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The theory of the line profile based on the absorption of X-ray diffraction and its experimental demonstration

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We have studied the theory of the X-ray diffraction (XRD) absorption peak profile (Liu, K. et al., Adv X-ray Anal, 2010, 54, 17-23) in detail by further theoretical derivation and by verification of the experimental line profile of a standard sample. It was obtained that the deviation between theory and experiment is less than 9% for the standard samples, by ignoring the line profiles in the range of diffraction angle less than 60°, for which the instrumental broadening could not be ignored. And the theoretical formula between FWHM and the Bragg angle 2θ was derived which can be called as the ARF. The results show that the Caglioti's relations should be replaced by the formula derived in this work.
Keywords: XRD, absorption line profile, FWHM, Caglioti's relation.

Проведено детальное исследование профиля пика поглощения при рентгеновской дифракции (Liu, K. et al., *Adv X-ray Anal*, **54**, 17, 2010) путем дальнейшего развития теории и сравнения с экспериментальным профилем линии стандартного образца. Полученное расхождение между теорией и экспериментом для стандартных образцов не превышало 9%, если пренебречь профилем линий в диапазоне углов дифракции меньше 60°, для которых необходимо учитывать приборное уширение. Выведена теоретическая формула, связывающая полную ширину на уровне половинной амплитуды и брэгговским углом 2θ, которую можно назвать функцией разрешения поглощения. Результаты показывают, что соотношения Кальоти должны быть заменены формулами, полученными в настоящей работе.

Теорія профілю лінії піку поглинання при дифракції Х-променів та її експериментальна демонстрація. *Лю Кецзя, Сюе Інь, Чень Кунь*
Проведено детальне дослідження профілю піку поглинання при дифракції Х-променів (Liu, K. et al., *Adv X-ray Anal*, **54,** 17, 2010) шляхом подальшого розвитку теорії та співставлення з експериментальним профілем лінії стандартного зразка. Отримане розходження між теорією та експериментом для стандартних зразків не перевищувало 9%, якщо знехтувати профілями ліній в діапазоні кутів дифракції менше 60°, для яких треба враховувати уширення, пов'язане з приладом. Виведено теоретичну формулу, що пов'язує повну ширину на рівні половини максимуму та брегівським кутом 2θ , яку можна назвати функцією розділення поглинання. Результати показують, що співвідношення Кальоті необхідно замінити формулами, отриманими в цій роботі.

1. Introduction

XRD line profiles provide lots of information of a crystalline sample. It is well known that, the intensity line can be calculated by the intensity theory and the interplanar spacing, d, can be calculated via the Bragg's equation. However, the line profiles, or the line shapes, cannot be analysised by any theory even for an ideal case. This is probably due to the XRD theory that the XRD line profiles of an ideal sample, collected on an ideal instrument, does not have a defined shape, but the interference function obtained by the grating , i.e., the intensity line would has an infinitely small angle distribution and very strong intensity at exact Bragg angle.

In contrast, there is no experimental evidence showing the interference function line profile. In other words, all observed diffraction peaks have the non-zero width; for common XRD instruments, an observed peak usually has the width of 0.1 degree in full width at half maximum (FWHM). To the author's knowledge, the observed interference function-like peak has not been reported.

In the real cases, the XRD line profiles will be broadened by the sample conditions and imperfect experiment. These conditions can be the imperfection of a crystalline sample, such as the point imperfections, dislocations in the crystals and its small size. As we all known, the imperfectly designed diffractometer (the light source, optical instruments and optical path conditions) is another source for XRD line broadening. However, all imperfections can be eliminated in theory; therefore, the XRD ideal line profile would have been observed. We have proposed [1, 2] that, at least, one of the"hidden effects"may prevent any XRD line profile forms in the shape of a interference function in reality even in the ideal case, and which is the absorption of the sample.

Therefore, a theory of the absorption line profile (ALP) is proposed, in our previous papers, that is, the LP of the XRD is different from that of the grating, and a new formula of the LP is obtained, and a few experimental demonstrations were given.

In paper is arranged bellow, first, one review the main results of the ALP, and then give the demonstration of line profiles by comparing the 24 peaks of a standard sample (LaB_6) with the calculated one in the following section. In Sec.3 a new Instrument Resolution Function (IRF) derived by the ALP is given, which gives the variation of the Full width at Half Maximum (FWHM) vs diffraction angle (2θ). And this relationship is named as the Resolution function of the absorption (RFA) in this paper, and the comparison between calculated and the experiment of the sample is also performed. It hopes that the new IRF should replace the Cagliotti's relations [3] which is a semi-empire formula proposed more than 50 years ago.

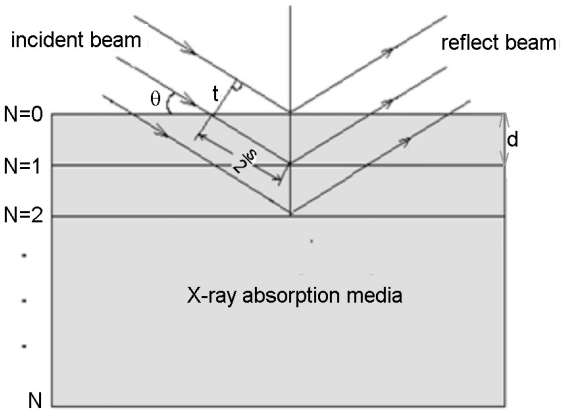

Fig. 1. Schematic diagram of X-ray reflection by crystalline planes

2. Brief review for the derivation of the absorption line profiles

In a powder XRD diffraction analysis, the path length of light beams of different depth of crystal face reflected propagation in the sample medium is different (Fig.1) so the wave amplitude attenuation is also different. The diffraction beams are the superposition of damped waves, rather than the non-absorption case of the grating interference. We obtain the diffraction intensity with the absorption considered [2]

$$I = A_0 A_0^* = \\ = I_0 \frac{1 + e^{-2\sqrt{\mu s}(N+1)} \cos[(N+1)\phi]}{1 + e^{-2\sqrt{\mu s}(N+1)} - 1 + e^{-\sqrt{\mu s}} \cos(\phi)} \quad (1)$$

Where N is the total number of the layers,

$$\phi = 2\pi \frac{\Delta l}{\lambda} = 2\pi \frac{2d \sin\theta}{\lambda},$$

Δl is optical path difference, μ is the absorption of a sample, s is the path difference between two nearby X-ray beams which immerged in the material, one can calculate s (Figure 1) by d as $s = 2d / \sin\theta$, where θ is the Bragg's angle, d is the interplanar spacing and λ is the wave length. One can verify that by setting μ=0, Equation (1) will be the interference function. Therefore, Equation (1) is a more general intensity function than the interference function.

When the grain in the sample is big so that $N \to \infty$, then Equation (1) can be simplified as

$$I = I_0 \frac{1}{1 + e^{-2\sqrt{\mu s}(N+1)} - 2e^{-\sqrt{\mu s}} \cos(\phi)} \quad (2)$$

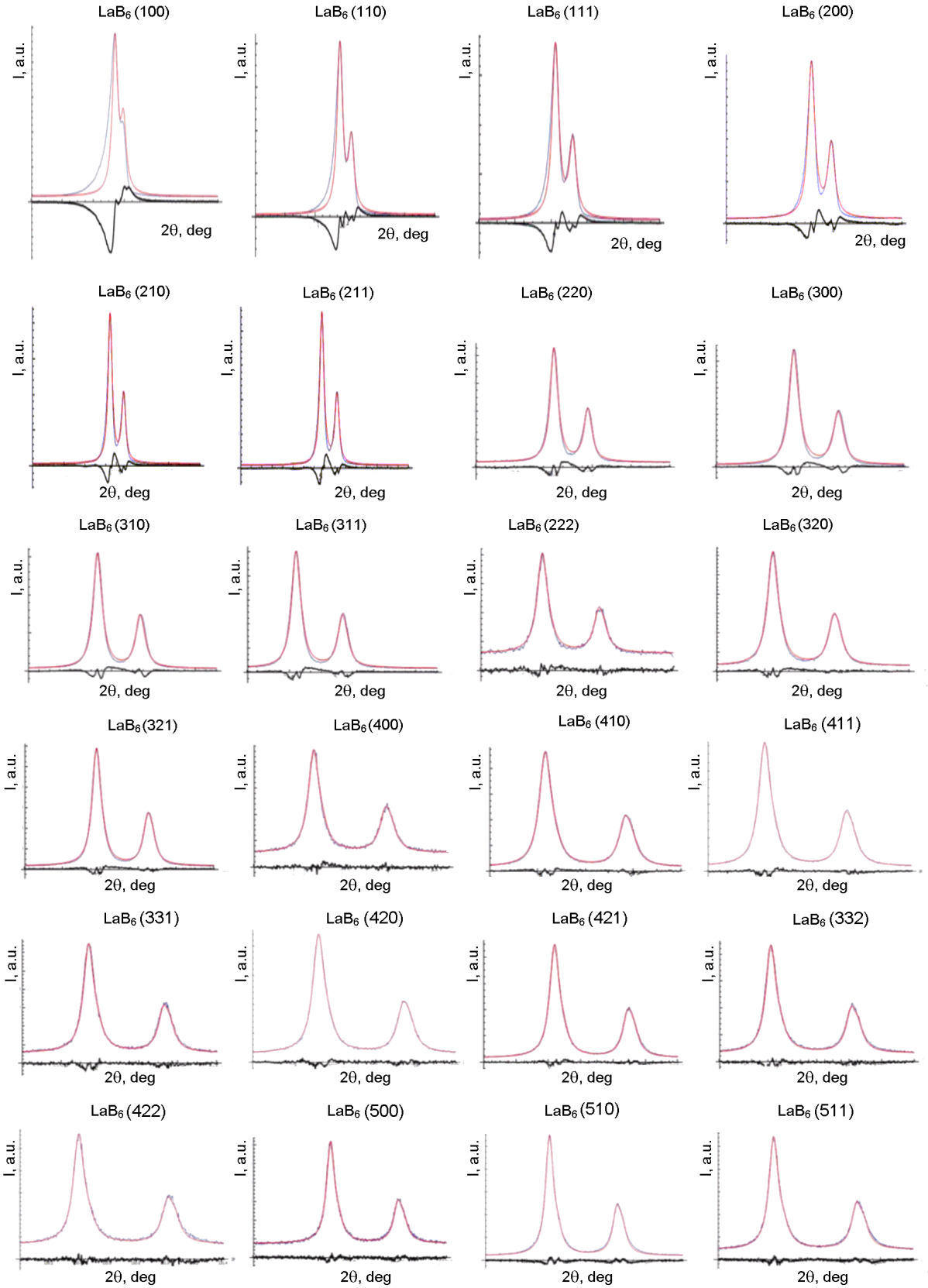

Fig. 2. X-ray diffraction line-profiles of the experiment (blue) and the theoretical (red) for the standard sample SRM660a LaB_6.

Table 1. Relative intensities I_0 (areas), wavelengths λ for representing the Cu $K\alpha$ spectrum by four Lorentzians

Emission line	λ (Å)	Relative I_0
$K\alpha$1a	1.540591	1
$K\alpha$1b	1.541064	0.1289
$K\alpha$2a	1.54436	0.3902
$K\alpha$2b	1.544686	0.1207

Equation (2) was verified by some experimental results for a few elemental crystals of individual diffraction angle line profiles [1-2]. It was given a whole range of the demonstration systematically by the LaB_6.

It is assumed that the absorption of a sample is the main reason of the formation of XRD line profiles, however, in the following quantitative calculation, other factors that can cause the peak broadening should also be considered, but not be discussed in detail in this paper. In order to do this assume that the absorption is the main case so that other effects can be account in to a single coefficient called the effective absorption coefficient express by μ_{eff}, which will replace – μ_l in Equation (2) in the following sections.

3. Experimental verification of the LP for LaB_6 in the whole range profiles

The LP of NIST standard sample of lanthanum hexaboride(LaB_6), was obtained by diffractameter the 24 full spectrum line profiles can be seen in Fig. 2. Experimental diffraction profiles of the diluted LaB_6 samples were collected with a conventional powder X-ray diffractometer (Pananytical X'PertPro MPD) with a Cu $K\alpha$ radiation tube as the X-ray source and a curved graphite monochromator on the diffracted-beam side. The voltage of 40kV and current of 40mA was adopted; a receiving slit of 0.15 mm width, and 1° -open divergence and scattering slits were used; the scanning speed was 1° /s and the step size was 0.03283°. However, the theory was calculated with the fitting effective absorption coefficient selection μ_{eff} and four [4] wavelengths of Cu $K\alpha$ target spectral line which can be given in Table 1.

Fig. 2 shows that peak curves are blue, the theoretical curves are red by using Equation (2), and the difference between theory and experiment for black peak curve is to give error curve of theory.

The effective absorption coefficient μ_{eff} obtains from experimental verification is 140 cm^{-1}, however, line absorption coefficient μ_l given in reference is 1099 cm^{-1} [5], the difference between them will not be discussed in the paper. The theoretical value is consistent with the experimental from the entire distribution range, the seventh peak to twenty-fourth peak error consistently less than 8%, but the first six peak fitting error is greater than 10%, which we believe that this is mainly due to instrumental broadening caused by the measurement error of the instrument itself. The error of small angle peaks and small angle lateral is large that should be caused by the plate specimen. However, while the large angle (2θ >60°) diffraction peaks is only related to the sample absorption, the flat sample error (i.e. instrumental broadening) will be negligible.

Fig. 2 shows that the FWHM of each peak is different with the diffraction angle from 20° to 160°, the width range of the FWHM is from 0.068° to 0.22° by calculating accordingly. The difference between the experiment with the calculation is also shown in the figures (in black), the maximum difference is less than 9% within large angle (2θ>60°) peak. Therefore, the theoretical prediction is in excellent agreement with the experimental results.

In contrast, both the Gauss fitting function and Lorentz fitting function which need 24 different parameters for peak fitting to peak shape simulate is only consistent with the shape of the curve, not refer to the nature of peak shape. The above theoretical peak only needs one peak shape parameter within the wide-angle range which can reflect the essence of the peak width due to sample absorption peak.

The above results illustrate the main formation of line profiles peak that caused by instrumental broadening should be in fact negligible, especially within large angles. The conclusion was that the absorption is the main reason of the formation of line profiles

4. The derivation of absorption resolution function(ARF)

The above peaks have been proved absorption peak can be used to quantitatively describe the line profiles. In this section, the line peaks will be further verified. The quantitative relationship between the Bragg angle 2θ and FWHM which represented the characteristics of peaks will be calculated, and this relationship will be verified on the basis of experiments.

Firstly, the derivation Δθ between FWHM and 2θ will be considered. By setting θ_B as Bragg angle, which is corresponding to the peak. And by setting Δθ as the deviation angle of θ_B due to the Bragg angle θ_B within the range distribution of FWHM about 1°,namely the Bragg angle can be described as $\theta = \theta_B \pm \Delta\theta$ to discuss the peak shape . The phase peak ϕ will be expanded as a function of Bragg devia-

tion angle and located in θ_B, now consider the Bragg formula can be

$$\phi = 2\pi \frac{2d\sin(\theta_B + \theta)}{\lambda} = \\ = 2\pi + 2\pi \frac{2d\sin\theta_B}{\lambda}\Delta\theta \quad (3)$$

The above formula has been assumed that the derivation of type angle is very small for 10^{-2}rad, so we retained only a term approximation, namely $\cos\Delta\theta\approx1$, $\sin\Delta\theta\approx\Delta\theta$.

By Equation (2) can be used to solve the FWHM. Let N as the deviation angle difference at half peak height, as shown in Figure 1, the numerical FWHM for $B = 2\Delta\theta_{1/2}$. And the $\theta_{1/2}$ can be solved by the point of the half peak intensity of the corresponding strength, namely $I_H = \theta_{1/2} = I_{max}/2$, it can be expanded as

$$\frac{I_0}{1 + e^{-2\sqrt{\mu s}} - 2e^{-\sqrt{\mu s}}\cos(\phi_H)} = \\ = \frac{1}{2}\left(\frac{I_0}{1 + e^{-2\sqrt{\mu s}} - 2e^{\sqrt{\mu s}}}\right) \quad (4)$$

where ϕ_H is the numericalφ when $\Delta\theta = \Delta\theta_{1/2}$, namely $\phi_H = \phi(\Delta\theta=\Delta\theta_{1/2})$.

Considering the above equation $2d/s = \sin\theta$, $\mu s = 2\mu d/(\sin\theta) = 4\mu d^2/\lambda$ and by series expansion approximation to simplify Equation (4) with $\cos x \approx 1–x^2/2!$, $e^x \approx 1 + x^2/1! + x^2/2!$ (x<1). Finally the half peak width of the crystal explicit function formula can be obtained.

$$B = 2\Delta(\theta_{1/2}) = \frac{1}{2\pi}\frac{\sqrt{\mu\lambda}}{\cos\theta_B} \quad (5)$$

The conclusion is that the half peak width of crystal is a bounded amount, rather than the infinite small which is represented by the interference function. And the full width at half maximum is about the function of the Bragg angle versus the sample absorption coefficient, even if the infinite crystal, the peak width is no longer represented by the interference function, and interference function is represented by setting the absorption coefficient μ=0. Because the formula is related with the sample absorption, so we call the relationship between B and 2θ of Equation (5) as the absorption resolution function (ARF), to distinguish IRF.

Now the absorption resolution function is compared with Caglioti's relations, Firstly the Cagliotti's relations is a semi empirical formula, rather than the ARF function is the theoretical formula which is deduced from the diffraction geometry and material absorption theory; secondly, the fitting coefficients of Caglioti's relations can only be obtained by fitting the experimental value without the exact physical meaning, but the absorption coefficient of ARF function has the definite physical meaning; finally, the Caglioti's relations needs three undetermined coefficients which can be obtained from the interference function, however, the ARF function is drawn from the new formula of XRD of Equation(2), and the absorption coefficient in principle can be obtained by experiments. Thus the ARF function has the more theoretical basis than Caglioti's relations.

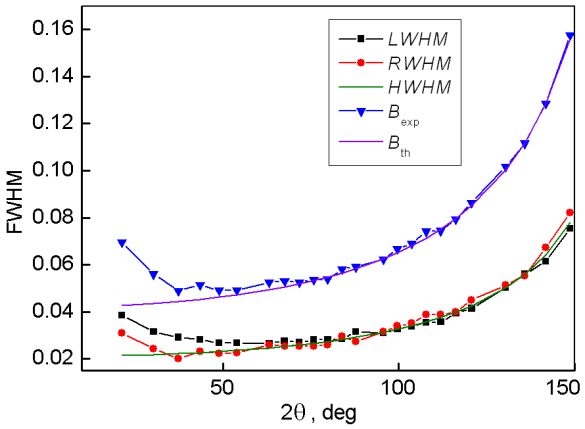

Fig. 3. FWHM of the experiment and the theory, take μ_{eff} =140 cm^{-1}

Considering the above discussion, the curves of Caglioti's relations and Equation (5) are not compared in the paper.

5. The experimental validation of the ARF function

The theoretical full width at half maximum (FWHM) of 24 peaks of the LaB_6 crystal peak under the effective absorption coefficient μ_{eff} =140 cm^{-1} by the ARF function, as shown in Fig. 3. In addition, the left and right of the experimental FWHM are not the same, it is reported that flat sample error only had effect on small angle of peaks [5], therefore, both the experimental left half width at half maximum (*LWHM*) and the right half width at half maximum (*RWHM*) measurement are also shown in Fig. 3. The theoretical half width at half maximum (*HWHM*) curve is also plotted in Fig. 3. The asymmetric experimental values will be a test of the instrumental errors.

It can be seen in Fig. 3 that the curves were increasing by the full width at half maximum increases as the diffraction angle 2θ increases. In the small angle, the difference between the theory (B_{th}) and the experiment (B_{exp}) is large that can be considered to be caused by the instrument broadening. However, the difference is small within the large angle. With considering the LWHM only caused by the flat sample error, the results show that the FWHM is

mainly caused by the sample absorption. And the HWHM compares with the LWHM and RWHM, we can obtain that the divergence of LWHM in small angle which should be caused by the flat sample error.

6. Conclusions

The purpose of this study is to propose a novel point of the absorption broadening of the XRD line profiles in this paper, and give the further theoretical derivation and experimental verification. We can draw the following conclusions:

Two different crystal full spectrum line profiles are verified with the standard LaB_6 specimen. The theoretical calculation is consistent with the experiments within the full spectrum peak. The maximum deviation of the standard samples between the theory and the experiments is less than 8% during $2\theta>60°$, the flat sample instrumental broadening may be the main reason of the deviation of small angle. So that the instrumental broadening only has influence on the small angle instead of the effect of full spectrum line profiles. It can further prove that the absorption peak is an important reason of the formation of XRD peak.

The paper derives the theoretical formula of the FWHM with 2θ that can be called as the ARF, and it should be replaced of the Caglioti's relations.

The quantitative system verification of the absorption peak is given in this paper. It proves that the absorption of incident X-ray sample is the main reason of the formation of the line profiles. And the previous theory of the interference function peak should be abandoned.

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