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X-ray Studies on the Structure of Graphitic Carbons

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The disorder in the layer stacking of graphitic carbons is interpreted in terms of a statistical distribution for the positional correlation between adjacent layers and stacking faults for the second layer influence.

Experimental data show the variation of the root-mean-square values of the statistical distribution and the stacking fault parameters in the transition from non-graphitic carbons to graphite.

Introduction

The designation 'graphitic carbon' has been introduced by Franklin (1951) for those carbons in which three-dimensional correlations exist between the graphite layers. These correlations appear in the diffraction pattern as modulations of the intensity concentrated on all (*hk*) rods, whereas the 'non-graphitic carbon' shows modulations of the (00) rod only. The latter effect has been described by Biscoe & Warren (1942), who explain the absence of three-dimensional correlations by a random translation and rotation of the graphite layers ('turbostratic structure').

As a measure of the three-dimensional correlations, Franklin (1951) proposed the parameter p defined as the fraction of layers showing no three-dimensional correlations. Houska & Warren (1954) introduced the parameter P_1 defined as the probability for the occurrence of perfect correlation between two adjacent layers, a definition which has also been adopted by Maire & Méring (1957) and Méring & Maire (1960).

Franklin (1951) and Bacon (1951) have shown that there is a non-linear relationship between the average interlayer spacing and p. This non-linearity indicates that a model of ordered and disordered stacks of layers with unique interlayer spacings corresponding to each type of order is too simple. Franklin (1951) considered therefore different interlayer spacings at the limits between ordered and disordered regions.

Houska & Warren (1954), Maire & Méring (1957) and Méring & Maire (1960) have shown that there is a fluctuation of the interlayer spacing which can be assessed by studying the line profiles of the 00*l* bands. This fluctuation was attributed to a distribution of spacings in the disordered stacks of layers. The ordered stacks are considered to possess a unique interlayer spacing, that of perfect graphite, whereas the disordered stacks are supposed to have a constant average spacing.

The aim of this paper is to establish a more general model for the disorder in graphitic carbons and to show how the parameters based on this model can describe the transition from non-graphitic carbons to graphite.

Theoretical

Let the coherent scattering I be given by the basic equation of the kinematic scattering theory

$$I(\mathbf{s}) = \mathfrak{F}[\varrho^{*2}(\mathbf{r})], \tag{1}$$

where

$$\mathfrak{F} = \int_v \exp(2\pi i \mathbf{r}\mathbf{s})\, dv,$$

and

$$\varrho^{*2} = \int_v \varrho(\mathbf{y})\, \varrho(\mathbf{r}+\mathbf{y})\, dv_y\,.$$

$\mathbf{s}$ is the reciprocal space vector ($s = 2\sin\theta/\lambda$),
$\mathbf{r}$ the position vector in physical space,
$\varrho(\mathbf{r})$ the distribution of electron density, and
$\mathbf{y}$ an auxiliary variable in physical space.

In the case of a layer structure with identical layers, ϱ can be written as

$$\varrho = \varrho_l \star z = \int_v \varrho_l(\mathbf{y})\, z(\mathbf{r}-\mathbf{y})\, dv_y$$

where ϱ_l is the electron-density distribution within one layer and z the layer distribution. For the perfect hexagonal lattice of graphite one finds:

$$\varrho_l = \varrho_0 \star \sum_{p_1} \sum_{p_2} \delta(\mathbf{r} - p_1\mathbf{a}_1 - p_2\mathbf{a}_2) \tag{2}$$

where ϱ_l is given by the content of the unit cell of the layer structure and $\mathbf{a}_1$ and $\mathbf{a}_2$ the unit-cell vectors. δ is the Dirac delta distribution, and p_1 and p_2 are ensembles of integers.

The layer distribution is given by:

$$z = \sum_m \delta[\mathbf{r} - m\mathbf{a}_3 - (-1)^m(\mathbf{a}_1 - \mathbf{a}_2)/6]$$

where $\mathbf{a}_3$ is the interlayer spacing and m the running index of the layer.

For perfect graphite, or for imperfect graphite with disorder in ϱ_l and z independent of each other, one can write:

$$\varrho^{*2} = \varrho_l^{*2} \star z^{*2} \tag{3}$$

We shall adopt this relationship and assume that the disorder in ϱ_l, although probably correlated to the disorder in z, is very small compared with that in z.

For perfect hexagonal graphite one finds

$$\frac{1}{N}z^{*2}=\sum_m \delta(\mathbf{r}-2m\mathbf{a}_3)+\tfrac{1}{2}\sum_m \delta\,\{\mathbf{r}-(2m+1)\mathbf{a}_3\pm(\mathbf{a}_1-\mathbf{a}_2)/3\}$$

when N, the total number of layers, tends to infinity.

If we now consider a disordered graphite structure we can first think of faults in the stacking of the layers which are due to the occurrence of *ABC* sequences. This means that $(1/N)z^{*2}$ can still be expressed by a regular array of delta distributions as shown in Fig. 1, but each delta distribution has a weight $A_{m,n}$ which is governed by the number of stacking faults and their distribution in space. It is, however, obvious that the disorder in graphitic carbons cannot be described by stacking faults alone. In order to explain the diffuseness of (hkl) lines for $(h-k)/3$ integral, one has to consider probability distributions around the ideal positions of the layers. We thus replace the delta distributions in $(1/N)z^{*2}$ by distributions $h_{m,n}$ of finite dimensions as shown in Fig. 1.

$(1/N)z^{*2}$ can thus be written generally as

$$\frac{1}{N}z^{*2}=\sum_m\sum_n A_{m,n}h_{m,n}\{\mathbf{r}-m\mathbf{a}_3-n(\mathbf{a}-\mathbf{a}_{12})/3\} \tag{4}$$

with the conditions $\sum_n A_{m,n}=1$ and $A_{m,n}=0$ if $(m+n)$ is odd or if $n>m$. The distributions $h_{m,n}$ are normalized

$$\int_v h_{m,n}\,dv=1\,.$$

Considering equations (1) and (3) one can write

$$I(\mathbf{s})=|F_l^2|\,.\,|Z^2| \tag{5}$$

when $F_l=\mathfrak{F}(\varrho_l)$ and $Z=\mathfrak{F}(z)$. From equation (4) follows

$$\frac{1}{N}|Z^2|=\sum_m\sum_n A_{m,n}\,H_{m,n}\exp\,[2\pi i\{m\mathbf{a}_3+n(\mathbf{a}_1-\mathbf{a}_2)/3\}\mathbf{s}] \tag{6}$$

when $H_{m,n}=\mathfrak{F}(h_{m,n})$.

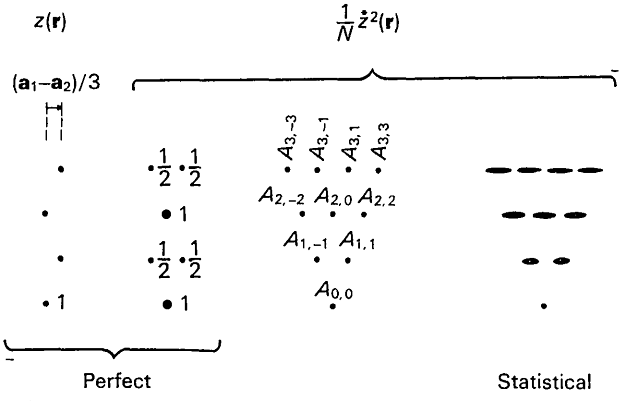

Fig. 1. Layer distribution $z(\mathbf{r})$ and layer correlation function $(1/N)z^{*2}(\mathbf{r})$ for perfect and imperfect graphite.

Owing to the two-dimensional periodicity in ϱ_l, F_l is different from zero only for $\mathbf{s}=(h_1b_1,\ h_2b_2,\ s_3)$, where $\mathbf{b}_1$ and $\mathbf{b}_2$ are the reciprocal unit-cell vectors of the layer structure, h_1 and h_2 integral numbers and s_3 the component of $\mathbf{s}$ in the $\mathbf{a}_3$ direction. $|Z^2|$ is thus only of interest in these regions, which are the (hk)-rods discussed by Biscoe & Warren (1942). Apart from the effect of the atomic scattering factor, F_l is constant along s_3 in each rod; the modulation of the intensity is thus given only by $|Z^2|$. As already known from the calculations of stacking faults in cubic and hexagonal metals, there are two kinds of modulation of these rods. For $(h_1-h_2)/3$ integral, one finds:

$$\frac{1}{N}|Z^2|=\sum_m\sum_n H_{m,n}A_{m,n}\exp\,(2\pi i m a_3 s_3) \tag{7}$$

and $(h_1-h_2)/3$ non-integral

$$\frac{1}{N}|Z^2|=\sum_m\Big[\sum_{\substack{n=0\\(\text{mod. }3)}}A_{m,n}H_{m,n}-\tfrac{1}{2}\sum_{\substack{n=1,2\\(\text{mod. }3)}}A_{m,n}H_{m,n}\Big]\,.\,\exp\,(2\pi i m a_3 s_3). \tag{8}$$

At this stage we introduce two assumptions:

1. The distributions $h_{m,n}$ depend only on m, the number of interlayer spacings which separate any pair of layers.
2. These distributions h_m depend only on interactions between adjacent layers; this means $h_m=h^{*|m|}$ where $\bigstar\,|m|$ stands for $|m|$ times convoluted and h stands for the next neighbour distribution.

Equation (7) becomes then:

$$\frac{1}{N}|Z^2|=\mathrm{Re}\,\frac{1+H\exp\,(2\pi i a_3 s_3)}{1-H\exp\,(2\pi i a_3 s_3)} \tag{9}$$

where Re stands for 'real part'.

This intensity distribution is that of a 'paracrystalline lattice factor' as described by Hosemann & Bagchi (1962) which, for a 'well-behaved' distribution h, shows maxima at s_3 approximately equal to integral multiples of $1/a_3$; the integral width B of the maxima is approximately:

$$B\simeq\frac{1}{2a_3}(1-|H|)\,. \tag{10}$$

To simplify equation (8) we make use of the approach given by Wilson (1942) in his calculations on stacking faults in hexagonal cobalt. Considering the summations over n one finds that P_m, defined as the probability of finding a layer in an equivalent position to any layer m spacings apart, is given by:

$$P_m=\sum_{\substack{n=0\\(\text{mod. }3)}}A_{m,n}.$$

Following Wilson (1942), we can write

$$P_m=\tfrac{1}{3}+\sum_i C_i x_i^m$$

where

$$x_1 = \tfrac{1}{2}(-\alpha + \sqrt{4 - 8\alpha + \alpha^2})$$
$$x_2 = -\tfrac{1}{2}(\alpha + \sqrt{4 - 8\alpha + \alpha^2})$$
$$C_1 = \tfrac{1}{3}(1 - (1-\alpha)/\sqrt{4 - 8\alpha + \alpha^2})$$
$$C_2 = \tfrac{1}{3}(1 + (1-\alpha)/\sqrt{4 - 8\alpha + \alpha^2}) \,.$$

In the case of graphite, α is the fractional number of rhombohedral stacking faults.

Equation (8) becomes thus

$$\frac{1}{N}\,|Z^2| = \tfrac{3}{2} \sum_i C_i \,\mathrm{Re}\, \frac{1 + x_i H \exp(2\pi i a_3 s_3)}{1 - x_i H \exp(2\pi i a_3 s_3)} \,. \tag{11}$$

For α smaller than 0·5, this intensity distribution shows two kinds of maxima related to the even and the odd values of the index l for hexagonal graphite. Provided that these maxima do not overlap too strongly, the integral widths are approximately

$$B_{\mathrm{even}} \simeq \frac{1}{2a_3}(1 - x_1|H|) \tag{12}$$

$$B_{\mathrm{odd}} \simeq \frac{1}{2a_3}(1 + x_2|H|). \tag{13}$$

We have so far considered lattices of infinite extension. To introduce finite dimensions we assume that no correlation exists between the disorder and the crystallite size. In this case, the intensity distribution I_L for an ensemble of crystallites of finite size (L) is obtained by the convolution of the intensity distribution for infinite size I_∞ with a distribution Φ_L which represents the effect of the shape functions (Ewald, 1940) of the ensemble of crystallites in reciprocal space.

$$I_L = I_\infty \bigstar \Phi_L \,.$$

The peaks in I_∞ are thus broadened further by the effect of finite dimensions, but this broadening is the same for all peaks.

Experimental

Six powder samples of organic compounds graphitized at different temperature have been measured with a Philips diffractometer, filtered Cu radiation and a xenon-filled proportional counter or Mo radiation and a scintillation counter, and pulse-height discrimination. The starting materials and the heat-treatment temperatures were the following:

Acenaphthylene; 2000, 2500, 3000 °C
Bifluorenyl; 2000, 3000 °C
Tetrabenzonaphthalene; 3000 °C.

The line profiles of the 00l, 10l, 11l, and 30l lines were measured as far as they could be reasonably separated from adjacent lines and the diffuse background, and appropriate corrections were applied for instrumental broadening. The evaluation was carried out in two ways. First, the intensity distribution along the (hk)-rods was reconstructed with the use of a plot of $ss_3\,I(s_3)$ *versus* f_c^2 as described by Franklin (1951). Secondly, the integral line width along s was converted into that along s_3 using the tangent plane approximation (von Laue, 1926) and the relations between integral widths of projections as described in the Appendix. The latter method proved to be a practical way of eliminating the finite width of the rod as indicated by the hk0 line profile provided the hkl lines are not too diffuse. The results were interpreted using equations (9) and (11) for a comparison of observed and calculated intensity distributions, and equations (10), (12) and (13) for the evaluation of integral widths of relatively sharp lines. The effect of crystallite size leads to appreciable corrections only for the 00l lines of lower order. Only the most ordered graphitized sample (acenaphthalene 3000 °C) showed well separated 30l lines, notably 304, whereas for all the other samples the modulations of the 30l rod could not be reconstructed unambiguously owing to the considerable overlap with modulation from other rods, especially 11l and 00l. This is unfortunate since it limits the information on $H(\mathbf{s})$ to a few values along 00l, 10l and 11l for most of the samples.

The average interlayer spacing was obtained from corrected peak positions of 00l lines of higher order since it was found that the position of the 002 line is affected by too many errors due to the diffractometer geometry as well as the absorption correction.

Results and discussion

Although the information on $H(\mathbf{s})$ is limited to a few values only, it appears that Franklin's approach $H = 1 - p$ for $(h+k)$ non-zero is not a good approximation since it implies identical intensity distributions along s_3 for $(h-k)/3$ integral on one hand and $(h-k)/3$ non-integral on the other, which has not been found. The experimental results are better approached with an H of the form:

$$H(\mathbf{s}) = \exp\left[-2\pi^2(\Delta_{12}^2 s_{12}^2 + \Delta_3^2 s_3^2)\right]$$
$$s_{12} = |\mathbf{s}_1 + \mathbf{s}_2| \,,$$

which means that the next neighbour distribution h can be represented by a three-dimensional Gaussian distribution with mean square deviations Δ_{12}^2 parallel and Δ_3^2 perpendicular to the layer planes. The latter value is obtained from the 00l lines; with the knowledge of Δ_3, Δ_{12} can be obtained from the lines $(h-k)/3$ integral, and with the knowledge of both values, α is obtained from the lines $(h-k)/3$ non-integral.

The values obtained in this way are shown in Figs. 2, 3, and 4. Furthermore, the values given by other authors for p or P_1 and the disorder in the $\mathbf{a}_3$ direction as well as some line profiles of 10l bands given by Franklin (1951) have been reinterpreted to yield the proposed parameters and are plotted together with the results of the present work.

The most striking feature is the perfection of the linear relationship between Δ_{12}^2 and $\bar{a}_3$ (Fig. 2) which is found to be

$$\bar{a}_3 = 3{\cdot}353 + 0{\cdot}425\,\Delta_{12}^2\ (\text{Å})\,. \qquad (15)$$

This result is rather unexpected, since no obvious reason can be seen for the mean square deviation parallel to the layer planes to be proportional to the average interlayer spacing. The range of validity of the linear relationship as well as the small scatter of the values measured by different authors seems to indicate, however, that this relationship is a genuine feature. It is interesting to note that with this model of disorder in graphitic carbons the average interlayer spacing of 3·44 Å is no longer a limiting value as in the case of the Franklin model, but merely an interlayer spacing for which Δ_{12} has a value which does not produce modulations of the (11) rod strong enough to be detected by the usual techniques. If one extrapolates to $\bar{a}_3 = 3{\cdot}44$ Å in Fig. 2, one obtains $\Delta_{12} = 0{\cdot}45$ Å which is still small compared with the unit-cell dimension in the $(\mathbf{a}_1 - \mathbf{a}_2)$ direction. Thus a carbon with the 'turbostratic' value of the inter-layer spacing, 3·44 Å, may yet possess partial correlation.

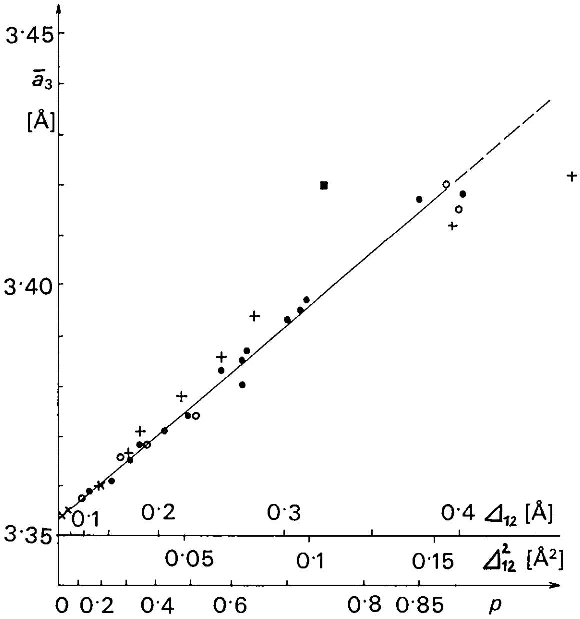

Fig. 2. Average interlayer spacing $\bar{a}_3$ as function of the mean square displacement $\Delta_{12}{}^2$ of adjacent layers parallel to the layer planes. Present work ○. Values calculated from data of: Franklin (1951) ●, Bacon (1951) ×, Houska & Warren (1954) ■, Méring & Maire (1960) +.

A plot of Δ_3 *versus* $\bar{a}_3$ (Fig. 3) does not reveal a simple relationship between these two parameters. The values scatter relatively strongly, and the scatter does not seem to be due to experimental errors or differences in the methods of evaluation only. A comparison of the Δ_3 values with the corresponding values of $\bar{a}_3 - a_{3\,\mathrm{min}}$ (Fig. 3, broken line) shows that, over a large range, the r.m.s. deviations around $\bar{a}_3$ are far larger than the difference between $\bar{a}_3$ and the possible minimum value of a_3. This result seems to indicate that the disorder is not simply due to faults in the stacking of relatively free layers since in that case one would expect Δ_3 to be proportional to $\bar{a}_3 - a_{3\,\mathrm{min}}$. To explain the results one might think of special kinds of disorder effect like those due to dislocations, cross-links and, perhaps, tetrahedral carbon atoms. It is possible that the scatter of the experimental data is partly due to basic differences in the kinds of disorder present in the various samples.

For α, the fraction of rhombohedral stacking sequences, only a few values are available, which do not allow a detailed discussion of the relationship between this parameter and $\bar{a}_3$. It seems, however, that a preference for hexagonal stacking sequences is developed only at $\bar{a}_3$-values lower than about 3·38 Å, and that even relatively well ordered graphitic carbons as, for example, the 3000 °C sample of acenaphthalene, contain still appreciable amounts of rhombohedral stacking sequences.

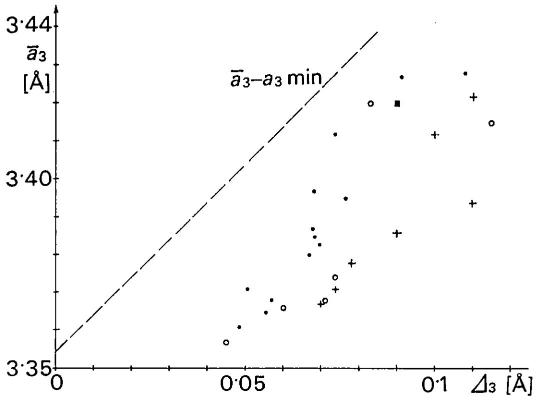

Fig. 3. Average interlayer spacing $\bar{a}_3$ as function of the r.m.s. displacement Δ_3 of adjacent layers normal to the layer planes. Present work ○. Values calculated from data of Franklin (1951) ●, Houska & Warren (1954) ■, Méring & Maire (1960) +. Broken line: $\bar{a}_3 - a_{3\,\mathrm{min}}$.

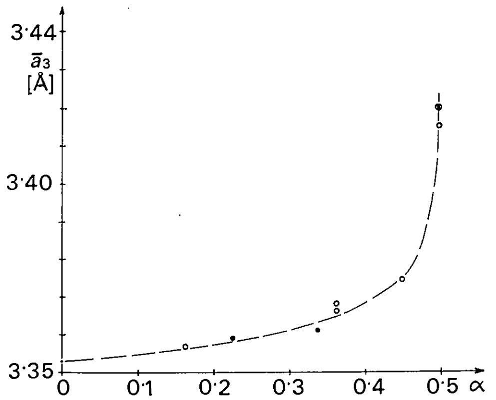

Fig. 4. Average interlayer spacing as function of the fraction of rhombohedral stacking sequences α. Present work ○. Values calculated from data of Franklin (1951) ●, Houska & Warren (1954) ■.

Summing up one can state that the relatively simple model for the structure of graphitic carbons proposed in this work enables one to make a consistent interpretation of the interference effects which can be assessed by powder techniques. It is possible that a refinement could be obtained by studying oriented samples.

The author is indebted to Drs H. Tompa and R. Gevers for stimulating discussions during the course of this work, and to Mr J. P. Pauwels for technical assistance.

APPENDIX

The integral width of projections of a multi-dimensional distribution

A problem frequently encountered in the evaluation of line widths is the calculation of the integral width of the projection of a three-dimensional distribution onto any given direction from the line widths of projections onto other directions. A general solution of this problem can be found as follows:

Let $\Phi(s)$ be a spherically symmetrical distribution and $\varphi(r)$ its Fourier transform. The content of s-space is then given by:

$$\int_v \Phi dv_s = \varphi(0) = w\,.$$

Let Φ be such that w is real and positive-definite.

The projection of Φ on to a line, denoted $\{\Phi\}$, is given by the one-dimensional Fourier transform of φ, from which follows:

$$\{\Phi\}_{(0)} = \int_{-\infty}^{\infty} \varphi(r)dr = u\,. \tag{16}$$

The integral width of $\{\Phi\}$ is defined as

$$B = \int_{-\infty}^{\infty} \{\Phi\}ds/\{\Phi\}_{(0)} = w/u\,.$$

For B to be meaningful, u has to be positive-definite.

We now replace the variable s in $\Phi(s)$ by $|T\mathbf{s}|$ where T is a non-degenerate tensor the determinant of which is considered to have a positive-definite value v.

We now define the distribution $\Phi_T(\mathbf{s})$ by:

$$\Phi_T(\mathbf{s}) = v\Phi(|T\mathbf{s}|)\,.$$

According to Fourier transform theory one finds:

$$\mathfrak{F}(\Phi_T) = \varphi[|(T^{-1})'\mathbf{r}|] = \varphi_T(\mathbf{r}) \tag{17}$$

where $(T^{-1})'$ is the transposed inverse of tensor T.

With this definition of Φ_T one finds:

$$\int_v \Phi dv_s = \int_v \Phi_T dv_s\,.$$

We now consider the projection of Φ_T onto a line the direction of which is defined by the unit vector $\mathbf{e}_j$ and denote this projection by $\{\Phi_T\}_j$. As for equation (16) one finds

$$\{\Phi_T\}_j(0) = \int_{-\infty}^{\infty} \varphi_T(r_j)dr_j \tag{18}$$

where

$$\mathbf{r}_j = r_j \,.\, \mathbf{e}_j\,.$$

Using equation (17) one obtains:

$$\varphi_T(r_j) = \varphi[|(T^{-1})'\mathbf{e}_j|r_j]$$

After a change of variables in (18), one finds:

$$\{\Phi_T\}_j(0) = u/|(T^{-1})'\mathbf{e}_j|$$

The integral width B_j of a projection of Φ_T onto a line in the direction $\mathbf{e}_j$ is thus

$$B_j = B\,.\,|(T^{-1})'\mathbf{e}_j|\,.$$

Let T, for example, be given by

$$T = \begin{pmatrix} k_1^{-1} & 0 & 0 \\ 0 & k_2^{-1} & 0 \\ 0 & 0 & k_3^{-1} \end{pmatrix}$$

and

$$\mathbf{s} = s_1\mathbf{e}_1 + s_2\mathbf{e}_2 + s_3\mathbf{e}_3$$

where $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ define a rectangular system of coordinates. If the integral widths of the projections of Φ_T on to the principal axis are denoted B_1, B_2 and B_3, one finds $B_1 = Bk_1$, $B_2 = Bk_2$ and $B_3 = Bk_3$. The integral width of the projections in an arbitrary direction $\mathbf{e}_j$ is then given by:

$$B_j = \sqrt{j_1^2B_1^2 + j_2^2B_2^2 + j_3^2B_3^2}$$

where j_1, j_2 and j_3 are the components of $\mathbf{e}_j$ in the directions $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$.

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