integrals by summations, it is desirable to evaluate the integrand at approximately the middle of the area increments. These are located by

$$r_m = [(m - \frac{1}{2})/m_R]R \\ m = 1, 2, \dots, m_R, m_R + 1, \dots, Km_R. \quad (20)$$

In selecting a subdivision in the angular coordinate ω , it is desired that the resulting area elements be of approximately constant size and have comparable orthogonal dimensions in order that all areas of the cross section will contribute with equal weight to the summation. This will necessitate a separate subdivision for each ring. It is convenient to exploit the fact that there exists a twofold angular symmetry about

$$\omega = (2\theta + \pi)/2.$$

The angular limits in Eqs. (5), (10), (11), and (16) can thus be reduced to π and the resulting integrals multiplied by two. These considerations lead to the following stipulation for the finite increments in ω .

$$\omega_{n,m} = \theta - (\pi/2) + (n - \frac{1}{2})\pi/3m, \quad n = 1, 2, \dots, 3m. \quad (21)$$

For the finite grid established by Eqs. (20) and (21), the area elements are given by

$$r\delta\omega\delta r = (m - \frac{1}{2})(\pi/3m)[(1/m_R)R]^2, \\ m = 1, \dots, Km_R. \quad (22)$$

The integrals for $A_{i,i}$ and $A_{i,j}$ may now be replaced by finite area increment summations. For computational

TABLE I. Summary of optical path lengths in cell and sample.

Zone for computing		$l_c(m, n; 2\theta)$	$l_s(m, n; 2\theta)$	r varies between	ω varies between
d	$A_{s,s}$ & $A_{s,sc}$	$\alpha + \beta - \eta - \nu$	$\eta + \nu - \sigma$	$0 \leq r \leq R$	$\theta - \pi/2 \leq \omega \leq \theta + \pi/2$
a_1	$A_{c,c}$ & $A_{c,sc}$	$\alpha + \beta - \sigma$	0	$R \leq r \leq KR$	$\sin^{-1}R/r \leq \omega \leq \theta + \pi/2$
a_0	$A_{c,c}$ & $A_{c,sc}$	$\alpha + \beta - \sigma$	0	$\frac{R}{\cos\theta} \leq r \leq KR$	$\theta - \pi/2 \leq \omega \leq -\sin^{-1}R/r$
b_0	$A_{c,c}$ & $A_{c,sc}$	$\alpha + \beta - \sigma - 2\nu$	2ν	$R \leq r \leq \frac{R}{\cos\theta} < KR$	$2\theta - \pi + \sin^{-1}R/r \leq \omega \leq \sin^{-1}R/r$
b_1	$A_{c,c}$ & $A_{c,sc}$	$\alpha + \beta - \sigma - 2\nu$	2ν	$\frac{R}{\cos\theta} \leq r \leq KR$	$-\sin^{-1}R/r \leq \omega \leq \sin^{-1}R/r$
c	$A_{c,c}$ & $A_{c,sc}$	$\alpha + \beta - \sigma - 2\nu - 2\eta$	$2\nu + 2\eta$	$R \leq r \leq \frac{R}{\cos\theta} \leq KR$	$\theta - \pi/2 \leq \omega \leq 2\theta - \pi + \sin^{-1}R/r$

$\theta = \sin^{-1} \frac{s\lambda}{4\pi}$
 $r_m = \frac{(m - \frac{1}{2})}{m_R} R$
 $\omega_{n,m} = \theta - \pi/2 + \frac{(n - \frac{1}{2})}{3m} \pi$

$\alpha(m, n; 2\theta) = [K^2 R^2 - r_m^2 \sin^2 \omega_{n,m}]^{\frac{1}{2}}$
 $\beta(m, n; 2\theta) = [K^2 R^2 - r_m^2 \sin^2(\omega_{n,m} - 2\theta)]^{\frac{1}{2}}$
 $\nu(m, n; 2\theta) = [R^2 - r_m^2 \sin^2 \omega_{n,m}]^{\frac{1}{2}}$
 $\eta(m, n; 2\theta) = [R^2 - r_m^2 \sin^2(\omega_{n,m} - 2\theta)]^{\frac{1}{2}}$
 $\sigma(m, n; 2\theta) = 2r_m \sin(\omega_{n,m} - \theta) \sin\theta$

purpose it is convenient to regard these integrals as a function of the scattering angle 2θ , rather than as a function of s .

$$A_{s,s}(2\theta) = \frac{2}{3m_R^2} \sum_{m=1}^{m_R} \sum_{n=1}^{3m} \left(1 - \frac{1}{2m}\right) e^{-\mu_s l_s(m, n; 2\theta)} \quad (23)$$

$$A_{s,sc}(2\theta) = \frac{2}{3m_R^2} \sum_{m=1}^{m_R} \sum_{n=1}^{3m} \left(1 - \frac{1}{2m}\right) e^{-\mu_s l_s(m, n; 2\theta) - \mu_c l_c(m, n; 2\theta)} \quad (24)$$

$$A_{c,c}(2\theta) = \frac{2}{3(K^2 - 1)m_R^2} \sum_{m=m_R+1}^{Km_R} \sum_{n=1}^{3m} \left(1 - \frac{1}{2m}\right) e^{-\mu_c l_c(m, n; 2\theta)} \quad (25)$$

$$A_{c,sc}(2\theta) = \frac{2}{3(K^2 - 1)m_R^2} \sum_{m=m_R+1}^{Km_R} \sum_{n=1}^{3m} \left(1 - \frac{1}{2m}\right) e^{-\mu_c l_c(m, n; 2\theta) - \mu_s l_s(m, n; 2\theta)} \quad (26)$$

The geometrical evaluation of the optical path lengths in sample and cell is straightforward in the case of $A_{s,s}$ and $A_{s,sc}$. When scattering from the cell is considered, however, the annular area must be subdivided into three parts, illustrated in Fig. 2, wherein: (a) the optical path lies completely within the cell material; (b) the optical path has one segment within sample material; and (c) the optical path has two segments within the sample material. The values for the optical path lengths which enter into Eqs. (23) through (26) are summarized in Table I.

The problem of computing the cylindrical absorption

factors for cell and sample as outlined above was programmed for the Burroughs 220 digital computer. The routine is capable of evaluating the absorption factors as a function of scattering angle and the geometric and absorption constants of the cell and sample. The time required to compute the four absorption factors for a given scattering angle was approximately 5 minutes per value of s with an m_R of 15. In a test case, the program accurately evaluated eight of the absorption factors given by Ritter.²

The computer program will be made available to interested parties on request.