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Expressing the extinction-free integral breadth

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Secondary extinction (SE) is inherently related to the pole density, P. The latter represents a crystalline volume fraction normalised to random distribution that contributes to reflection. In fact, any measured point inside the reflection range $2\Delta\theta$ is affected to a different extent by the SE due to variation of both pole density and energy distribution of the incident beam intensity, I_0. However, to evaluate a SE effect of the reflection as a whole, its integral intensity must account for pole density, $\overline{P}$, being dependent on integral breadth of reflection. Thus, the aim of the present study is to develop a technique for calculating the integral breadth of reflection using extinction free data of both its integral intensity and maximal intensity. The reformed data can be used for sensitive treatment of the SE effect in textures and powders including nanoscale materials as well.

Keywords: secondary extinction, integral breadth, textures, powders, microcrystalline, nanocrystallites.

INTRODUCTION

The effect of extinction is subject to extensive research in characterizing domain size and shape of real crystals in single-crystal diffractometry [1–4], while there is only little interest in conventional X-ray diffractometry, despite that extinction is an intrinsic property of textures. Knowing that secondary extinction effect on reflection profile distortion of textures is not justified, this compromises the correct assessment of the microstructure parameters. As a first step to adequate characterization of the microstructure, one needs a method for eliminating the extinction-induced profile distortion, since this distortion causes a respective reflection enlargement. Thus, the aim of the present study is to convert measured (extinction-affected) profile into a kinematical (extinction-free) one and thus to correctly assess the physical effect due to size-strain broadening controlled by integral breadth [5, 6]. In this context, by treating the SE problem we reconsidered and specified the behaviour of the coefficient *k,* empirically introduced earlier [7].

WHAT IS COEFFICIENT *k*?

Based on the relationship $k = (g/PI_0)(2\mu/S)$ between diffraction and extinction, we have found that the coefficient k is an irrational quantity [cm^{-3}] of the scattering space (Fig. 1). In the real space, $1/k$ is a crystalline volume [cm^3] covering those crystallites in the Bragg condition that do not contribute to an increase of the reflectivity and, hence, to the diffraction process. Just the ineffectiveness of this crystalline volume, $1/k$, weakens the level of interaction of the diffraction process by, PI_0, where P represents a crystalline volume fraction normalised to random distribution that contributes to reflection. By its very nature, the relationship between diffraction and extinction specifies the behaviour of the SE coefficients, k and g. We have specially proved that the constancy of k may exist only under *the same structural condition*, i.e. P = const., and proper variation of I_0 alone [8]. Let us analyse this problem.

To distinguish between the behaviour of k and g, we suppose a set of levels of interaction defined in particular. In this context, whereas the pole density P is held to be a constant, the incident beam intensity varies from level $I_{0,i}$ to level $I_{0,i*}$ caused by variation of the generator current from i to i*. Then the above relationship is rewritten as

$$k_i = (g_i/PI_{0,i})(2\mu/S), \quad (1a)$$

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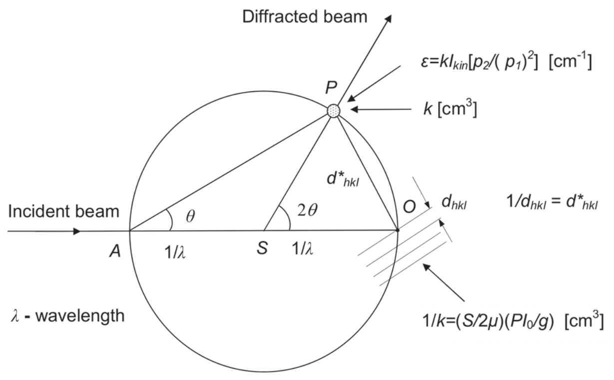

Fig. 1. Diffraction and extinction treated by means of scattering and real spaces. The scattering of X-rays 'operates' at the cross-section of the Evald's and projection spheres (P). The origin, O, of the real space is there, where the sample under study is situated, ε is the SE correction.

$$\begin{array}{lccc}
\mathrm{I}: & I_{kin,i};g_i;k_i & ----- & I_{0,i}=Ai(V-V_K)^n \\
 & k_i=k_{i*} & \updownarrow R_{i,i*} & i=2i* \\
\mathrm{II}: & I_{kin,i*};g_{i*};k_{i*} & ----- & I_{0,i*}=Ai*(V-V_K)^n \\
 & k_{i*}=k_{i**} & \updownarrow R_{i*,i**} & i*=2i** \\
\mathrm{III}: & I_{kin,i**};g_{i**};k_{i**} & ----- & I_{0,i**}=Ai**(V-V_K)^n \\
 & k_{i**}=k_{i***} & \updownarrow R_{i**,i***} & i**=2i*** \\
\mathrm{IV}: & I_{kin,i***};g_{i***};k_{i***} & ----- & I_{0,i***}=Ai***(V-V_K)^n
\end{array}$$

Fig. 2. Relationship between four levels of interaction defined by variation of the incident beam intensity from $I_{0,i}$ to $I_{0,i***}$. In the equations A is a constant, V_K is the critical excitation potential of the $K\alpha$ radiation, and n = 1.5 [6].

$$k_{i*} = (g_{i*}/PI_{0,i*})(2\mu/S), \tag{1b}$$

where it is accounted that g_i and g_{i*} are proportional to $I_{0,i}$ and $I_{0,i*}$, respectively, i.e.

$$(g_i/I_{0,i})/(g_{i*}/I_{0,i*}) = 1 \tag{2}$$

Dividing (1a) and (1b) by considering (2) yields

$$k_i = k_{i*}, \tag{3}$$

where k is an invariable independent of the level of interaction of the diffraction process. Therefore, any variation of $I_{0,i}$ does not change the value of k coefficient under P=const. and otherwise equal condition. To reveal the straight proportional dependence of g on (PI_0), one has to rewrite the same relationship between diffraction and extinction as

$$g = (PI_0)(kS/2\mu). \tag{4}$$

Evidently, at lower limiting values of either ($PI_0\to 0$) it is clear that only in the case of absent diffraction ($I_{kin}\to 0$), there is no extinction ($g\to 0$) (4). This is in accordance with Matheson's statement that 'extinction is only zero, in absolute sense, when diffracted power is identically zero' [9].

APPARENT EXTINCTION

One may show an apparent SE effect, i.e. a visible effect such as it is. To this end, a data acquisition technique called 'compensative condition' is elaborated. This condition requires XRD measurements of a reflection to be carried out by using a four-step design presented in Figure 2. To compensate a stepwise decrease of $I_{0,i}$ intensity controlled by the generator current density $i=i,i*,i**,i***$, the time $\tau=\tau,\tau*,\tau**,\tau***$ for data collection is step by step increased to give the same product of τ per a scanned step and current density i:

$$\tau i=\tau*i*=\tau**i**=\tau***i***=const. \tag{5}$$

Profiles were measured by a step scanning mode with conventional X-ray diffractometer using CuKα radiation separated by nickel filter. Figure 3 illustrates the apparent extinction effect. An extinction-free condition means that diffraction would be kinematical and then the profiles should overlap each

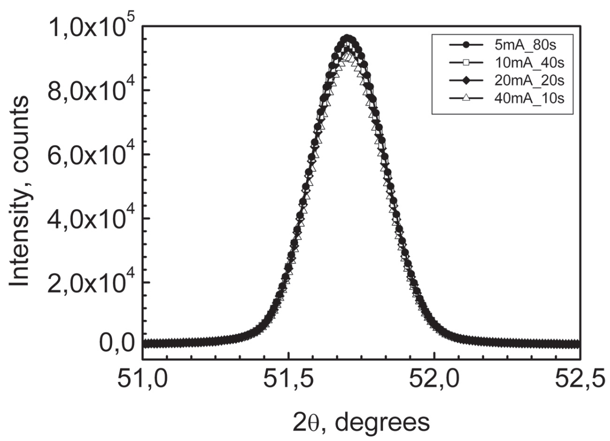

Fig. 3. A four-step measurement procedure applied to 200 reflections of Ni sample illustrates the apparent extinction effects such as they are.

other, i.e. they would be indistinguishable. Thus, for any of the neighbour levels of interaction, R_{i,i^*} ratios of the following type are valid:

$$I_{0,i}/I_{0,i^*} = I_{kin,i}/I_{kin,i^*} = g_i/g_{i^*} = i/i^* = R_{i,i^*} \quad \text{(6a,b,c,d)}$$

where,

$$I_{kin,i}/I_{kin,i^*} = R_{i,i^*} = \left\{\mu I_{m,i} / \left[\mu - k\ I_{m,i}\left(p_2/p_1^2\right)\right]\right\} / \left\{\mu I_{m,i^*} / \left[\mu - k\ I_{m,i^*}\left(p_2/p_1^2\right)\right]\right\} \quad \text{(7a,b,c,d).}$$

Here, (a, b, c, d) denotes equations corresponding to different combinations. Combining the ratios, R_{i,i^*}=$R_{i^{**},i^{***}}$, R_{i,i^*}=$R_{i^*,i^{**}}$, $R_{i,i^{**}}$=$R_{i^*,i^{***}}$, $R_{i^*,i^{**}}$=$R_{i^{**},i^{***}}$ among themselves and then solving them for k=const., i.e. k^s=k_i=k_{i^*}=$k_{i^{**}}$=$k_{i^{***}}$ and k^{max}=k_i=k_{i^*}=$k_{i^{**}}$=$k_{i^{***}}$ yield expressions of the type:

$$k^s = \frac{\left[\mu\left(I^s_{m,i^*} I^s_{m,i^{**}} - I^s_{m,i} I^s_{m,i^{***}}\right)\right]}{\left[I^s_{m,i^*} I^s_{m,i^{**}}\left(I^s_{m,i} + I^s_{m,i^{***}}\right) - I^s_{m,i} I^s_{m,i^{***}}\left(I^s_{m,i^*} + I^s_{m,i^{**}}\right)\right]\left(p_2/p_1^2\right)} \quad \text{(8a,b,c,d)}$$

$$k^{\max} = \frac{\left[\mu\left(I^{\max}_{m,i^*} I^{\max}_{m,i^{**}} - I^{\max}_{m,i} I^{\max}_{m,i^{***}}\right)\right]}{\left[I^{\max}_{m,i^*} I^{\max}_{m,i^{**}}\left(I^{\max}_{m,i} + I^{\max}_{m,i^{***}}\right) - I^{\max}_{m,i} I^{\max}_{m,i^{***}}\left(I^{\max}_{m,i^*} + I^{\max}_{m,i^{**}}\right)\right]\left(p_2/p_1^2\right)} \quad \text{(9a,b,c,d)}$$

These coefficients are used for calculation of kinematical intensities and thus to correctly assess the physical effect due to size-strain broadening defined accordingly by integral intensity $I^s_{kin,i}$ [rad] and maximal intensity ($I^{\max}_{kin,i}$) of reflection, both affected differently by SE:

$$I^s_{kin,i} = \left\{\mu I^s_{m,i} / \left[\mu - k^s I^s_{m,i}\left(p_2/p_1^2\right)\right]\right\} \quad \text{(10a,b,c,d)}$$

$$I^{\max}_{kin,i} = \left\{\mu I^{\max}_{m,i} / \left[\mu - k^{\max} I^{\max}_{m,i}\left(p_2/p_1^2\right)\right]\right\} \quad \text{(11a,b,c,d)}$$

The latter two equations are used to express extinction free integral breadth:

$$B_i = I^s_{kin,i} / I^{\max}_{kin,i} \quad \text{(12a,b,c,d)}$$

To illustrate the relationship between k, $1/k$, and P, it may be instructive to use a heuristic device [11]. Heuristic refers to experience-based techniques for problem solving, learning, or discovery that find a solution, which is not guaranteed to be optimal or perfect, but sufficient for immediate goals. In this context, Figures 4a, 4b and 4c represent the behaviour of k^s and k^{max} as well as $1/k^s$ and $1/k^{max}$ of a sharp texture (Ni38) and powders (both microstructured and nanocrystalline CeO_2). We have shown that de-

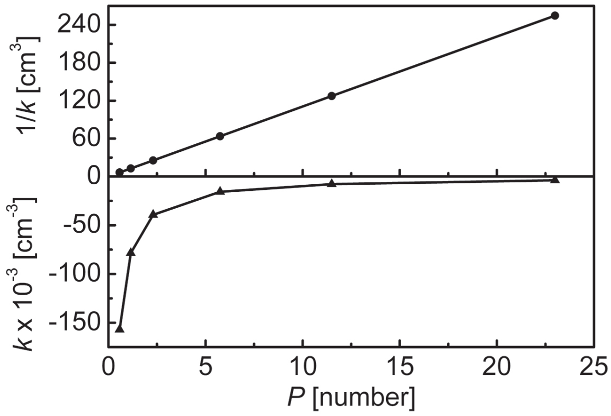

Fig. 4a. A heuristic device used to illustrate the relationship between k, $1/k$, and P. Highly textured Ni: B = 0.2413 [rad].

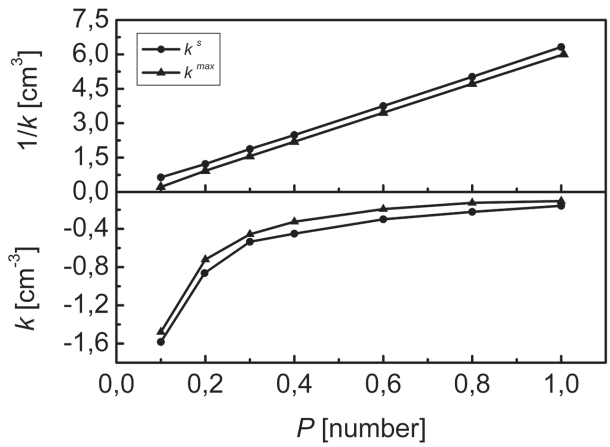

Fig. 4b. A heuristic device used to illustrate the relationship between k, $1/k$, and P. Nanosized CeO_2 : B = 1.1322 [rad].

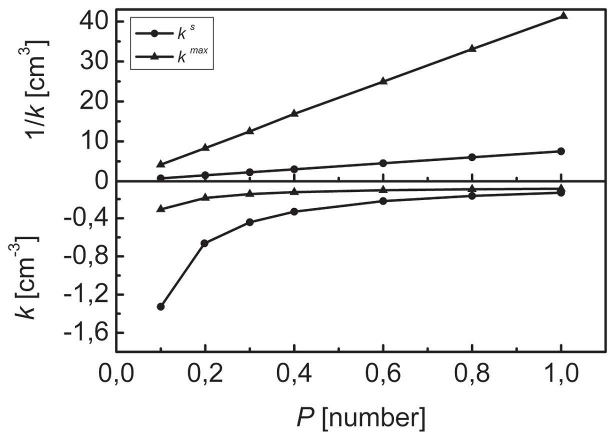

Fig. 4c. A heuristic device used to illustrate the relationship between k, $1/k$, and P. Microstructured CeO_2 sample: B = 0.1806 [rad].

pending on P ($0 < P < \infty$), k and $1/k$ vary in different ways. Whereas the coefficient k reaches to its limits ($-\infty < k < 0$) asymptotically, its reciprocal $1/k$ is straight proportional to P in the whole interval ($0 < 1/k < \infty$). These curves demonstrate how the coefficients k and $1/k$ depend on microstructure (crystalline size and strain) in terms of P. In particular, the behaviour of the coefficients k^s and k^{max} proves complete homogeneity of the nanosized sample. However, in case of microstructured sample CeO_2, the behaviour of $1/k^{max}$ exhibits a nearly defect-free structure.

CONCLUDING REMARKS

1. Under pole density P = const., the SE coefficient k is an irrational constant corresponding to the scattering space.

2. In the real space, $1/k$ defines crystallite volume in the Bragg condition that does not contribute to an increase of reflectivity.

3. Based on the constancy of k, a reformed methodology to observe, estimate, and nullify the SE effect is elaborated.

4. The main advantage of this methodology is that it allows for the capability of internal experimental checks revealing simply the real ability of the XRD apparatus to supply precise and accurate data.

5. The accuracy can only be achieved by care in experiment design and experiment realisation.

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ОПРЕДЕЛЯНЕ НА СВОБОДНА ОТ ЕКСТИНКЦИЯ ИНТЕГРАЛНА ШИРИНА

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(Резюме)

Вторичната екстинкция (ВЕ) е неотделимо свързана с полюсната плътност, P. Последната представлява нормирана в кратност на хаотично разпределение обемна фракция на кристалити, която дава приноси към рентгеново отражение. В действителност, всяка измерена точка вътре в областта $2\Delta\theta$ на рентгеновото отражение е въздействана в различна степен от ВЕ, дължаща се на двете: полюсната плътност и разпределението на енергията (интензитета) на падащия сноп рентгенови лъчи, I_0. Обаче, за да бъде оценен ефекта на ВЕ върху рентгеновото отражение като цяло, неговия интегрален интензитет трябва да отчита полюсна плътност, $\overline{P}$, която е зависима от интегралната ширина на рентгеновото отражение. Така дефинирана, целта на настоящето изследване е да се развие техника за изчисляване на интегралната ширина, използвайки свободни от екстинкция данни на двата му параметъра: интегрален интензитет и максимален интензитет. Реформираните данни могат да бъдат използвани за чувствително третиране на ефекта на ВЕ в текстури и прахове, включвайки нано-размерни материали също така.