On Secondary Extinction

N. Kato

Department of Crystalline Materials Science, Faculty of Engineering, Nagoya University,
Chikusa-ku, Nagoya, Japan

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Dedicated to Professor Dr. G. Hildebrandt on his 60th Birthday

For the purpose of extinction correction in crystal analysis, the secondary extinction factor y is discussed in the light of the new approach developed by the present author. The mosaic crystal model is adopted. A comparison is made between the present theory and the conventional theory (CT) through functional analysis of y in general cases and numerical analysis in the special case of parallel slab crystals. The y values of CT are underestimated by about 4% and 30% at $y = 0.5$ and 0.15, respectively. For $y \gtrsim 0.7$, CT is practically correct.

1. Introduction

The present author has developed a "statistical dynamical theory" [1]–[6]. The diffraction phenomena in a wide range of crystal perfection from ideal crystals to ideally mosaic crystals can be understood by this new approach.

Although the theory intends to solve the extinction problems it is not very popular and the traditional approach is still widely used. One of the reasons is that the new theory includes unfamiliar concepts and has remained in a fundamental stage of development. It seems, therefore, worth while to demonstrate how the extinction factor y is to be calculated and to show the numerical difference between the results expected by the present theory (PT) and the conventional theory (CT) in some simple cases.

Only secondary extinction will be discussed because it is most seriously concerned in the practices of crystal analysis. For the same reason, the model of mosaic crystals is adopted although the present theory is more versatile. With this model, not only the general expression but the concrete expressions in a few special cases are presented for the "correlation length", which is a central quantity in the present extinction theory. In the course of arguments, also some well-known results in CT are reformulated and critically discussed. Finally, numerical examples of the differences of y in CT and PT are given in the case of parallelsided crystals.

2. The Correlation Length τ

In the present theory, the lattice phase factor, G, its correlation function $f(z)$, and the two kinds of correlation lengths (τ_1, τ_2) are important quantities. They are defined as follows;

$$G = \exp 2\pi i (\bar{\boldsymbol{g}} \cdot \boldsymbol{u}), \tag{1}$$

$$f(z) = \langle G(0) \cdot G^*(z) \rangle, \tag{2}$$

$$\tau_1 = \int_0^\infty f(z)\,\mathrm{d}z, \quad \tau_2 = \int_0^\infty \{f(z)\}^2\,\mathrm{d}z, \tag{3a, b}$$

where $\bar{\boldsymbol{g}}$ is the reflection vector of a (hypothetical) perfect crystal and $\boldsymbol{u}$ is the displacement of the lattice point from the position in the perfect state, therefore being a function of position. By taking $G(0)$ and $G(z)$ at A and B, respectively, $f(z)$ is defined by the ensemble average $\langle\ \rangle$ of their product, where z is the distance between A and B. Meanwhile, only the second order correlation is considered.

The general form of $f(z)$ is illustrated in Fig. 1, and can be represented by

$$f(z) = E^2 + (1 - \mathrm{E}^2)\, g(z), \tag{4}$$

where

$$E = \langle G \rangle \tag{5}$$

is called the "static Debye Waller factor" and $g(z)$ is referred to as the "intrinsic correlation function". In this paper, the integrability of $f(z)$ is assumed. In other words, E is assumed to be zero. In general, $f(z)$ should be replaced by $g(z)$.

The present theory is free in its formalism from a specific model of the lattice distortion. The model

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Reprint requests to Dr. N. Kato, Department of Crystalline Materials Science, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya/Japan.

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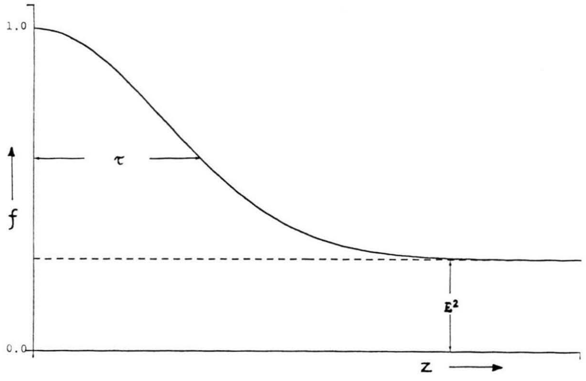

Fig. 1. Correlation function $f(z)$. See (4).

dependence comes out through the expression of τ which is obtained only by giving the model of lattice distortion. Since this paper aims mainly at comparing the present approach with the conventional one, we shall start from the model similar to mosaic crystals.

2.1. The Model

The model is enunciated in the next paragraph. The basic ideas have been explained in Appendix A of a previous paper [2]. The "combination model" in it is the one discussed in this section.

If one takes a position A in the crystal, the surrounding region satisfies the Bragg condition with a deviation angle φ from the exact one. The probability is denoted by $\Phi(\varphi)$. When X-rays propagate through A in the specific direction $\vec{s}_0$ (or $\vec{s}_g$) by a distance l, the crystal no longer satisfies the Bragg condition with the same deviation angle. Outside this distance, the lattice phase is assumed to be random with respect to the lattice phase at A. The probabilistic distribution of the distance is denoted by $L(l)$, l being called "coherent length". Since the original position A will be on the half way of the total coherent length in the sense of probability, the total coherent length or the crystallite size must be statistically

$$S = 2\langle l\rangle = 2\int_0^\infty l L(l)\,\mathrm{d}l\,. \tag{6}$$

The model implies that the crystal consists of crystallites with a misorientation larger than the angular spread of the diffraction due to each crystallite.

2.2. Calculation of τ's

The procedures of calculating τ are also explained in the Appendix of the paper mentioned above [2]. Here, they are extended further for the later discussion. We shall introduce the Fourier transform of $f(z)$,

$$Z(\xi) = \sqrt{\frac{2}{\pi}}\int_{-\infty}^{+\infty}\Phi(\varphi)\,\mathrm{d}\varphi\int_0^\infty L(l)\,\frac{\sin(\xi+\alpha\varphi)\,l}{\xi+\alpha\varphi}\,\mathrm{d}l\,, \tag{7}$$

where

$$\alpha = 2\pi(\sin 2\theta_\mathrm{B}/\lambda)\,. \tag{8}$$

Then, one can calculate τ's by use of Parseval's theorem in the Fourier transform,as follows:

$$\tau_1 = \sqrt{\frac{\pi}{2}}\,Z(0)\,, \tag{9a}$$

and,

$$\tau_2 = \tfrac{1}{2}\int_{-\infty}^{+\infty}\{Z(\xi)\}^2\,\mathrm{d}\xi\,. \tag{9b}$$

It is easily seen that $Z(\alpha\varphi)$ is the convolution of $\Phi(\varphi)$ and the function

$$C(\eta) = \int_0^\infty l L(l)\,[\sin\eta l/\eta l]\,\mathrm{d}l\,, \tag{10}$$

where

$$\eta = \alpha\varphi\,. \tag{11}$$

Denoting the Fourier transforms of $\Phi(\eta/\alpha)$ and $C(\eta)$ as $\Phi(z)$ and $C(z)$, respectively, one can write

$$f(z) = \Phi(z)\,C(z)\,. \tag{12}$$

With this relation, τ_2 can be rewritten in the form

$$\tau_2 = \tfrac{1}{2}\int_{-\infty}^{+\infty}\{\Phi(z)\,C(z)\}^2\,\mathrm{d}z\,. \tag{13}$$

When the functional forms of $\Phi(\varphi)$ and $L(l)$ are simple, τ_1 and τ_2 can be expressed in terms of the parameters characterizing $\Phi(\varphi)$ and $L(l)$. Some examples are listed in Table 1.

2.3. The Properties of the sinc Transformation

The function $\sin x/x$ is often called sinc function, so that here the relation (10) is called sinc transformation. It is worth knowing the general properties of $C(\eta)$ for characterising τ_1 and τ_2 because, often, the analytical expression of $C(\eta)$ is difficult to obtain directly from $L(l)$.

Table 1. The functions of $\Phi(\varphi)$ and $L(l)$ are normalized in the range $(-\infty, +\infty)$ and $(0, \infty)$ respectively. The functions $C(\eta)$ satisfy the require-ments of a, b, and c of 1.3 in the text. $x = \bar{\alpha}/g$, where $\bar{\alpha} = (\sin 2\theta_{\mathrm{B}}/\lambda)\bar{l}$.

Case	$\Phi(\varphi)$	$L(l)$	$C(\eta)$	$\tau_1/\bar{l}$	$\tau_2/\bar{l}$
a	G	$\bar{G}_1$	$\tilde{G}$	$(1+2x^2)^{-1/2}$	$(1/\sqrt{2})(1+2x^2)^{-1/2}$
b	L	$\bar{E}$	$\tilde{L}$	$(1+x)^{-1}$	$(1/2)(1+x)^{-1}$
c	L	$\bar{E}_1$	L_2	$(1+\frac{1}{4}x)/(1+\frac{1}{2}x)^2$	$(9/16)(1+\frac{2}{3}x)/(1+\frac{1}{2}x)^3$

$G = \sqrt{2}g \cdot \exp\{-2\pi g^2 \varphi^2\}$ $\quad \bar{G}_1 = \frac{\pi}{2}(l/\bar{l}^2)\exp\left\{-\frac{\pi}{4}(l/\bar{l})^2\right\}$ $\quad \tilde{G} = \bar{l}\exp\left\{-\frac{1}{\pi}(\bar{l}\eta)^2\right\}$

$L = 2g/(1+(2\pi g\varphi)^2)$ $\quad \bar{E} = (1/\bar{l})\exp\{-(l/\bar{l})\}$ $\quad \tilde{L} = \bar{l}/(1+(\bar{l}\eta)^2)$

$\bar{E}_1 = (2/\bar{l})^2 l \exp\{-(2l/\bar{l})\}$ $\quad \tilde{L}_2 = \bar{l}/(1+((\frac{1}{2}\bar{l}\eta)^2)^2$

a) When the distribution $L(l)$ is appreciable only for a large l, the following asymptotic form is valid:

$$\sin\eta l/\eta l \to \pi\,\delta(\eta)/l\,. \tag{10a}$$

Then, owing to the normalization of $L(l)$ the integration of l gives

$$C(\eta) \to \pi\,\delta(\eta)\,. \tag{10b}$$

b) When η is sufficiently small,

$$\sin\eta l/\eta l \to 1 \tag{11a}$$

irrespective of l, so that

$$C(\eta) \to \langle l\rangle\,. \tag{11b}$$

c) Since

$$\int_{-\infty}^{+\infty} \frac{\sin x}{x}\,\mathrm{d}x = \pi\,, \tag{12a}$$

$$\int_{-\infty}^{+\infty} C(\eta)\,\mathrm{d}\eta = \pi \tag{12b}$$

irrespective of the details of the normalised $L(l)$ or $\langle l\rangle$.

When an analytical form $C(\eta)$ is postulated instead of $L(l)$, the properties mentioned above serve as the guide lines of the postulate. For example, if one postulates a Gaussian form or a Lorentzian form for $C(\eta)$, one must take

$$C(\eta) = \langle l\rangle \exp - \frac{1}{\pi}(\langle l\rangle\eta)^2 \tag{13a}$$

$$= \langle l\rangle/[1+(\langle l\rangle\eta)^2]\,. \tag{13b}$$

In this connection it is worthwhile to consider the meaning of the approximate treatments which are often used in the conventional secondary extinction theory (for example Becker and Coppens [7]). They postulated ad hoc

$$D(\eta) = \int_0^\infty \left(\frac{\sin\eta l}{\eta l}\right)^2 l L(l)\,\mathrm{d}l \tag{14a}$$

$$\sim \langle l\rangle \exp\left\{-\frac{1}{\pi}(\eta\langle l\rangle)^2\right\} \tag{14b}$$

$$\sim \frac{4}{3}\langle l\rangle \bigg/ \left[1+\left(\frac{4}{3}\eta\langle l\rangle\right)^2\right]. \tag{14c}$$

The form (14b) can be justified by the same arguments described above for $C(\eta)$. In this case, the integral

$$\int_{-\infty}^{+\infty} \left(\frac{\sin x}{x}\right)^2 \mathrm{d}x = \pi \tag{15}$$

should be used instead of (12a). One of the reasons of the success of the conventional extinction theory lies in the coincidence of the integral results of (12a) and (15). One notices, however, that in the Lorentzian case the scaling factor 4/3 is excessive.

3. Integrated Intensity

3.1. *General Remarks*

Under the conditions, $E = 0$ and $\tau \ll \Lambda$ (extinction distance*, the following energy transfer equations (ETE) are valid:

$$\partial I_0/\partial s_0 = -(\mu_0+\sigma)\,I_0 + \sigma I_{\mathrm{g}}\,, \tag{16a}$$

$$\partial I_{\mathrm{g}}/\partial s_{\mathrm{g}} = -(\mu_0+\sigma)\,I_{\mathrm{g}} + \sigma I_0\,, \tag{16b}$$

where s_0 and s_{g} are the coordinates along the direction of 0 and G beams, respectively, μ_0 is the photoelectric linear absorption coefficient, and the coupling constant is given by

$$\sigma = 2\,\tau_2/\Lambda^2\,. \tag{17}$$

Equations (16) are similar to the ETE's in CT. The physical implications, however, are different. In PT σ is constant. Equations (16) hold for the amounts of total energy carried by the 0 and G beams, respectively. In CT, the coefficient σ is re-

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* $\Lambda^{-1} = |\varkappa_{\mathrm{g}}| = (\lambda/v)(e^2/mc^2)\,|F_{\mathrm{g}}|\,C$ and $Q = (\lambda/\sin 2\theta_B)/\Lambda^2$ [v: The volume of unit cell; C: Polarization factor].

garded as a function of the glancing angle φ of the incident beam, namely

$$\sigma(\varphi) = Q\Phi(\varphi) * (\alpha/\pi) D(\alpha\varphi) = Q(\alpha/\pi) W(\varphi), \qquad (18)$$

where $D(\eta)$ is defined by (14a) and $*$ implies the convolutional integral. $(\alpha/\pi) W$ is a normalised distribution function.

The integrated intensity is defined by

$$R_g = \iint I_g \, \mathrm{d}X_E \, \mathrm{d}X_A \qquad (19\text{a})$$

in PT, whereas it is given by

$$R_g = \iint \mathrm{d}X_E \, \mathrm{d}X_A \int I_g(\varphi) \, \mathrm{d}\varphi \qquad (19\text{b})$$

in CT. Here, $\mathrm{d}X_E$ and $\mathrm{d}X_A$ are the surface elements perpendicular to the 0 and G directions, respectively, and the integrals are carried out over the entrance and exit surfaces. We assert that $\int \mathrm{d}\varphi$ is redundant.

3.2. A Special Example

In order to see the structure of PT in comparison with CT, the symmetrical Laue case of parallel sided crystals is considered. The integrated intensity is given by

$$R_g = (Q/\sigma) \sinh \sigma T \cdot \exp\{-(\mu_0 + \sigma) T\}, \qquad (20\text{a})$$

where $T = T_0/\cos\theta_B$, T_0 being the crystal thickness. A more general expression is given by (16) in [6].

The corresponding expression of CT is

$$R_g = \int_{-\infty}^{+\infty} \sinh \sigma T \cdot \exp\{-(\mu_0 + \sigma) T \, \mathrm{d}\varphi\}, \qquad (20\text{b})$$

where (18) is assumed for σ.

3.3. The Functional Form $\eta = R_g/QT$ of Extinction Factor

The expression (20a) is very straightforward. y can be written in the form

$$y = f_p(\Sigma_2, M), \qquad (21\text{a})$$

where

$$\Sigma_2 = 2(\tau_2/\Lambda)(T/\Lambda), \quad M = \mu_0 T. \qquad (22\text{a, b})$$

The expression (21a), in fact, is applicable also to the more general cases, where R_g is given by (19a), provided that the crystal shape is specified by a single parameter. For example, for cylinders or spheres it is sufficient to replace T by the radius R.

The expression (20b) is rather complex, in general. y must have the form

$$y = \mathscr{F}_c(\Sigma, M; W/W(0)), \qquad (21\text{b})$$

where

$$\Sigma = 2[W(0)/\Lambda](T/\Lambda) \qquad (22\text{c})$$

and $\mathscr{F}_c$ is a "functional" depending on the form of the function $W(\varphi)$. The expression (21b) can be simplified only when W is characterized by a single variable

$$w = g\varphi \qquad (23)$$

as in the case of a Gaussian or Lorentzian distribution. In this case, the integral of any function of $W(\varphi)/W(0)$ must be proportional to g^{-1}. Thus, it turns out that

$$y = (gQT)^{-1} f_c(\Sigma, M), \qquad (24)$$

where f_c is an ordinary function.

Furthermore, $(\alpha/\pi) W(\varphi)$ is a normalized function so that $(\alpha/\pi) W(0)/g$ must be a constant (K) irrespective of α and g. On the other hand, it is very reasonable to assume $D(\eta)$ to be the same as $C(\eta)$, because they have the same properties as discussed in Section 1.3. With this assumption and from (7) and (9a) one can see that $W(0) = \tau_1$ so that

$$(\alpha/\pi)\tau_1 = Kg. \qquad (25)$$

Thus, rewriting $K f_c/\Sigma$ as f_c, one can conclude that the extinction factor has the form

$$y = f_c(\Sigma_1, M), \qquad (26)$$

where

$$\Sigma_1 = 2(\tau_1/\Lambda)(T/\Lambda). \qquad (27)$$

Obviously, the functional forms of f_p and f_c are different. In the specific cases of (20a) and (20b), with the use of Gaussian distribution for $W(\varphi)$ they have the following forms, respectively:

$$\exp M \cdot f_p(x, M) = \sum_{n=1}^{\infty} \frac{1}{n!} (-2x)^{n-1}, \quad x = \Sigma_2, \qquad (28\text{a})$$

$$\exp M \cdot f_c(x, M) = \sum_{n=1}^{\infty} \frac{1}{\sqrt{n}\, n!} (-2x)^{n-1}, \quad x = \Sigma_1. \qquad (28\text{b})^*$$

The functions are drawn in Figure 2.

It is worth noting that the distribution $W(\varphi)$ is Gaussian if we assume both $\Phi(\varphi)$ and $C(\eta)$ to be

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* For numerical calculation for $\sum_1 \gtrsim 1$, the original form (20b) has to be used.

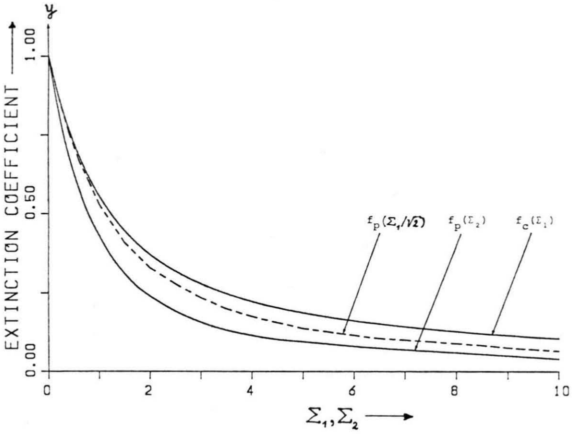

Fig. 2. Comparison of y in the conventional theory $[f_c(\Sigma_1)]$ and the present theory $[f_P(\Sigma_1/\sqrt{2})]$ in the parallel-sided slab crystals.

Gaussian (case a of Table 1). Then $\tau_1 = \sqrt{2}\tau_2$, so that $\Sigma_1 = \sqrt{2}\Sigma_2$. From the expressions (28a, b), PT and CT would give the same result up to the first power of x. The dotted line of Fig. 2 is $f_p(\Sigma_1/\sqrt{2})$, which should be compared with $f_c(\Sigma_1)$.

4. Discussion and Conclusions

The present theory is simpler and more versatile than the conventional theory. The theoretical framework is independent of the model of crystal perfection. Once the extinction function like (21a) has been obtained for a particular form of the crystal it can be used universally. The independent variables are Σ_2 and M, which characterize the crystal perfection and absorption, respectively.

The parameter Σ_2 is model-dependent through the correlation length τ_2. In this paper, for making comparison between CT and PT, τ_2 was calculated on the basis of the mosaic model. The general expression is given by (9b) in terms of the angular and size distributions of the blocks, $\Phi(\varphi)$ and $L(l)$. The explicit expressions for some particular cases are listed in Table 1.

Conventionally, instead of $L(l)$ the averaged intensity diffraction function of the blocks, $D(\eta)$ in the present notation, is introduced. Rigorously speaking, however, the averaged amplitude diffraction function of the blocks, $C(\eta)$, must be used. Nevertheless, one can admit that $D(\eta)$ is practically the same as $C(\eta)$. Using this conventional approach and assuming Gaussian distributions for $\Phi(\varphi)$ and $C(\alpha\varphi)$, one can see that $\tau_1 = \sqrt{2}\tau_2$ (case a of Table 1). In the parallel sided crystals, the results expected by PT and CT coincide up to the first power of Σ_2. The discrepancy, however, increases with increasing Σ_2. The relative difference is the order of 4% and 30% for the y-values 0.5 and 0.15, respectively.

The fact that τ_1 is propertional to τ_2, however, is accidental. As shown in the case c of Table 1, the proportionality of τ_1 and τ_2 is not valid in general. Moreover, sometimes the ad hoc assumption of using $D(\eta) = C(\eta)$ instead of $L(l)$ leads to a false conclusion. As shown in the case b of Table 1, one must take the $\bar{E}$ distribution for obtaining a Lorentzian form of $C(\eta)$. The $\bar{E}$ distribution is unrealistic in crystalline materials because it is maximum at $l = 0$.

Finally, a remark on the effects of primary extinction may be made. According to the present theory, the effects must be classified into two types. One appears due to the finiteness of E in the correlation function (see (4)), namely due to the overall perfection of the crystal. Then, the coherent component of the intensity plays a significant role. This effect can be put out of considerations in mosaic crystals because then E must be intrinsically zero.

Another effect will appear through the higher order correlation of the lattice phase factor, namely the local perfection of the crystal. The effect has been discussed in [6]. Then, the correlation length τ_2 must be appearently reduced and the reduction factor is represented as a power series of $(1/\Lambda)^2$.

This situation is intuitively expected by inspecting the expression (7) of this paper, where the kinematical theory is assumed within the domain of coherence so that the diffraction function $\{\sin \zeta l/\zeta\}$ is averaged over the coherent domains. When the coherent length $S = 2\langle l \rangle$ is comparable to Λ, ζ must be replaced by $[\zeta^2 + (1/\Lambda)^2]^{1/2}$ according to the dynamical theory. Although the fundamental justification is required through the approach of [6], this intuitive substitute is promising within the domain of the mosaic model.

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