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Non-linear elastic behaviour of carbon fibres of different structural and mechanical characteristic

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Abstract: Five types of polyacrylonitrile, PAN, based carbon fibres, differing in modulus, breaking strain and in crystallite orientation, have been studied. Non-Hookean behaviour was investigated by computing the tangent tensile and compression moduli as a function of strain, from the axial stress–strain response obtained in standard tensile, compression, as well as in modified flexural tests of unidirectional carbon/epoxy composites. The dependences of the tensile modulus on tensile strain of the carbon fibres were extracted from data obtained in single-filament tensile tests. Analytical expresssions for the tensile modulus–tensile strain and compression modulus–compression strain dependences in the performed test were deduced. The structural characterization of the carbon fibres was performed by X-ray diffraction on bundle of parallel fibres. The interlayer spacing d_{002} and the apparent lateral dimension of the crystallites L_c were deduced by processing the 002 diffraction profiles. The established modulus–strain dependences were correlated with the fibre characteristics (breaking strain and mean modulus values), as well as with the characteristic of the 002 difraction profile and the d_{002} and L_c values.

Keywords: carbon fibres, carbon/epoxy composites, non-linear elasticity, crystallite preferential orientation.

INTRODUCTION

The tensile modulus of carbon fibres increases with increasing tensile strain,[1–4] while the compression modulus decreases with increasing compression strain.[6–8] This makes stress–strain response of carbon fibres non-Hookean. Such behaviour has been observed for carbon fibres themselves, as well as for their unidirectional composites.[5–8] The non-Hookean stress–strain response of carbon fibres is reversible and is unaffected by loading and unloading cycles up to at least 40 % of the tensile strength. This suggests that the non-linear behaviour of carbon fibres is real non-Hookean elastic behaviour.

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In this paper the results of a study of the non-Hookean behaviour of carbon fibres with different mechanical properties (modulus and breaking strain) are presented. Tensile tests on carbon single-filaments and standard axial (tensile, compression) and modified flexure test[8] on coupons of unideractional carbon fibre/epoxy resin composites were performed. The tangential Young's modulus and strain values were extracted from test data and a linear expression between the tangent moduli and strain were deduced

$$E_{ax} = E_0 (1 + \gamma_{ax}\varepsilon_{ax}) \quad (1)$$

The coefficient γ_{ax}, describing the variation of E with ε_{ax} is a measure of the degree of non-linearity.

The γ_{ax} values for all the tested carbon fibres were correlated to the fibre breaking strain and the mean modulus values, as well as to structural characteristics of the fibres, determined using X-ray diffraction analysis of bundles of parallel fibres. Special attention was paid to the parameter *FWHM* (full width at half-maximum peak height) for the (002) planes as a possible measure of the preferred axial orientation of the crystallites along the fibre axis, *i.e.*, orientation of the basal plane of turbostratic carbon to the *a*-axis.

EXPERIMENTAL

Materials

The tested commercial carbon fibres types were: high strength Torayca T 300; fibres of enhanced breaking strain (Union Carbide THORNEL A, Enka TENAX HTA, Grafil HYSOL XA-S) and high modulus, Sigry Sigrafil HM carbon fibres, the characteristics of which are given in Table I.

TABLE I. Characteristics of the employed carbon fibres, from the producer's data sheets

Fibre	Diameter μm	Density/kg m^{-3}	Strength MPa	Modulus/GPa	Breaking strain/mm m^{-1}
Tarayca T 300	7	1740	2800	226	11.0
Thornel A	7	1730	3100	230	15.0
Tenax HTA	7	1770	3900	240	15.6
Hysol XA-S	7	1780	3100	270	15.5
Sigrafil HM	6.6	1800	2570	445	6.5

The tested carbon/epoxy laminates were obtained from four commercial unidirectional carbon fibre/epoxy resin prepregs:

– Brochier Vicotex 108, with Torayca T 300 carbon fibres, laminate label B
– Hexcel F263, with Union Carbide Thornel A carbon fibres, laminate label F,
– Hexcel M 39, with ENCA Tenax HTA carbon fibres, laminate label M and
– Hexcel NCHR, with ENCA Tenax HTA carbon fibres, laminate label NH.

The used prepregs were cured at 175 °C, except Vicotex 108, which was cured at 120 °C.

Mechanical tests

All mechanical test were performed with an M 1185 INSTRON Universal Testing Machine. The tensile test were performed on Tenax HTA, Hysol XA-S and Sigrafil HM fibres, on axially aligned sin-

gle-filaments (centre-line mounted on a slotted tab), according the ISO 11566 standard. During the test, the applied load (P) and fibre extension (I) were recorded on the machine chart, as an I–P curve. From this curve, the quantities of fibre elongation, ΔL, and fibre compliance, C, given as:

$$\Delta L = \mathrm{I}\,\frac{H}{S} \qquad C = \frac{\Delta L}{\Delta P} = \frac{IH}{PS} \tag{2}$$

(where H is the cross head and S the chart speed) were deduced, as the data necessary for the calculation of the experimental tensile fibre characteristics, the strength σ_f and the failure strain ε_f^{exp}

$$\sigma_f = \frac{4}{\pi\Phi_f^2} P_{max} \qquad \varepsilon_f^{exp} = \frac{CP_{max}}{L_0} \tag{3}$$

where Φ is the fibre diameter.

From single filament tensile tests with different gauge length (L_0), for the tested carbon fibres, the system compliance values ($C_s = 8.25 \times 10^{-4}$ m N^{-1}) were derived according to Annex A of the above-mentioned Standard Document and the through (corrected) fibre strain value ε_f^{coor} was deduced as:

$$\varepsilon_f^{corr} = \varepsilon_f^{exp} - C_s \frac{P}{L_0} \tag{4}$$

Then the tangential through modulus values for successive individual strain intervals were calculated (the correlation coefficient of the linear regression, r, was not lower than 0.98) by the definition:

$$E_f = \frac{d\sigma}{d\varepsilon^{corr}} \tag{5}$$

The tangential moduli values, in the range from zero up to breaking strain, were correlated to the corresponding strain interval mean value ε_f^{corr} values and the linear expression

$$E_f = E_0\,(1 + \gamma_{ax}\varepsilon_{ax}) \tag{6}$$

for the tested carbon fibres, as well as for the tested UDC(0) were derived. The values of E_0 and γ_{ax} parameters together with the values of correlation coefficient r for the tested fibres und UDC(0) are summarized in Table II.

The tensile test on B, F, M and NH UDC(0) coupons were performed using the ISO 527-5 standard tensile method. The B-UDC(0) coupons were also tested in compression in accordance to the ISO 14126 standard test method (using a Celanese compression test fixture), as well as in a modified standard (ISO 14125) flexure test.[8] During the tensile, compression and modified flexure test, the longitudinal strains were monitored using strain gauges. The systematic error in recording the load was less than 1 %, for a measurement strain lower than 0.5 %.

The coefficient of variation of the determination of the fibre modulus at $\varepsilon_f = 0.003$ was ± 7.0 %, while that for the determination of UDC(0) at $\varepsilon_f = 0.004$, it was lower than ± 6.0 %.

In a modified three point flexure test, with a span to depth ratio equal to 32, measurements of the axial strain of both outer coupon surfaces were performed using strain gauges attached at a distance x from the middle point. The axial stress at point x was calculated using the equation:[8]

$$\sigma_x = \frac{3}{2}\frac{PL}{bd^2}\left(1 - \frac{2x}{L}\right) \tag{7}$$

From the axial and modified flexure test on the B-UDC(0) coupons, $E - \varepsilon_{ax}$ dependences were derived for the tensile and compression range (Fig. 1). For the F, M and NH-UDC(0) coupnos, the $E - \varepsilon_{ax}$ expressions were only derived for tensile range (Table II).

Structural characterization of the fibres

The structural characterization of fibres by X-ray difraction analysis included the determination of the apparent crystallite size (lateral dimension) L_c and the lattice constant d_{002} (the The X-ray diffraction patterns were recorded using a Siemens diffractometer, type D500, with a Röntgen tube with a copper anode. The $K_{\alpha 1}$ rays of wavelength $\lambda = 0.154050$ nm were used. The $K_{\beta 1}$ X-ray waves were eliminated with a nickel filter. The diffractions were performed on bundles of parallel fibres and the L_c and d_{002} values (Table III) were deduced from the (002) diffraction profile, *i.e.,* L_c from the positions of the diffraction angle (2θ) and the full width at half maximum intensity peak (*FWHM* = *B*) using the Scherrer equation, $L_c = K\lambda/B \cos\theta$ were the shape factor *K* is equal 0.89, and d_{002} using the Bragg Law, $d_{002} = n\lambda/2 \sin\theta$ where, $n = 1$ for the (002) diffraction profile.

The functions of the diffractometer were controlled by a microprocessor using the software package DIFFRAC^{plus}. The EVA program of the package was used for the following operations: the graphical processing and analogue presentation of the diffraction diagrams, the elimination of $K_{\alpha 2}$ component of the radiation and the computing and digital presentation of the data, *i.e.,* computing the position, area, intensity and width at half intensity of the peaks, as well as calculating the values of the interlayer spacing. The *FWHM* values were calculated without taking into account the correction for the instrumental broading of the 002 peak, amounting 0.09°.

RESULTS AND DISCUSSION

The values obtained from the standard tensile and modified flexure test on B-UDC(0) coupons were the same, while γ_C value deduced from the modified flexure test was lower than that derived from the standard compression test in the Celanesse fixture (Fig. 1). In addition, the value derived from the standard compression test was higher than the γ_T value, while the γ_C value derived from the modified flexure test was lower.

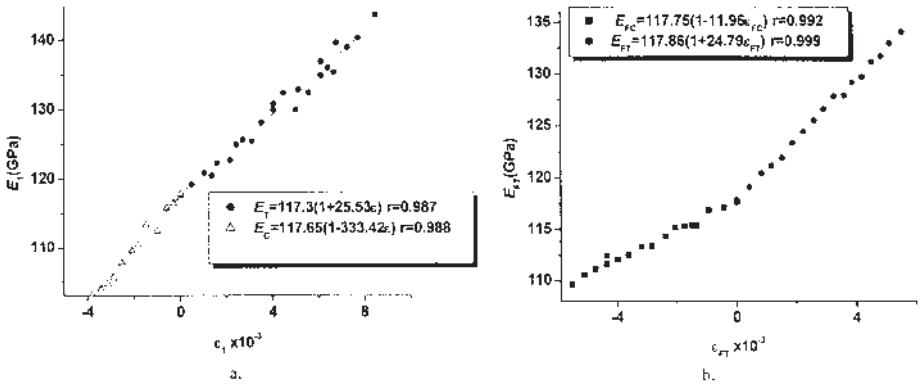

Fig. 1. Dependences of the axial modulus on strain, derived from standard axial (a) and modified flexure tests (b) for B-UDC.

The lower γ_T than γ_C value from the standard axial test is, according to Harper and Neumann,[6] explained by the buckling mechanism of the fibres, which could cause a reduction of the modulus with compressive strain, while it could not account for the increase in the modulus with tensile strain. Consequently, the γ_C value deduced from the modified flexure test was lower than that deduced from the

standard compression test, because the buckling of the fibres, as a progressive failure mechanism under compressive load, is more intense in the coupon during the standard compression test than on the upper outer surface of the bent coupon. In the Celanesse fixture, the shear between the gripes and coupon tabs contributes to a reduction of E_C and an increase of γ_C, as well.

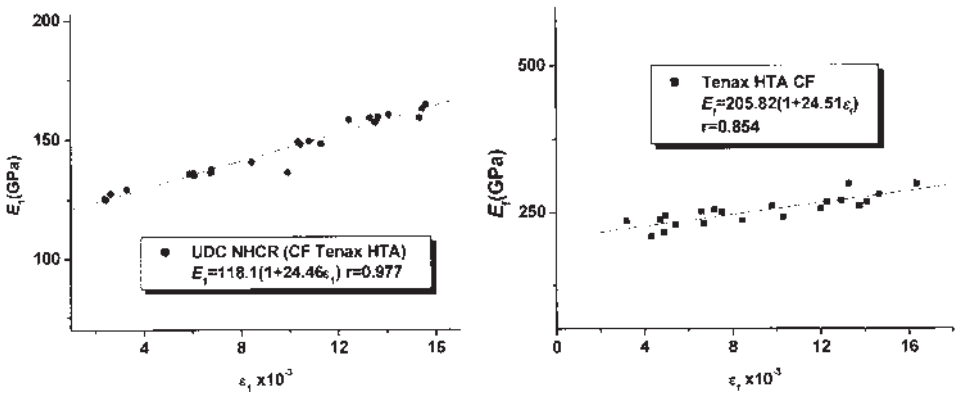

Fig. 2. Dependences of the axial modulus on strain. (a) of NHCR UDC(0) coupons reinforced with Tenax HTA fibres tested on tension and (b) of Tenax HTA carbon fibres tested in the single filament tensile test.

The γ_T values deduced from the single-filament tensile test of Tenax HTA carbon fibres and that from the tensile test of UDC(0) NHCR coupons reinforced with the same fibres, are identical (Fig. 2). It is easy to see that the correlation of the UDC coupons data is much better than that of the fibre data, due to the more precise measurement of strain in the UDC coupon test than in the single filament test. The same occurred with the other tested fibres and with the UDC reinforced with the same fibres (Table II). Thus, the linear correlation of the $E - \varepsilon$ values for the fibres is worse than that for UDC. Also, the r values the linear correlation of data obtained from the modified flexure test are slightly higher than from the standard axial test (Fig. 1).

TABLE II. Parameters of $E_f = E_0(1 + \gamma_{ax}\varepsilon_{ax})$ expression of the non-linear behaviour of the fibres, deduced from test on carbon single-filaments and on carbon/epoxy UDC(0) coupons

UDC(0) – standard tensile(T) compession (C) and modified flexure (MF) tests								
UDC(0)	Fibres	Test	ε_v^*/mm m^{-1}	E_0/GPa	γ_{ax}	r[1)]	E_f^{mean} [2)]/GPa	$FWHM$[4)]/°
Brochier Vicot. 108	Torayca T300	T	10.2	117.4	25.2	0.987	219±15	5.25
		MFT		117.8	24.8	0.999	219±15	
Hexcel F263	Thornel A	T	15.0	107.4	22.8	0.909	240±29	5.33
Hexcel HNCR	Tenax HTA	T	15.6	118.1	24.5	0.997	240±21	5.20

TABLE II. Continued

UDC(0) – standard tensile(T) compession (C) and modified flexure (MF) tests								
UDC(0)	Fibres	Test	ε_v^*/mm m^{-1}	E_0/GPa	γ_{ax}	$r^{1)}$	$E_f^{mean\ 2)}$/GPa	$FWHM^{4)}$/°
Hexcel M30	Tenax HTA	T	15.6	118.6	27.3	0.756	240±33	5.24
Brochier Vicot. 108	Torazca T 300	C	10.2	117.7	33.5	0.988	147±20	5.25
		MFC		117.9	12.0	0.992	178±7	
CARBON FIBRES – single filament tensile tests (SFTT)								
Producer	Fibres	Test	ε_v^*/mm m^{-1}	E_0/GPa	γ_{ax}	$r^{1)}$	$E_f^{mean\ 2)}$/GPa	FWHM$^{4)}$/°
SIGRY	Sigrafil HM		6.5	458.3	7.1	0.863	472±4	1.69
GRAFIL	Hysol Xa-S	SFTT	14.0	208.3	18.1	0.954	242±20	4.16
ENCA	Tenax HTA		15.2	205.8	24.5	0.854	253±26	5.20

[1]Correlation coefficient of linear regression; [2]mean fibre modulus data calcualted from UDC(0) experimental results, *via* the rule of mixture; [3]experimental fibre mean modulus values; [4]*FWHM* - full width at thalf-maximum height for 002-profile

The γ_T values for B-UDC(0) with high strenth fibres of first generation and for F, M and NH-UDC(0) coupons (all reinforced with carbon fibres of enhanced breaking strain) were mutually similar (Table II). This is due to similar conditions of fibre processing.[9,10]

For the high strain Hysol XA-S carbon fibres in the single-filament tensile test, a somewhat lower γ_T value (18.8) was evaluated, while for the high modulus Sigrafil HM carbon fibres a rather low γ_T value (7.2) was found (Table II).

The determined values of the coefficient γ_{ax} as a measure of the degree of non-linear elasticity of the carbon fibres, are correlated to the mean modulus values, as well as to the characteristics of the X-ray diffraction pattern (Fig. 4) and with the parameters of the structure of the carbon fibres (Table III).

The only distinct peak present in all the diffraction patterns of the tested carbon fibres (Fig. 4) is the 002 peak, with a maximum intensity at $2\theta = 25–26°$. The Hysol and Sigrafil fibres were covered with epoxy sizing before the X-ray diffraction analysis. For this reason, a peak at about 12° appeared on the diffraction patterns of these fibres (Fig. 4, patterns 5 and 6).

From Tables II and III, it can be seen that the values decrease with decreasing interlayer spacing (d_{002}) and width of the 002 reflection (*FWHM*). Simultaneously, the apparent lateral dimension of the crystallites, L_c increases.

The present results (Table II) show that the γ_T values are inversely proportional to the mean modulus values of the carbon fibres, which is a well-known phenomenon.[11–13] The experimental mean modulus value of the Twaron fibres, making an exception to this generalisation, is higher than that of the Hysol fibres. The found value is higher than the one reported by the producer (Table I) and the value determined from the UDC(0) modulus values.The observed disparity between the values of the modulus of the Twaron fibres can be ascribed to different strain inter-

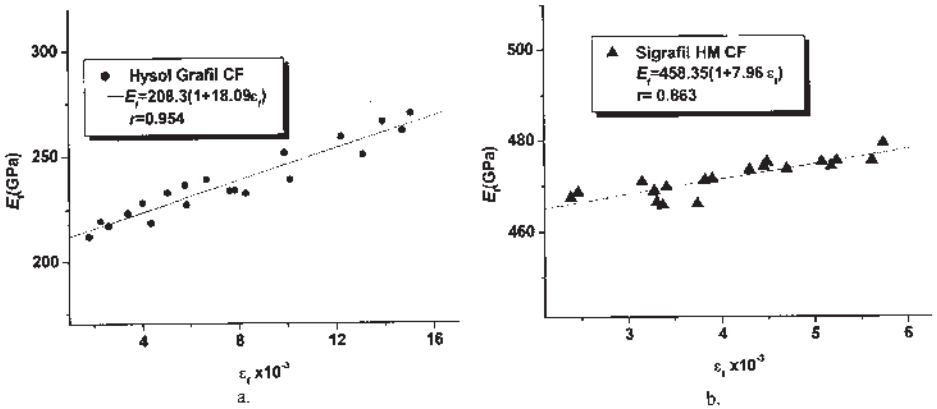

Fig. 3. Dependences of the tensile modulus on strain derived from single-filament tensile tests of Hysol XA–S (a) and Sigrafil HM carbon fibres (b).

vals employed for the different measurements of the mean modulus. For this reason, research in the field of the study of non-Hookean elasticity is directed to the correlation of non-linearity with the parameters of the carbon fibre structure determined by X-ray diffraction alaysis.

Loidl *et al.*[14] measured the Young modulus of nanocrystallites of carbon single filaments loaded in tension by *in-sity* X-ray microbeam diffraction. They concluded that the half-width of the 002 reflection decrease nearly linearly with increasing load. With the increasing tensile load, both the modulus and strain also increase. Hence, Loidl's conclusion is in full agreement with the above cited statement on the relation between the present *FWHM* and γ_C results.

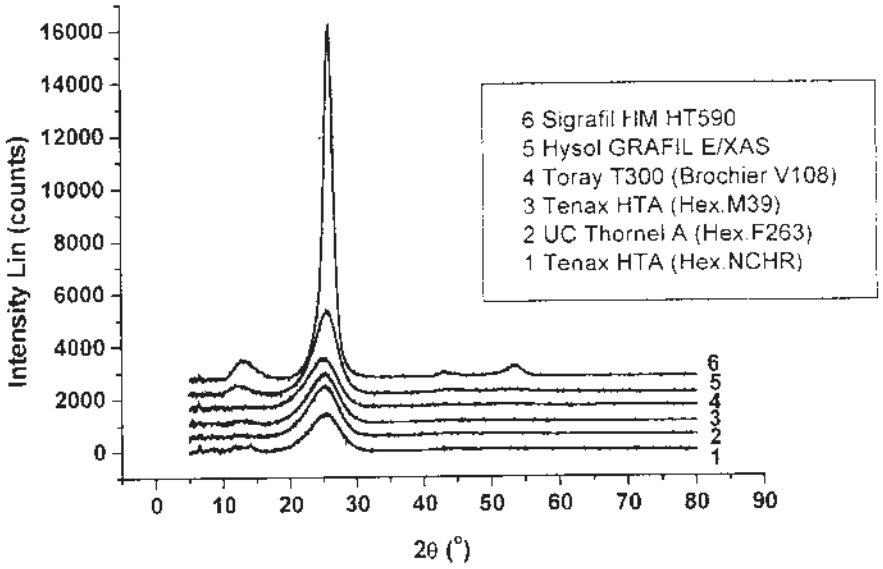

Fig. 4. X-Ray diffraction patterns of the tested fibres showing the (002) peak.

It is generally accepted that the variation in the Young modulus with strain is a measure of axial preferred orientation in carbon fibres.[13] However, it would be difficult to claim that the full width at half maximum intensity peak (*FWHM*) of the (002) peak is a measure of the preferred orientation of the crystallites along the fibre axis. The commonly accepted comprehension of a measure of the preferred orientation of the crystallites along the fibre axis is the full width at half maximum intensity of 002 reflection profile, obtained in an azimuthal scan.[15]

TABLE III. Characteristics of the profile of the (002) diffraction peak and the parameters of the carbon fibre structure

Material	2θ/°	*FWHM*/°	d_{002}/nm	L_c/nm
Graphite	25.31		0.335	
Sigrafil HM	26.00	1.69	0.341	4.77
Hysol XA-S	25.42	4.09	0.346	1.97
Tenax HTA	25.23	5.28	0.353	1.54
Torayca T 300	25.19	5.22	0.355	1.53
UC Thornel A	25.07	5.28	0.358	1.52

CONCLUSIONS

The stress-strain response of the tensile of carbon fibres and carbon fibre/epoxy resin unidirectional composites, with different fibre characteristics, were investigated and non-linear elastic behaviour of the carbon fibres was observed.

The lateral dimension of the crystallites and the interlayer spacing, as characteristics of the structure of carbon fibres, were determined by X-ray diffraction analysis of bundles of parallel fibres from the characteristics of the 002 peaks of the recorded diffractograms.

For the investigated carbon fibres and the unidirectional carbon fibre/epoxy resin composites, expressions for the dependence of the modulus on strain and the values of the parameter γ_{ax}, as a measure of non-linear elasticity, were derived.

Obtained γ_{ax} values were correlated to values of the mean modulus of the fibres, as well as to characteristics of the fibre crystallite structures. It was found that the value of the coefficient of non-linear elasticity of the fibre crystallite structures. It was found that the value of the coefficient of non-linear elasticity is lower in fibres of higher modulus and that it decreases with decreasing interlayer spacing of the fibre crystallite structure and the width at maximum intensity of the 002 reflection on X-ray diffractograms. Simultaneously, the apparent lateral dimension of the crystalites increases.

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ИЗВОД

НЕЛИНЕАРНО ЕЛАСТИЧНО ПОНАШАЊЕ КАРБОНСКИХ ВЛАКАНА РАЗЛИЧИТИХ СТРУКТУРНИХ И МЕХАНИЧКИХ КАРАКТЕРИСТИКА

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Проучавано је пет квалитета карбонских влакана различитих вредности модула, деформације кидања и параметара структуре. Нехуковско еластично понашање је проучавано одређивањем тангентних модула затезања и компресије као функције деформације из података изведених из стандардних тестова затезања и компресије и модификованих тестова савијања епрувета унидирекционих композита карбонска влакна/епоксидна смола. Зависност модула затезања од деформације угљаничних влакана извођена је из података добијених у тестовима затезања карбонских монофиламената. Утврђено је да је степен нелинеарне еластичности влакана мањи код влакана већег модула и да опада са смањењем растојања између графенских слојева и са порастом величине кристалита у карбонским влакнима. Пораст димензије кристалита у правцу управном на графенске равни одређен је на основу смањивања ширине на половини максималног интензитета рефлексије (002) равни на дифрактограмима.

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