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On the Choice of θ:2θ Scan in Neutron Diffraction

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The conditions under which undistorted measurements of Bragg intensities can be carried out with the use of various modes of scan including Werner's optimum scan have been examined. It is shown that in the conventional $\theta:2\theta$ mode of scan undistorted estimates of Bragg intensities can be obtained with a fixed angular aperture in front of the detector, whereas in Werner's optimum scanning mode, although the required detector aperture is a minimum, it changes from reflexion to reflexion. The fact that the relative intensities of Bragg reflexions in the $\theta:2\theta$ mode are independent of the angular aperture in front of the detector has been experimentally verified. Simple expressions for the scan widths and the divergences of the integrated intensity distributions sensed by the detector in different modes of equatorial scans have been derived. The general expressions for the optimum scanning ratio g, the width of the crystal rocking curve σ and the width of the Bragg scattered beam δ have been checked analytically, and cast in a simplified form. They have also been experimentally evaluated for a typical neutron diffractometer and found to be in good agreement with the theoretical predictions.

Introduction

Recently, Werner (1971, 1972) has proposed an optimum scanning procedure for the measurement of integrated intensities of Bragg reflexions. According to Werner, the intensity $I(\gamma,\varphi)$ of the Bragg beam scattered from the sample at an angle γ (away from the nominal $2\theta_S$) for a given setting of the crystal $\varphi=\theta-\theta_S$ is given by

$$I(\gamma,\varphi)=I_0 \exp\{-\tfrac{1}{2}[(\gamma-g\varphi)^2/\delta^2+\varphi^2/\sigma^2]\} \qquad (1)$$

where g is the optimum scanning ratio, δ is the width of the Bragg scattered beam and σ is the width of the crystal rocking curve. All three depend on the instrument parameters and on the scattering angle. The expression for these and for I_0 are given in Appendix A. The expressions for g, δ and σ have been checked analytically and an error in Werner's expression for g has been corrected.

Very recently, the optimum scanning ratio has been experimentally verified by Pantazatos & Werner (1973) for a diffractometer with relatively large divergence ($\alpha_0\to\infty$) of the in-pile collimator. All the examples discussed in Werner's (1971) paper also belong to this special category, in which the error in his expression for g referred to above becomes quite unimportant.

According to equation (1), if the detector is moved through an angle $g\varphi$ as a function of the crystal angle φ, the centre line of the detector will remain aligned to the centre of the diffracted beam for each angular setting of the crystal while it sweeps through a Bragg peak. Consequently, the required angular aperture in front of the detector is a minimum, thus enabling the background counting to be reduced. Also, coupling the detector and the crystal motions in this optimum ratio g is not a constraint in most of the automatic diffractometers currently in use, since the detector and the crystal are usually driven independently. However, there is an important drawback to the use of this optimum scanning mode. In order to measure the Bragg intensities in a relatively undistorted way one has also to vary the angular aperture of the detector as a function of the width of the diffracted beam. Most of the diffractometers in current use do not have this flexibility of varying the detector aperture continuously. In typical diffractometers δ (FWHM) can range from near zero ($\simeq\eta_S$) to well over a degree (see Fig. 2, for example). If the transmission function of the detector aperture is assumed to be rectangular, the latter has to be nearly three times as large as δ in order to accept up to 98% of the beam intensity. Therefore, if the optimum mode is to be used with a *fixed* detector aperture, the latter has to be three times as large as the maximum δ in order to measure all Bragg intensities with an accuracy of better than 2%. This may mean using detector apertures as large as 2 to 3° (FWHM). This would be self-defeating since the main advantage of the optimum scanning mode is expected to be in the reduction of the required detector apertures.

In this paper we show that in the conventional $\theta:2\theta$ mode of scanning it is possible to obtain relatively undistorted estimates of Bragg intensities with a fixed detector aperture even if the latter is not large enough to accept all the reflected neutrons as the specimen crystal is swept through a Bragg peak.

The divergence of the integrated intensity distribution sensed by the detector in various modes of scan

By integrating equation (1) over φ we get

$$I(\gamma)=\int I(\gamma,\varphi)\mathrm{d}\varphi$$
$$=I(0)\exp\{-\gamma^2/[2(\delta^2+g^2\sigma^2)]\}\,. \qquad (2)$$

The angular width of this distribution corresponds to the angular width of the integrated intensity distribution, or to the overall angular width of the Bragg scattered neutrons as the specimen crystal is swept through a Bragg peak. Therefore, if the integrated intensity is to be measured with a stationary detector positioned at the centre of this distribution (*i.e.* by using the ω-scan technique), the angular aperture of the detector should be proportional to the width α_ω of this distribution

$$\alpha_\omega=[\delta^2+g^2\sigma^2]^{1/2}.$$

On substitution for g, δ and σ this simplifies to

$$\alpha_\omega=\left[\frac{4(a+1)^2\alpha_1^2\eta_M^2+(2a+1)^2\alpha_0^2\alpha_1^2+4a^2\alpha_0^2\eta_M^2}{4\eta_M^2+\alpha_0^2+\alpha_1^2}\right]^{1/2}$$
$$=(\delta)_{\eta_S\to\infty}\,. \quad (3)$$

Obviously, α_ω depends on the scattering angle through the dispersion parameter a $(=\varepsilon_S \tan\theta_S/\varepsilon_M \tan\theta_M)$.

However, if the intensity is measured by moving the detector in coupling with the crystal, the effective angular width of the integrated intensity distribution as sensed by the detector will be different. When the scanning ratio is g', the overall angular width of the Bragg-scattered neutrons as sensed by the moving detector can be obtained from the integral

$$I(\xi)=I_0\int\exp\left[-\varphi^2/2\sigma^2\right]\exp\left[-(\xi+g'\varphi-g\varphi)^2/2\delta^2\right]\mathrm{d}\varphi$$
$$=I_0\left[\frac{2\pi\,\sigma^2\delta^2}{\delta^2+(g-g')^2\sigma^2}\right]^{\frac{1}{2}}$$
$$\times\exp\left\{-\xi^2/2[\delta^2+(g-g')^2\sigma^2]\right\}, \quad (4)$$

where ξ $(=\gamma-g'\varphi)$ is the angle of a divergent ray with the detector centre line. The width α of this distribution is

$$\alpha_{g'}=[\delta^2+(g-g')^2\sigma^2]^{1/2}.$$

In the optimum scanning mode $g'=g$,

$$\alpha_{\text{opt}}=\alpha(g'=g)=\delta\,.$$

In the conventional $\theta:2\theta$ mode of scanning $g'=2$,

$$\alpha_{\theta:2\theta}=\alpha(g'=2)=[\delta^2+(g-2)^2\sigma^2]^{1/2}.$$

On substitution for g, δ and σ this simplifies to

$$\alpha_{\theta:2\theta}=\left[4\eta_S^2+\frac{4\alpha_1^2\eta_M^2+\alpha_0^2\alpha_1^2}{4\eta_M^2+\alpha_0^2+\alpha_1^2}\right]^{1/2}. \quad (5)$$

It is clear from equation (5) that the angular width or the *overall* angular divergence $\alpha_{\theta:2\theta}$ of the integrated intensity distribution as sensed by the moving detector in the conventional $\theta:2\theta$ mode of scanning is a constant for a given instrument and sample. This enables the undistorted measurement of Bragg intensities with a finite detector aperture in the $\theta:2\theta$ mode of scanning.

Fractional loss in integrated intensity due to finite detector aperture

If the intensity $I(\gamma,\varphi)$ is measured with a detector of finite angular aperture (α_2) with its centre line along γ, the measured intensity will be

$$I_m(\gamma,\varphi)=\int I(\gamma',\varphi)\exp\left[-\frac{(\gamma-\gamma')^2}{2\alpha_2^2}\right]\mathrm{d}\gamma'$$
$$=I_0\alpha_2\delta\left(\frac{2\pi}{\alpha_2^2+\delta^2}\right)^{1/2}\exp\left[-\varphi^2/2\sigma^2\right]$$
$$\times\exp\left[-\frac{(\gamma-g\varphi)^2}{2(\alpha_2^2+\delta^2)}\right] \quad (6)$$

when the scanning ratio is g', γ and φ will be coupled in the ratio $g':1$ with $\gamma=0$ corresponding to $\varphi=0$. Therefore, the measured intensity at the crystal setting φ would be

$$I_m(g'\varphi,\varphi)=I_0\alpha_2\delta\left(\frac{2\pi}{\alpha_2^2+\delta^2}\right)^{1/2}\exp\left[-\frac{\varphi^2}{2\sigma^2}\right]$$
$$\times\exp\left[-\frac{(g'-g)^2\varphi^2}{2(\alpha_2^2+\delta^2)}\right] \quad (7)$$

and the measured integrated intensity $\mathscr{I}_M$ would be given by

$$\mathscr{I}_M=\int I_m(g'\varphi,\varphi)\mathrm{d}\varphi$$
$$=\frac{2\pi I_0\delta\sigma\alpha_2}{[\alpha_2^2+\delta^2+(g'-g)^2\sigma^2]^{1/2}}$$
$$=\mathscr{I}_T\frac{\alpha_2}{[\alpha_2^2+\delta^2+(g'-g)^2\sigma^2]^{1/2}} \quad (8)$$

where $\mathscr{I}_T(=2\pi I_0\delta\sigma)$ is the total integrated intensity scattered by the sample crystal as it sweeps through a Bragg peak. On substitution for I_0, δ and σ the expression* for $\mathscr{I}_T$ reduces to

$$\mathscr{I}_T=\frac{(2\pi)^{3/2}p_Sp_M\alpha_0\alpha_1\eta_S\eta_M\cot\theta_M}{(4\eta_M^2+\alpha_0^2+\alpha_1^2)^{1/2}}\,.$$

Using equation (8) one gets the following expression for the fractional loss in integrated intensity

$$\Delta\mathscr{I}/\mathscr{I}=1-\mathscr{I}_M/\mathscr{I}_T$$
$$=1-\frac{\alpha_2}{[\alpha_2^2+\delta^2+(g'-g)^2\sigma^2]^{1/2}}\,. \quad (9)$$

* To be complete this expression has to be multiplied by the integrated transmission due to the vertical divergence of the collimators. Since the wavelength angle correlation arising out of vertical divergences is very small, throughout this paper, as in Werner's (1971) paper, we have neglected the effect of vertical divergences.

When $g'=2$, $\Delta\mathscr{I}/\mathscr{I}$ becomes independent of a and is given by

$$(\Delta\mathscr{I}/\mathscr{I})_{g'=2} = 1 - \frac{\alpha_2(4\eta_M^2+\alpha_0^2+\alpha_1^2)^{1/2}}{[(\alpha_2^2+4\eta_S^2)\,(4\eta_M^2+\alpha_0^2+\alpha_1^2)+4\alpha_1^2\eta_M^2+\alpha_0^2\alpha_1^2]^{1/2}}\,.$$

Hence, in the conventional $\theta{:}2\theta$ mode of scanning, the fractional loss in integrated intensity due to fixed

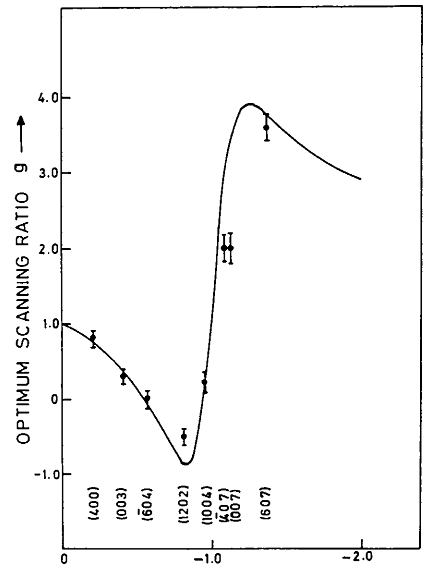

Fig. 1. Comparison of the observed and calculated optimum scanning ratios for various reflexions from a single crystal of L-cystine.2HCl in parallel geometry. The scattering angle is given by $a=\varepsilon_S \tan\theta_S/\varepsilon_M \tan\theta_M$ with $\theta_n=32{\cdot}5°$. The ratio calculated (solid curve) from equation (i) (see Appendix A) corresponds to values (FWHM) of $\alpha_0=1{\cdot}35°$, $\alpha_1=1{\cdot}25°$, $\eta_M=0{\cdot}20°$ and $\eta_S=0{\cdot}01°$.

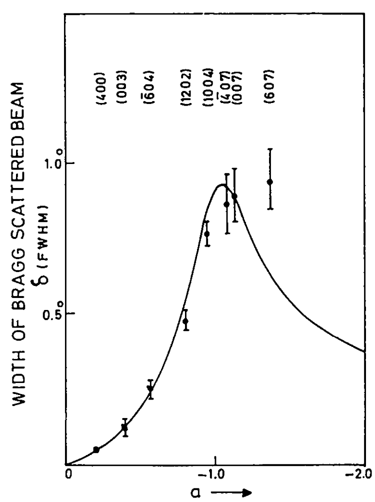

Fig. 2. Variation of the observed and calculated (solid curve) values of the width of the Bragg scattered beam δ for various reflexions from L-cystine.2HCl as a function of $a=\varepsilon_S \tan\theta_S/\varepsilon_M \tan\theta_M$.

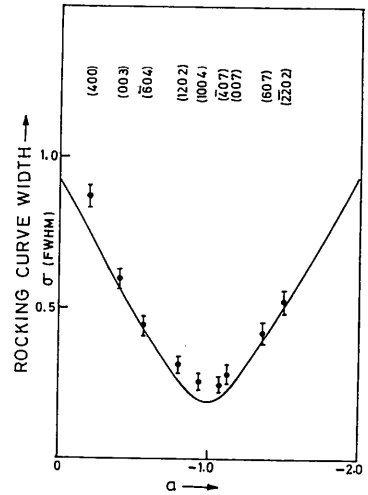

Fig. 3. Variation of the observed and calculated (solid curve) values of the rocking curve width σ for various reflexions from L-cystine.2HCl as a function of $a=\varepsilon_S \tan\theta_S/\varepsilon_M \tan\theta_M$.

detector aperture is independent of the scattering angle and remains a constant for all reflexions.

Widths of scans

Using equation (7) one gets the following expression for the characteristic width $\langle\Delta\varphi\rangle$ of the scan when the scanning ratio is g',

$$\langle\Delta\varphi\rangle_{g'} = \sigma\left[\frac{\alpha_2^2+\delta^2}{\alpha_2^2+\delta^2+(g'-g)^2\sigma^2}\right]^{1/2}. \tag{10}$$

In the optimum scanning mode $g'=g$,

$$\langle\Delta\varphi\rangle_{\rm opt} = \sigma\,. \tag{10a}$$

In the ω scan $g'=0$,

$$\langle\Delta\varphi\rangle_{\omega} = \sigma\left[\frac{\alpha_2^2+\delta^2}{\alpha_2^2+\delta^2+g^2\sigma^2}\right]^{1/2}. \tag{10b}$$

In the $\theta{:}2\theta$ scan $g'=2$,

$$\langle\Delta\varphi\rangle_{\theta:2\theta} = \sigma\left[\frac{\alpha_2^2+\delta^2}{\alpha_2^2+\delta^2(2-g)^2\sigma^2}\right]^{1/2}. \tag{10c}$$

On substitution for g, δ and σ the above expression for $\langle\Delta\varphi\rangle_\omega$ can be seen to be the same as Caglioti & Ricci's (1962) expression for $B_{1/2}$ and Cooper's (1968) expression for φ_M; and the expression for $\langle\Delta\varphi\rangle_{\theta:2\theta}$ is the same as the expression for $A_{1/2}$ given by Caglioti, Paoletti & Ricci (1960) except that the former is in θ space while the latter is in 2θ space. Substituted expressions for $\langle\Delta\varphi\rangle_\omega$ and $\langle\Delta\varphi\rangle_{\theta:2\theta}$ are given in Apendix B.

Experimental results

The general expressions for g, δ and σ given in the Appendix have been experimentally verified on our diffractometer, 3DFAD (Momin, Sequeira & Chidambaram, 1974) using a typical crystallographic sample.

The specimen crystal (L-cystine. 2HCl) in the shape of a triangular prism with height $\simeq 5$ mm and volume $\simeq 42$ mm^3 was mounted with its b axis along the φ axis of the diffractometer and bathed in the incident beam ($\lambda = 1{\cdot}170$ Å, $2\theta_M = 65°$) which was 1 cm in diameter. The estimated angular divergences α_0 and α_1 of the in-pile and secondary collimators were 1·35° and 1·25° (FWHM) respectively. The mosaic spreads η_M of the monochromator (Ge 115) and η_S of the sample were 0·20° and 0·01° (FWHM) respectively. To measure the optimum coupling g, the centre of the diffracted beam was located by step-scanning it using a narrow aperture on the detector for two stationary-crystal orientations for each reflexion. If γ_1 and γ_2 are the locations of the diffracted beam for crystal orientations φ_1 and φ_2

$$g = \frac{\gamma_2 - \gamma_1}{\varphi_2 - \varphi_1}.$$

φ_1 was set corresponding to the peak value of the intensity with the detector wide open and φ_2 at (φ_1 + 0·10°). The angular width of the diffracted beam δ was also estimated using the same scans; the width of the rocking curve σ was measured using a wide

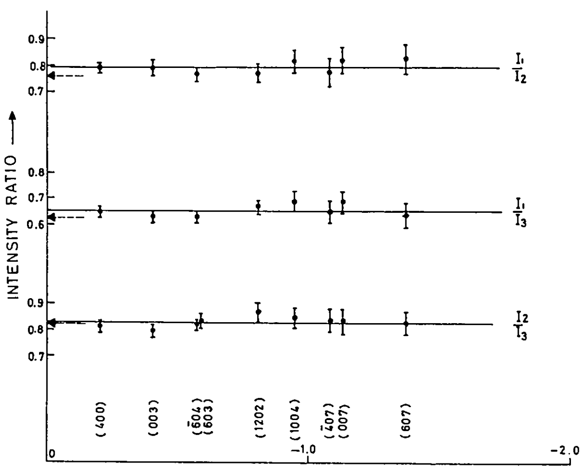

Fig. 4. Ratios of the integrated intensities measured with three different apertures on the detector for various reflexions from L-cystine.2HCl. Intensities I_1, I_2 and I_3 correspond to detector apertures (FWHM) of 0·8°, 1·2° and 2·0° respectively. The solid lines indicate the observed averages and the arrows indicate the theoretically expected values of the ratios.

aperture on the detector. The experimental results along with the calculated values are shown in Figs. 1, 2 and 3. The agreement between the observed and calculated values is quite good, considering that no instrument parameters have been adjusted to fit the observations.

The fact that the fractional loss in integrated intensity due to the finite detector aperture is independent of the scattering angle in the θ:2θ mode of scanning has also been verified experimentally using the diffractometer 3DFAD. Intensities of a few reflexions from the same single crystal of L-cystine.2HCl have been recorded using three different apertures in front of the detector. The angular widths (FWHM) of these apertures were 0·80°, 1·20° and 2·00° as compared with the value of 0·94° (FWHM) for $\alpha_{\theta:2\theta}$ calculated using equation (5). For each reflexion the ratios I_1/I_2, I_1/I_3 and I_2/I_3 of the integrated intensities I_1, I_2 and I_3 obtained with the three apertures have been plotted as a function of the parameter a in Fig. 4. The fact that these ratios are independent of a shows that all the intensities have been uniformly scaled by the detector aperture without introducing any distortions. Conversely, the results prove that the relative values of integrated intensities do not depend on the size of the detector aperture. The average observed values of 0·794, 0·652 and 0·830 for the ratios I_1/I_2, I_1/I_3 and I_2/I_3 respectively are also close to the theoretically expected values of 0·757, 0·625 and 0·825.

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APPENDIX A
Expressions* g, δ, σ and I_0

$$g=\frac{2(a+1)\,(a+2)\alpha_1^2\eta_M^2+(2a+1)\,(a+1)\alpha_0^2\alpha_1^2+2a^2\alpha_0^2\eta_M^2}{(a+2)^2\alpha_1^2\eta_M^2+(a+1)^2\alpha_0^2\alpha_1^2+a^2\alpha_0^2\eta_M^2+\eta_S^2(4\eta_M^2+\alpha_0^2+\alpha_1^2)} \tag{i}$$

$$\delta=\left[\frac{a^2\alpha_0^2\alpha_1^2\eta_M^2+\eta_S^2\{4(a+1)^2\alpha_1^2\eta_M^2+(2a+1)^2\alpha_0^2\alpha_1^2+4a^2\alpha_0^2\eta_M^2\}}{(a+2)^2\alpha_1^2\eta_M^2+(a+1)^2\alpha_0^2\alpha_1^2+a^2\alpha_0^2\eta_M^2+\eta_S^2(4\eta_M^2+\alpha_0^2+\alpha_1^2)}\right]^{1/2} \tag{ii}$$

$$\sigma=\left[\eta_S^2+\frac{(a+2)^2\alpha_1^2\eta_M^2+(a+1)^2\alpha_0^2\alpha_1^2+a^2\alpha_0^2\eta_M^2}{(4\eta_M^2+\alpha_0^2+\alpha_1^2)}\right]^{1/2} \tag{iii}$$

$$I_0=(2\pi)^{1/2}p_Sp_M\cot\theta_M\left[\frac{4(a+1)^2}{\alpha_0^2}+\frac{4a^2}{\alpha_1^2}+\frac{(2a+1)^2}{\eta_M^2}+\frac{a^2}{\eta_S^2}\right]^{-1/2} \tag{iv}$$

where, $a=\dfrac{\varepsilon_S\tan\theta_S}{\varepsilon_M\tan\theta_M}$ is the dispersion parameter.

$(\varepsilon_S/\varepsilon_M)=-1$ for parallel geometry.
$=+1$ for antiparallel geometry.

α_0,α_1 = Effective width parameters of the primary and secondary collimators having Gaussian transmission functions of the form

$$T(\gamma_i)=\exp\left(-\gamma_i^2/2\alpha_i^2\right).$$

γ_i is the angle of a divergent ray with the nominal ray direction.

η_M,η_S = Mosaic spreads of the monochromator and sample crystals whose reflectivities as a function of of the mosaic misorientation angle Δ_i are of the form

$$P(\Delta_i)=p_i\exp\left(-\Delta_i^2/2\eta_i^2\right)$$

* In Werner's (1971) expression for g, the first term in the numerator has been wrongly given as $2(a^2+3a+1)\alpha_1^2\eta_M^2$.

APPENDIX B
Final expressions for the widths of ω and $\theta:2\theta$ scans

$$\langle\Delta\varphi\rangle_\omega=\left[\eta_S^2+\frac{\dfrac{(a+2)^2}{\alpha_0^2}+\dfrac{(a+1)^2}{\eta_M^2}+\dfrac{a^2}{\alpha_1^2}+\dfrac{a^2}{\alpha_2^2}}{\dfrac{4}{\alpha_0^2\alpha_1^2}+\dfrac{1}{\alpha_0^2\eta_M^2}+\dfrac{1}{\alpha_1^2\eta_M^2}+\dfrac{4(a+1)^2}{\alpha_0^2\alpha_2^2}+\dfrac{(2a+1)^2}{\eta_M^2\alpha_2^2}+\dfrac{4a^2}{\alpha_1^2\alpha_2^2}}\right]^{1/2}$$

$$\langle\Delta\varphi\rangle_{\theta:2\theta}=\left[\frac{\dfrac{(a+2)^2}{\alpha_0^2}+\dfrac{(a+1)^2}{\eta_M^2}+\dfrac{a^2}{\alpha_1^2}+\dfrac{a^2}{\alpha_2^2}+\eta_S^2\left\{\dfrac{4}{\alpha_0^2\alpha_1^2}+\dfrac{1}{\alpha_0^2\eta_M^2}+\dfrac{1}{\alpha_1^2\eta_M^2}+\dfrac{4(a+1)^2}{\alpha_0^2\alpha_2^2}+\dfrac{(2a+1)^2}{\eta_M^2\alpha_2^2}+\dfrac{4a^2}{\alpha_1^2\alpha_2^2}\right\}}{\dfrac{4}{\alpha_0^2\alpha_1^2}+\dfrac{1}{\alpha_0^2\eta_M^2}+\dfrac{1}{\alpha_1^2\eta_M^2}+\dfrac{4}{\alpha_0^2\alpha_2^2}+\dfrac{1}{\eta_M^2\alpha_2^2}+\dfrac{4\eta_S^2}{\alpha_2^2}\left\{\dfrac{4}{\alpha_0^2\alpha_1^2}+\dfrac{1}{\alpha_0^2\eta_M^2}+\dfrac{1}{\alpha_1^2\eta_M^2}\right\}}\right]^{1/2}.$$