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PAACFIT: a program for analysing positron annihilation angular correlation spectra

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PAACFIT: a Program for Analysing Positron
        Annihilation
        Angular Correlation Spectra

by

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CONTENTS

1. INTRODUCTION

In a measurement of angular correlation of positron annihilation, a spectrum is obtained which in many cases may be assumed to be a sum of central Gaussian curves, symmetrical side-peak Gaussians, and a background. The computer program PAACFIT was developed to perform the analysis necessary to extract the peak parameters from such spectra.

2. Mathematical Model of the Spectrum

The measured spectrum is first analysed by the processing and editing code PAAC. This gives an output spectrum

$$(\theta_i, \ y_i, \ \sigma_i) \quad i = 1, \ \ldots, n \tag{1}$$

on punched cards, which is fed as input to PAACFIT. θ_i are the angles (in mrad); in general they will not be equidistant.
y_i are the counts corrected for background, and σ_i associated standard deviations. We want to make a least-squares fit of a mathematical model

$$f(\theta) = \sum_{j=1}^{k_c} C_j \exp[-p_j^2 \ (\theta - \theta_0)^2] + \tfrac{1}{2} \sum_{j=1}^{k_s} S_j \{ \exp[-q_j^2 \ (\theta - \theta_0 + \omega_j)^2] + \exp[-q_j^2$$
$$(\theta - \theta_0 - \omega_j)^2] \} \tag{2}$$

to the spectrum (1). The model has k_c central peaks and k_s side peak pairs. θ_0 is the angular position of the central peaks, and ω_j is the angular distance from sidepeak pair no. j to θ_0. The absolute intensity of a central peak is

$$I_j^c = \sqrt{\pi} \ \frac{C_j}{P_j} \tag{3}$$

and of a sidepeak pair:

$$I_j^s = \sqrt{\pi} \ \frac{S_j}{q_j} \tag{4}$$

The sharpness parameters p_j and q_j are related to the fwhm by

$$\text{fwhm} \ j^c = \frac{c}{P_j} \quad \text{and fwhm } j^s = \frac{c}{q_j} \tag{5}$$

with $c = 2\sqrt{\log 2}$. In particular, (2) degenerates to a sum of central Gaussians if $k_s = 0$. Of the parameters in (2), θ_0 is always adjustable and ω_j always fixed. Some or all of the remaining parameters are adjustable, depending on the prescribed constraints (see eq. (13) and (14)).

3. The Least-Squares Technique

In formulating the least-squares condition, one could compare the y_i from the spectrum (1) simply to the model value $f(\theta_i)$ obtained from (2). However, some computational advantages are gained (simpler handling of the constraints (14) and (17) and of the statistics), if we replace $f(\theta_i)$ by an interval average

$$f_i = \frac{1}{V_{i+1} - V_i} \int_{V_i}^{V_{i+1}} f(\theta)d\theta \tag{6}$$

The new angles V_i are related to θ_i by

$$
\left.
\begin{array}{l}
V_1 = \frac{3}{2}\theta_1 - \frac{1}{2}\theta_2 \\[2mm]
V_i = \frac{1}{2}(\theta_{i-1} + \theta_i), \quad i=2, \ldots, n \\[2mm]
V_{n+1} = \frac{3}{2}\theta_n - \frac{1}{2}\theta_{n-1}
\end{array}
\right\} \tag{7}
$$
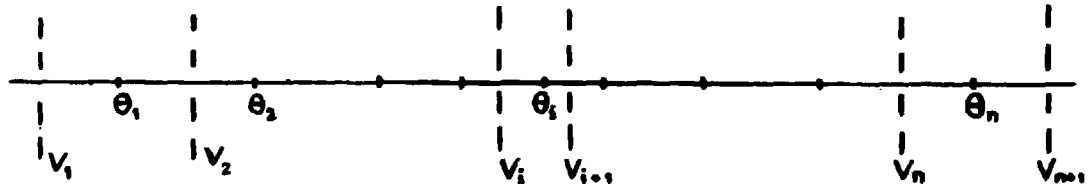
The expression (6) for $f_i = f_i(b)$, which depends on the parameter vector b, turns out to be

$$f_i(b) = \frac{1}{\Delta V_i} \left(\sum_{j=1}^{k_c} \Delta C_{ji} + \sum_{j=1}^{k_s} \Delta S_{ji} \right) \tag{8}$$

Δ is the difference operator with respect to index i; further,

$$C_{ji} = \frac{I_j^c}{2} \; erf\, [\, p_j(V_i-\theta_0)\,] \tag{9}$$

$$\text{and} \quad S_{ji} = \frac{I_j^s}{4}\left\{ \; erf[\; q_j(V_i-\theta_0+\omega_j)\,] + erf\,[\,q_j(V_i-\theta_0-\omega_j)\,]\,\right\} \tag{10}$$

b has $2(k_c+k_s)+1$ components; k_c+k_s intensity parameters, k_c+k_s sharpness parameters, and θ_0:

$$I_1^c, \; \ldots \; , \; I_{k_c}^c \; ; \; I_1^s, \; \ldots \; , \; I_{ks}^s \; ;$$

$$P_1, \; \ldots \; , \; P_{kc}; \quad q_1, \; \ldots \; , \; q_{ks}; \quad \theta_0 \tag{11}$$

According to the least-squares principle we shall find parameters (11) so that

$$\phi = \sum_{i=1}^{n} w_i\,[\,y_i - f_i\,(b)\,]^2 \tag{12}$$

where w_i are weights of the data points, becomes minimum. The parameters may vary without any restrictions, or, alternatively, constraints of different types can be imposed on them. In this work permissible constraints will be of the following two types:

(a) A fixed value is assigned to one or more of the sharpness parameters p and q (or the corresponding fwhm)

(13)

(b) m linear combinations of the (absolute) intensities equal zero ($m< k_c+k_s$) (14)

If we define the relative intensity to be

$$i_j^c = \frac{I_j^c}{I} \quad \text{for a central peak}$$

$$\left.\begin{array}{l} \\ \\ \end{array}\right\} \tag{15}$$

$$\text{and} \quad i_j^s = \frac{I_j^s}{I} \quad \text{for a sidepeak pair} \qquad ,$$

where I is the total intensity of all peaks,

$$I = \sum_{j=1}^{k_c} I^c_j + \sum_{j=1}^{k_s} I^s_j \qquad , \qquad (16)$$

then we observe that:

$$\text{relative intensity} = q_\ell = \text{constant} \quad (\ell = 1, \ldots, m) \qquad (17)$$

is a set of constraints that is a special case of (b) above.
Constraints of type (a) are realized simply by deleting the
fixed p and q from the parameter list. The vector of adjustable
parameters then becomes:

$$b = (I^c_1, \ldots, I^c_{k_c}, I^s_1, \ldots, I^s_{k_s}, P_1, \ldots, P_{k_{cv}}, q_1, \ldots, q_{k_{sv}}, \theta_0)^T \qquad (18)$$

where k_{cv} and k_{sv} are the number of central peaks and sidepeak
pairs with variable fwhm, and T stands for transpose.

Our model (8) is linear in the absolute intensities, but non-
linear in the peak sharpnesses and in θ_0. Marquardt's iteration
technique [11] is used in the subspace of nonlinear parameters [21].
The same method was applied successfully in the program POSITRONFIT[3,4],
which analyses position lifetime spectra. The iterations start from
a guessed initial set of the nonlinear parameters and are terminated
when Φ has proved to be stationary. A detailed description of the
applied ideas is given in an earlier report[21] that is the basis of
the subsequent analysis. The decomposition of the parameter vector
in its linear and nonlinear components reads

$$b = \begin{bmatrix} \alpha \\ \beta \end{bmatrix} \text{ with}$$

$$\alpha = (I^c_1, \ldots, I^c_{k_c}; I^s_1, \ldots, I^s_{k_s}) \; T \qquad (19)$$

and

$$\beta = (P_1, \ldots, P_{k_{cv}}; q_1, \ldots, q_{k_{sv}})^T ; \qquad (20)$$

then the model f_i (b) is linear in α and nonlinear in β. The dimen-
sion of α is $k\alpha = k_c + k_s$, and that of β is $k_\beta = k_{cv} + k_{sv} + 1$.

Now (8) can be written

$$f_i = \sum_{j=1}^{k_\alpha} \alpha_j \, u_{ij} \tag{21}$$

with $u_{ij} = u_{ij}(\beta)$, and the formulae from the semi-linear least-squares analysis[21] can be used. Let $\alpha = \alpha(\beta)$ be the solution of α conditioned on β, i.e., the α-vector (cf.(19)) that for a fixed β (cf. (20)) minimizes Φ(cf. (12)) under the possible constraints (13), (14), (17). It can be shown[21] that α is determined by solution of the linear system

$$
\begin{array}{c} k_\alpha \\ m \end{array}
\overset{\begin{array}{cc} k_\alpha & m \end{array}}{\left[\begin{array}{c|c} C & K^T \\ \hline K & \Theta \end{array}\right]}
\left[\begin{array}{c} \alpha \\ \hline \mu \end{array}\right]
=
\left[\begin{array}{c} \gamma \\ \hline \Theta \end{array}\right]
\tag{22}
$$

The submatrix C has the elements $c_{jj_1} = \sum_i w_i \, u_{ij} \, u_{ij_1}$, and the vector γ the components $\gamma_j = \sum_i w_i \, y_i \, u_{ij}$. Θ is here a zero matrix (or vector). K contains the k_α coefficients of each of the m constraints of type (14); these constraints read $K\alpha = \Theta$. In the special case (17) the coefficients of K turn out to be

$$k_{\ell j} = \delta_{jj_\ell} - q_\ell \qquad (j=1,\ldots,\, k_\alpha; \quad \ell=1,\ldots,m) \tag{23}$$

δ_{ij} is the Kronecker delta, and j_ℓ $(1 \le j_\ell \le k_\alpha)$ is the term no. (cf. (19)) associated with constraint no ℓ. μ is the vector of Lagrangian multipliers appropriate for the present constraint-minimum problem; no explicit use will be made of μ.

In the nonlinear β- iterations we shall need the quantities

$\frac{\partial f_i}{\partial \beta_{j'}}$; as $\alpha = \alpha(\beta)$, these can be expressed by

$$\frac{\partial f_i}{\partial \beta_{j'}} = \sum_{j_1=1}^{k_\alpha} \left[\frac{\partial \alpha_{j_1}}{\partial \beta_{j'}} \, u_{ij_1} + \alpha_{j_1} \frac{\partial u_{ij_1}}{\partial \beta_{j'}} \right]$$

$$(j' = 1, \ldots, k_\beta) \qquad (24)$$

Hence, to evaluate $\frac{\partial f_i}{\partial \beta_j'}$, $\frac{\partial \alpha_j}{\partial \beta_j'}$ has to be evaluated, and this can be done by taking the derivative of both members of (22) with respect to $\beta_{j'}$. The result can be expressed as a matrix equation

$$
\begin{array}{c}
 \quad k_\alpha \qquad m \qquad k_\beta \qquad\qquad k_\beta \\[4pt]
\begin{array}{c} k_\alpha \\[20pt] m \end{array}
\left[\begin{array}{c|c} C & K^T \\ \hline K & \Theta \end{array} \right]
\left[\begin{array}{c} A' \\ \hline M' \end{array} \right]
=
\left[\begin{array}{c} E \\ \hline \Theta \end{array} \right]
\end{array}
\qquad (25)
$$

A' contains the unknown derivatives $a_{jj'} = \frac{\partial \alpha_j}{\partial \beta_{j'}}$. E has the elements:

$$
e_{jj'} = \sum_i w_i \left[\frac{\partial u_{ij}}{\partial \beta_{j'}} (y_i - f_i) - u_{ij} \sum_{j_1=1}^{k_\alpha} \alpha_{j_1} \cdot \frac{\partial u_{ij_1}}{\partial \beta_{j'}} \right] \qquad (26)
$$

M' contains the derivatives of the Lagrangian multipliers and is not used explicitly. In specializing (26) to the present model, it is practical to introduce some abbreviations:

$$ t_i = V_i - \Theta_0 $$

$$ ER_{ij} = \tfrac{1}{2} \Delta erf \ (p_j t_i)/\Delta V_i $$

$$ EX_{ij} = \frac{1}{\sqrt{\pi}} \Delta \exp (-p_j^2 t_i^2)/ \Delta V_i $$

$$ TEX_{ij} = \frac{1}{\sqrt{\pi}} \Delta (t_i \exp (-p_j^2 t_i^2))/\Delta V_i \qquad (27) $$

$$ ERS_{ij} = \tfrac{1}{4} \Delta \left\{ erf [q_j(t_i + \omega_j)] + erf[q_j(t_i - \omega_j)] \right\}/\Delta V_i $$

$$EXS_{ij} = \frac{1}{2\sqrt{\pi}} \Delta \left\{ \exp\left[-q_j^2 (t_i + \omega_j)^2 \right] + \exp\left[-q_j^2 (t_i - \omega_j)^2 \right] \right\} / \Delta V_i$$

$$TEXS_{ij} = \frac{1}{2\sqrt{\pi}} \Delta \left\{ (t_i + \omega_j) \exp\left[-q_j^2 (t_i + \omega_j)^2 \right] + (t_i - \omega_j) \exp\left[-q_j^2 (t_i - \omega_j)^2 \right] \right\} / \Delta V_i$$

The expression for u_{ij} becomes:

$$j \leq k_c: \quad u_{ij} = \frac{\Delta C_{ji}}{\Delta V_i \cdot I_j^c} = ER_{ij}$$

$$(28)$$

$$k_c < j \leq k_c + k_s: \quad u_{ij} = \frac{\Delta S_{joi}}{\Delta V_i \cdot I_{jo}^s} = ERS_{ijo} \quad (j_o = j - k_c)$$

The expression in brackets in (26), h_i, can now be evaluated.
We find:

1) $j \leq k_c$, $j' \leq k_{cv}$

$$(29)$$

$$h_i = TEX_{ij} \cdot \left[\delta_{jj'} (y_i - f_i) - \alpha_{j'} ER_{ij} \right]$$

2) $j \leq k_c$, $k_{cv} < j' \leq k_{cv} + k_{sv}$ $(j'' = j' - k_{cv})$

$$(30)$$

$$h_i = - \alpha_{k_c + j''} ER_{ij} TEXS_{ij''}$$

3) $j \leq k_c$, $j' = k_\beta$

$$h_i = - \beta_j EX_{ij} (y_i - f_i) + ER_{ij} \left\{ \sum_{j_1=1}^{k_c} \alpha_{j_1} P_{j_1} EX_{ij_1} + \sum_{j_1=1}^{k_s} \alpha_{k_c + j_1} Q_{j_1} EXS_{ij_1} \right\} \quad (31)$$

4) $k_c < j \leq k_c + k_s$ $(j_o = j - k_c)$, $j' \leq k_v$.

$$h_i = - ERS_{ijo} \alpha_{j'} TEX_{ij'} \qquad (32)$$

5) $k_c < j \leq k_c + k_s$ $(jo = j - k_c)$, $k_{cv} < j' \leq k_{cv} + k_{sv}$ $(j'' = j' - k_{cv})$

$$h_i = TEXS_{ij''} [\ \delta_{joj''} (y_i - f_i) - \alpha_{k_c + j''}\ ERS_{ijo}\ ] \tag{33}$$

6) $k_c < j \leq k_c + k_s$ $(jo = j - k_c)$, $j' = k_\beta$

$$h_i = -q_{jo}\ EXS_{ijo}\ (y_i - f_i) + ERS_{ijo} \left\{ \sum_{j_1=1}^{k_c} \alpha_{j_1} P_{j_1}\ EX_{ij_1} + \sum_{j_1=1}^{k_s} \alpha_{k_c + j_1}\ q_{j_1}\ EXS_{ij_1} \right\} \tag{34}$$

Now we consider the Marquardt procedure [1],[2] in the space of

$$\beta = (p_1, \ldots, p_{k_{cv}}, q_1, \ldots, q_{k_{sv}}, \theta_0)^T = (p, q, \theta_0)^T \tag{35}$$

for minimizing $\phi = \sum_i w_i [y_i - f(x_i; \beta)]^2$ for variation of β without constraints $[f(x_i; \beta)$ is an abbreviation for $f(x_i; \alpha(\beta); \beta).]$

This method is derived from the familiar Gauss-Newton iteration technique by addition of positive terms to the elements of the diagonal of the matrix A corresponding to the system of "normal equations"

$$Ad = g \tag{36}$$

A stands for $P^T W P$. P, W, and g have the elements

$$P_{ij} = \frac{\partial f_i}{\partial \beta_j}\ ,\ w_{ii'} = \delta_{ii'}\ \text{and}$$

$$g_j = \sum_{i=1}^{n} w_i (y_i - f_i) \frac{\delta f_i}{\delta \beta_j}\ (j \leq k_\beta).$$

$\beta = (\beta_1, \ldots, \beta_{k_v})^T$ refers to a guessed or previously iterated non-linear parameter vector. d is the resulting correction vector to β. The Marquardt modification of (36) reads

$$(A + \kappa D^2) d = g \tag{37}$$

D is a diagonal matrix with its elements scaled according to A, $d_{ij} = \delta_{ij} (a_{ij})^{\frac{1}{2}}$. The additional parameter, κ, that is at our disposal provides for interpolation between the Gauss-Newton method

($\mathbf{m}$=o) and a gradient-like method ($\mathbf{m}$ = ∞). Details in Marquardt's iterative strategy are given elsewhere [1,2,3].

To set up eq. (37) we shall need the elements $p_{ij} = \frac{\partial f_i}{\partial \beta}{}_j$ of P. From $\alpha = \alpha(\beta)$ is obtained

$$\frac{\partial f_i}{\partial \beta_{j'}} = \sum_{j_1=1}^{k_\alpha} \left[\frac{\partial \alpha_{j_1}}{\partial \beta_{j'}} u_{ij_1} + \alpha_{j_1} \frac{\partial u_{ij_1}}{\partial \beta_{j'}} \right] (j' \leq k_\beta) \tag{38}$$

The derivatives $\frac{\partial u_{ij}}{\partial \beta_{j'}}$ are given by:

1) $j \leq k_c$, $j' \leq k_{cv}$: $\delta_{jj'} \, TEX_{ij}$

2) $j \leq k_c$, $j' = k_{cv} + j''$: 0

3) $j \leq k_c$, $j' = k_\beta$: $-p_j \, EX_{ij}$ (39)

4) $j = k_c + jo$, $j' \leq k_{cv}$: 0

5) $j = k_c + jo$, $j' = k_{cv} + j''$: $\delta_{joj''} \, TEXS_{ijo}$

6) $j = k_c + jo$, $j' = k_\beta$: $-q_{jo} \, EXS_{ijo}$

4. Statistical Analysis

In this section are given the results of a statistical analysis[21] of the least-squares problems with constraints of the present type. This analysis assumes

(i)   an ideal model

(ii)   small fluctuations of the data ordinates (count numbers) around their means.

(iii)   "statistical weighting"

Concerning (i) we know that model (2) is not an ideal model. We have no general theory which indicates that the measured curves can be represented by the model. However, experiments have shown that in many cases parts of the curves or the whole curve can be fitted well by use of one or several Gaussian curves.

(ii) is justified if the total number of counts in the spectrum is sufficiently large. This is generally true in this application.

(iii) concerns the choice of the weights, w_i, of the data points in the expression for ϕ (eq(12)). These have hitherto been regarded as arbitrary coefficients,but several advantages will be gained[21] if the so-called statistical weighting is chosen,

$$w_i = \frac{1}{\sigma_i^2} \qquad (40)$$

σ_i^2 is the variance of the ith data ordinate y_i and is estimated by the auxiliary program PAAC. With assumptions (i)- (iii) it is possible[21] to compute the covariance matrix, Q, of the statistical variable b [the vector that minimizes (12)]. The result is that Q is obtained by deletion of the last m [cf (14)] rows and columns from the inverse of the matrix

$$H = \begin{array}{cc} & \begin{array}{cc} k & m \end{array} \\ \begin{array}{c} k \\ \\ \\ m \end{array} & \left[\begin{array}{c|c} A & R^T \\ \hline R & \theta \end{array} \right] \end{array} \qquad (41)$$

Here, the matrix $A=p^T W p$ refers to all $k=k_\alpha+k_\beta$ parameter components (in contrast to A for the β-iterations, eq. (36)), so in this case P is an n x k matrix with the elements $P_{ij} = \frac{\partial f_i}{\partial b_j}$. R is related to the set of general constraints

$$k_\ell \ (b) = 0 (\ell = 1, \ldots, m) \qquad (42)$$

by $r_{\ell j} = \frac{\partial K_\ell}{\partial b_j}$. In the present case R becomes an extention of K (cf. (22) and (23)),

$$R = \begin{array}{c} \\ m \end{array} \begin{array}{cc} k_\alpha & k_\beta \\ \left[\begin{array}{c|c} K & \theta \end{array} \right] \end{array} \qquad (43)$$

In the special case of no constraints, $Q = A^{-1}$.

We want to express the parameters as well as the associated statistics in terms of relative intensities

$$i_j = \frac{\alpha_j}{\sum\limits_{j=1}^{k_\alpha} \alpha_j} \qquad (44)$$

and fwhm (eqs(5)). The new parameter vector

$b_1 = (i_1, \ldots, i_{k_\alpha}, \varphi_1, \ldots, \varphi_{k_{cv}+k_{sv}}, \theta_0)^t$, where φ has been written

for fwhm, has the covariance matrix $Q_1 = JQJ^T$. J is the Jacobian of the transformation $b \rightarrow b_1$,

$$
J = \begin{bmatrix}
\dfrac{i_1(1-i_1)}{\alpha_1} & & & -\dfrac{i_1^2}{\alpha_1} & & & & & \\
& \diagdown & & & & & \theta & & \\
-\dfrac{i_{k_\alpha}^2}{\alpha_{k_\alpha}} & & \dfrac{i_{k_\alpha}(1-i_{k_\alpha})}{\alpha_{k_\alpha}} & & & & & \theta & \\
\hline
& & & & -\dfrac{\varphi_1^2}{c} & & & & \\
& \theta & & & & -\dfrac{\varphi_1^2}{c} & 0 & & \\
& & & & & 0 & \diagdown & & \\
\hline
& & \theta & & & & & & 1
\end{bmatrix}
\quad (45)
$$

where $c = 2\sqrt{\log 2}$. Q_1 contains in particular the variances of the parameters in the diagonal. The minimal sum-of-squared-errors Φmin will approximately have a χ^2- distribution with $q = n - k_{free}$ degrees of fredom, where

$$
k_{free} = k_\alpha + k_\beta - m = k_c + k_s + k_{cv} + k_{sv} + 1 - m \qquad (46)
$$

q is always so large that this χ^2-distribution is close to a normal distribution with mean q and variance 2q. Hence the quantity

$$
s^2 = \frac{\Phi min}{q} \qquad (47)
$$

will be approximately normal $(1, \sqrt{\tfrac{2}{q}})$. S^2 will be denoted "the variance of the fit ". It serves as an indicator of the validity of our model [cf. assumption (i)] ; S^2-values substantially greater than 1 suggest that our model is not a good representation of the measured spectrum.

5. Description of the Code PAACFIT

5.1 Structure

The fortran program PAACFIT (AEK P-673)consists of a driver program and the subroutines GAUSFT, DISP, COLDEC, and COLSOL.

The driver program contains all the input and most of the output instructions. It carries out all the statistical analysis.

GAUSFT is the iterative least-squares fitting routine. It passes to the driver program converged values of the model parameters.

DISP produces a table with data as well as fit ordinates and a lineprinter display of the deviations.

COLDEC and COLSOL are used in the solution of linear systems with symmetric matrices and for inversion of such matrices. COLDEC performs an extended Cholesky decomposition, and COLSOL solves the system on the basis of this decomposition. The two subroutines are called from the driver program during the statistical calculations, and from GAUSFT.

5.2 Input

All input data are read from punched cards. The data are divided into five consecutive blocks.

BLOCK1 is a single card containing the word JOB and a job number, IJOB. The format is A3,I7. If "JOB" is not recognized, an error message is printed. IJOB<0 signals the end of the job stream.

BLOCK2 is a single card containing the print-out option IPRINT, format I 10. IPRINT=0 causes print-out of the main results. IPRINT=1 gives in addition a print-out of the parameters at each iteration, and IPRINT=2 furthermore a table with data as well as fit ordinates and a graphical display of the deviations.

BLOCK3 is a single card containing the length of the table N, format I10.

BLOCKS 4 and 5 both start with a text card with one of the words NEW or REP, format A3. If the card is a REP card, this will be the entire contents of that block, and the corresponding block data from the previous job are repeated. If neither "NEW" or "REP" is recognized, an error message occurs.

BLOCK4 contains the spectrum data. The first card after a NEW card is a text card with a description of the spectrum (col. 1-72). The next items are the angle table $(X(I),I=1,N)$, format 10F8.2; the count-rate table $(Y(I), I=1,N)$, format 16F5.0; and the standard-deviation table $(SIGMA(I),I=1,N)$, format 16F5.0. These tables constitute the punched output from the PAAC program. (cf.(1), sec. 2).

BLOCK5 contains information on number of terms, parameter guesses and constraints. The first card after a NEW card holds the five integers KC, KS, KCF, KSF, M, format 5I10. KC is the number of central peaks, KS the number of sidepeak pairs in the model. Of these, KCF central fwhm and KSF sidepeak fwhm are fixed. $|M|$ is the number of constraints on the intensities. If KS>0, a card follows with the sidepeak positions, format 2E10.5. The next card contains all the KC initial values (guessed followed by fixed) of the central fwhm, format 5E10.5. If KS>0, a card follows with the KS initial values (guessed followed by fixed) of the sidepeak fwhm, format 2E10.5. The next card holds the guessed value for the angle-zero θo, format E10.5. If M>0, M of the relative intensities are fixed. In this case, the next data item is a pair of cards with the numbers $(JL(L),L=1,...,M)$ and $(RINTF(L),L=1,...,M)$, format 6I10/6E10.5; JL(L) is the term no. associated with constraint no. L (the numbering of terms is defined from the previous card(s) with the central fwhms followed by the sidepeak fwhms), and RINTF(L) is the corresponding fixed relative intensity in percent. If M<0, $|M|$ linear combinations of the absolute intensities equal zero,

$$\sum_{j=1}^{KC+KS} k_{\ell_j} \alpha_j = 0;$$

in this case the next data item contains $|M|$ cards so that card number ℓ holds the coefficients $k_{\ell j}$ with the identifier COMB (J,L) $(J=1,..., KC+KS)$, format 7E10.5. The option M<0 may be used to fix ratio between intensities or the sum of certain relative intensities.

Restrictions on the input data in the present version (1/7 1973) of PAACFIT are: $N \leq 100$, $0<KC\leq 5$, $0 \leq KS \leq 2$, $0 \leq |M| < KC + KS$, $0 \leq KCF \leq KC$, $0 \leq KSF \leq KS$.

6. Experience with the Program.

The program has until now been used in about 500 analyses of
more than 100 different angular correlation curves. Most of the
results will be published in detail in other papers. In figures
1 and 2 are shown some of the curves. These figures were computer-
plotted by use of the program PAACDRAW. The fitting parameters of
the curves, determined by the PAACFIT analyses, are given in table
1 and the fitting curves are plotted in the figures.

As mentioned earlier (sec 4) we normally have no theory indi-
cating that the model is ideal. In practice, however, we frequent-
ly measure curves which, wholly or in part, can be fitted well by
one Gaussian (e.g. the broad component of many metal curves). Our
experience is that we have been able to fit well all the curves
we have analysed. In a typical case of a bell-shaped curve with
no sidepeaks a one -Gaussian fit is rather bad, a two-Gaussian
fit is fairly reasonable, and three Gaussians fit very well with
parameters that are already not too well determinded (see the
cystine parameters in table 1.)A four-Gaussian fit will normally
be so uncertain that much computing time is used and some of the
fitting parameters attain unacceptable values (e.g. intensities
of thousands of precent or very large fwhm's). We want to empha-
size that the model can contain so many fitting parameters that a
good fit can nearly always be obtained, and thus extreme care must
be exercised in the final correlation of the parameters to some
physical quantities.

Before we used the program for analysis of the measured curves
we analysed some calculated curves. For example we analysed a cal-
culated curve with a shape close to the shape of the a-axis ice
curve. The program found the same intensities and fwhm's as used in
the calculation, except for the fwhm's of the very narrow central
and side peaks, where the program found 0.7815 instead of 0.8
mrad and 0.5749 mrad instead of 0.6 mrad respectively. This very
small error arises because the measured numbers y_i are compared
to interval averages for the model curve in the fitting procedure
(cf. sec. 3) It can be reduced if more points are measured on the
narrow peaks. We have also tested the program many times by e.g.

varying the initial guesses of the fwhm's or by analysing different curves measured for identical sample conditions.

A more detailed discussion of a series of analyses of the a-axis ice curves will illustrate some of the problems we encountered in the fitting procedures. At low temperatures the curves consisted of a broad component, a narrow component, and a sidepeak pair, while at higher temperatures also a middle-broad component was found. We wanted especially to get good values for the intensities of the narrow central and side peaks (due to annihilation of delo-calized para-positronium (para Ps)) and of the middlebroad component (due to localized para-Ps). At first we analysed nearly all the a-axis curves by use of three central Gaussians and one pair of side-peak Gaussians. The side-peak positions were calculated by use of the ice lattice parameters. The fitting was good, but for many of the curves the values of the fitting parameters were not acceptable. For example the fwhm's of the side peaks sometimes attained values of 5 to 10 mrad at some of the highest temperatures, where the side peaks were rather small. For the a-axis - 182°C curve (see fig. 1) the broad component was well fitted by two Gaussians (84.6757% with fwhm = 10.3941 mrad and - 1.0130% with fwhm = 5.8701 mrad). A one-Gaussian fit of the broad component was rather bad and three Gaussians did not give a smaller variance of the fit.

We then analysed the curves by use of four central Gaussians and a pair of side-peak Gaussians. The shape of the broad component was fixed to the shape found at -182°C by use of fixed fwhm's(fwhm$_3$ = 5.8701 mrad and fwhm$_4$ = 10.3941 mrad) and one linear - combina-tion - of-intensities constraint, $84.6757 \times i_3 + 1.013 \times i_4 = 0$. Again the parameters for some of the higher temperature curves were unacceptable. The reason was that the larger angle parts of the curves strongly influenced the intensity of the broad component, and hence the side peaks and middle-broad component were to some extent used to compensate a too small or a too large broad compo-nent at smaller angles.

From theory we expected that the broad component would be ap-proximately independent of temperature except for a small correc-tion of the intensity. This was found to be roughly in agreement with the results of the first analyses. We therefore analysed the

curves by use of four central Gaussians and one pair of side -
peak Gaussians with the broad component fixed to the shape used
before and an intensity calculated by use of lifetime data. The
parameters were now fairly acceptable but for some curves they
were still somewhat too uncertain. We analysed once more using
fixed side-peak fwhm's with a theoretical temperature dependence.
The fwhm's for the middle-broad curves for temperatures above
$-40°C$, where the middle-broad components were well defined, were
then found to be very constant. For 11 curves we found $fwhm_2$
$= 3.94±0.09$ mrad.

In the final analyses we therefore also fixed $fwhm_2$ to be
3.94 mrad. This gave a variance of the fit close to the best
values obtained in the analyses, where all the parameters were
free, and the parameters, which were free to vary, were well de-
fined. The ice curves for other orientations and for HF-doped
ice were treated similarly. Manual treatments of some of the
curves have been published in ref. 5. The ice curves given in Fig.
1 and table 1 are the results of the final analysis. The complete
lineprinter output for curve 1 (c-axis, $-181°C$) is shown as the
test run output in appendix 2.

In Fig. 2 (see also table 1) are shown curves for cystine,
acetylmethionine and γ-irradiated (30 Mrad) acetylmethionine.
In acetylmethionine γ-irradiation reduces the amount of Ps formed.
Para-Ps annihilation results in a middle-broad component in the
angular correlation curves. We assumed that the rest of acetyl-
methionine curves, the broad component, had the same shape as the
cystine curve, where no Ps is formed. For the cystine curve three
Gaussians were necessary to give a good fit. Hence, we analysed
the acetylmethione curves by use of four Gaussians, one for the
middle-broad component and three to fit the broad component, using
two linear - combination - of - intensities constraints and fixed
fwhm's to fix the shape of the broad component to the shape of
cystine curve. The intensities of the middle-broad curves in Fig. 2
and table 1 therefore give the amount of para-Ps formed. A manual
treatment of the same curves have been published in ref. 6. This
example illustrates how a curve may be separated into two parts,
of which one has a fixed shape, by use of the linear - combination -

of - intensities constraints.

In sec. 4 it was pointed out, that on the assumption of an ideal model, the distribution of the "variance of the fit", s^2 (cf.(47)), should be approximately normal with mean value 1 and with s.d. $= \sqrt{\frac{2}{q}} \approx 0.17$ (in our application q was always near 70). Except for a very few cases we found much larger values, typically about 4. The reason is of course that the model is not ideal. Firstly, the curves cannot always be fitted by use of only Gaussians. Secondly, the curves contain small errors due to different experimental effects. For example, the narrow peaks are not completely symmetrical because of a small asymmetry of the resolution curve of the set-up owing to the variation of the position-penetration depth of the ice sample. The curves measured with the smallest statistical counting uncertainties gave the largest Φ - values, as expected.

The computing time on a Burroughs B 6700 was roughly 10 to 20 seconds, this corresponds roughly to 1-2 sec. on an IBM 370/165, depending on the number of points in the curves (typically around 75) and on the constraints used. The number of iterations to obtain convergence was usually of the order of 14 for unconstrained fits and around 7 for heavily constrained fits.

We conclude that the program is a very useful tool for the analysis of angular correlation curves. It may of course also be used for the analysis of symmetrical curves obtained in other experiments (e.g. the resolution curve of a positron lifetime set-up). As the program can handle negative intensities, curves of many different shapes can be analysed. In particular the possibility of using different constraints in the analysis has been found to be very applicable. The main problems of an analysis is to use the constraints in an intelligent way in order that the fitting parameters can be correlated unambiguously to the physical quantities. In other words, it is nearly always possible to obtain a good fit, but it may be very difficult to make out the meaning of the fitting parameters.

7. References

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2) P. Kirkegaard, Some Aspects of the General Least-Squares Problem for Data Fitting, Risø-M-1399 (1971).

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4) P. Kirkegaard and M. Eldrup, The Least-Squares Fitting Programme POSITRONFIT: Principles and Formulas, Risø-M-1400 (1971)

5) O. Mogensen and M. Eldrup, Proc. Conf. Phys. Chem. Ice, Ottawa (1972), to be published.

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```
JnB     5
        2
       77

NEW
H2O-C=1.51      T=-180.9°C
-12.74  -12.11  -11.48  -10.85  -10.22   -9.59   -8.96   -8.34   -7.71   -7.33
 -7.00   -6.82   -6.57   -6.32   -6.07   -5.82   -5.56   -5.19   -4.81   -4.43
 -4.19   -3.93   -3.67   -3.42   -3.17   -2.92   -2.67   -2.41   -2.16   -1.91
 -1.74   -1.53   -1.34   -1.15   -0.97   -0.78   -0.59   -0.40   -0.21   -0.02
  0.17    0.36    0.55    0.73    0.92    1.11    1.30    1.49    1.74    1.99
  2.25    2.50    2.75    3.00    3.25    3.51    3.76    4.01    4.39    4.77
  5.14    5.40    5.65    5.90    6.15    6.40    6.66    6.91    7.29    7.92
  8.54    9.17    9.80   10.43   11.06   11.69   12.32

 183   240   394   510   747   999  1321  1748  2300  3106  3789  4120  4234  4045  4279
4588  5010  5443  5793  6289  6773  7142  7612  7967  8180  8419  8573  8758  8810  9214
9477  9570 10506 12104 15703 20866 26839 30302 28042 25631 15851 14110376  9492  9308  9198
8927  8762  8408  8373  8175  7917  7682  7350  6834  6485  6037  5581  5013  4746  4479  4097
4089  4041  3993  3585  2701  2038  1460  1151   871   643   460   319   194

  13    15    19    21    26    32    34    40    46    50    58    66    62    60
  64    67    70    72    75    78    80    83    84    85    86    87    88    89    99
 100    93    98   105   117   138   156   166   160   143   130   105    97    93    92
  90    89    88    87    86    85    84    82    80    71    68    64
  61    72    60    57    50    43    40    32    28    24    22    17    16

NEW
  3     2     2     2     2     2

3.315   6.630
1.      3.70       10.53
0.950   0.950
0.00

     3                    4
83.660  0.559
JnB    -1
```

```
JOB NO  5

X-TABLE
   -12.76  -12.13  -11.48  -10.95  -10.22   -9.56   -8.96   -8.36   -7.71   -7.33
    -7.06   -6.62   -6.57   -6.32   -6.07   -5.82   -5.56   -5.19   -4.81   -4.63
    -4.16   -3.93   -3.67   -3.42   -3.17   -2.92   -2.67   -2.41   -2.16   -1.91
    -1.74   -1.53   -1.36   -1.15   -0.97   -0.78   -0.59   -0.40   -0.21   -0.02
     0.17    0.36    0.55    0.73    0.92    1.11    1.30    1.49    1.74    1.99
     2.25    2.50    2.75    3.00    3.25    3.51    3.76    4.01    4.35    4.77
     5.16    5.40    5.65    5.90    6.15    6.40    6.66    6.91    7.29    7.92
     8.56    9.17    9.80   10.43   11.06   11.69   12.32

Y-TABLE
    183   240   350   516   767   999  1321  1748  2300  2723  3106  3789  4120  4230  4065  4279
   4500  5010  5443  5793  6287  6773  7142  7612  7791  7967  8180  8619  8573  8750  8810  9214
   9477  9570 10500 12100 15700 20000 26000 30300 22820 20422560 15050 11210 10376  9492  9300  9190
   8927  8762  8600  8373  8176  7917  7662  7350  6834  6605  6037  5581  5013  4746  4479  4097
   4089  4041  3993  3585  2701  2030  1460  1151   871   643   460   319   194

SIGMA-TABLE
    13   15   19   21   25   32   34   40   46   50   53   58   66   62   60   62
    66   67   70   72   75   78   80   83   86   86   87   88   96   89   99
   100   93   98  105  117  130  156  166  160  143  130  105   97   93   92   92
    90   89   88   87   56   85   84   82   85   77   80   71   66   71   66   61
    61   72   60   57   53   43   40   37   29   26   22   17   16

INITIAL VALUES OF NONLINEAR PARAMETERS
CENTRAL FWHMS (FIRST THOSE TO BE FITTED)
   1.0000E+00 3.7000E+00 1.0590E+01
SIDEPEAK FWHMS (FIRST THOSE TO BE FITTED)
   9.5000E-01 9.5000E-01
THETA0-GUESS
   0.0000

ITERATION NO  1
SHARPNESS OF CENTRAL PEAKS
    .1665109E+01
THETA0
    0.
INTENSITY OF CENTRAL PEAKS
    .2083066E+05   -.1997830E+04    .1084945E+06
INTENSITY OF SIDEPEAKS
    .7249397E+03    .1632774E+04
PHI =    .88492730E+03
KAPPA =    .2000E-01
A

ITERATION NO  2
SHARPNESS OF CENTRAL PEAKS
    .1695327E+01
THETA0
    -.8759983E-02
INTENSITY OF CENTRAL PEAKS
    .1917170E+05   -.1926519E+03    .1087215E+06
INTENSITY OF SIDEPEAKS
    .7204562E+03    .1529167E+04
PHI =    .18158231E+03
KAPPA =    .2000E-02
A

ITERATION NO  3
SHARPNESS OF CENTRAL PEAKS
    .1930607E+01
THETA0
    -.6612020E-02
INTENSITY OF CENTRAL PEAKS
    .1894000E+05    .5408727E+02    .1087414E+06
INTENSITY OF SIDEPEAKS
    .7465092E+03    .1518089E+04
PHI =    .18791169E+03
KAPPA =    .2000E-03
A

ITERATION NO  4
SHARPNESS OF CENTRAL PEAKS
    .1932920E+01
THETA0
    -.6692729E-02
INTENSITY OF CENTRAL PEAKS
    .1892550E+05    .6936444E+02    .1087427E+06
INTENSITY OF SIDEPEAKS
    .7465976E+03    .1517464E+04
PHI =    .18784181E+03
KAPPA =    .2000E-04
A

ITERATION NO  5
SHARPNESS OF CENTRAL PEAKS
    .1933073E+01
THETA0
    -.6635490E-02
INTENSITY OF CENTRAL PEAKS
    .1892462E+05    .7038331E+02    .1087426E+06
INTENSITY OF SIDEPEAKS
    .7465982E+03    .1517423E+04
PHI =    .18786150E+03
KAPPA =    .2000E-05
A

ITERATION NO  6
SHARPNESS OF CENTRAL PEAKS
    .1933083E+01
THETA0
    -.6634331E-02
INTENSITY OF CENTRAL PEAKS
    .1892456E+05    .7045012E+02    .1087426E+06
INTENSITY OF SIDEPEAKS
    .7465982E+03    .1517420E+04
PHI =    .18786150E+03
KAPPA =    .2000E-06
A
```

```
*********************************
H2O-C-1.S1    T=-100.9'C
*********************************
```

CONVERGENCE OBTAINED AFTER   6 ITERATIONS
VARIANCE OF THE FIT =   2.053
ITS DISTRIBUTION SHOULD BE APPROXIMATELY NORMAL (1,0.167)
EXCESS PROBABILITY =   0.00 PCT

NUMBER OF CENTRAL PEAKS   = 3   NUMBER OF SIDEPEAK PAIRS = 2
NUMBER OF FIXED CENTRAL FWHM = 2   NUMBER OF FIXED SIDE FWHM = 2

NUMBER OF CONSTRAINTS FOR RELATIVE INTENSITIES = 2
FIXED RELATIVE INTENSITIES FOR PEAKS NO   3   4
PERCENTUAL INTENSITIES   83.6600   0.5590

POSITION OF SIDEPEAKS   3.3150   6.6300

LENGTH OF TABLE = 77

INTENSITIES OF CENTRAL PEAKS IN PCT   14.5594   0.0542   83.6600
STANDARD DEVIATIONS   0.0888   0.0965   0.0000

INTENSITIES OF SIDEPEAK PAIRS IN PCT   0.5590   1.1674
STANDARD DEVIATIONS   0.0000   0.0377

FWHM FOR CENTRAL PEAKS   0.8614   3.7000   10.5900
STANDARD DEVIATIONS   0.0048

FWHM FOR SIDEPEAK PAIRS   0.9500   0.9500

ANGLE-ZERO THETAO (MRAD)   -0.0063
STANDARD DEVIATION   0.0018

AREA CHECK   AREA FROM FIT = 1.29511E+05
               AREA FROM TABLE = 1.29416E+05

MATRIX OF TOTAL CORRELATIONS
(RELATIVE INTENSITIES, FREE FWHMS, THETAO)

```
 1.000 -0.921  0.000  0.000 -0.001  0.615 -0.014
-0.921  1.000  0.000  0.000 -0.390 -0.595  0.016
 0.000  0.000  0.000  0.000  0.000  0.000  0.000
 0.000  0.000  0.000  0.000  0.000  0.000  0.000
-0.001 -0.390  0.000  0.000  1.000  0.073 -0.008
 0.615 -0.595  0.000  0.000  0.073  1.000 -0.011
-0.014  0.016  0.000  0.000 -0.008 -0.011  1.000
```

X	TABLE Y	FIT Y	DEVIATION (FIT-TABLE) IN SIGMA UNITS
-12.740	1.8300E+02	1.7516E+02	
-12.110	2.4000E+02	2.5921E+02	
-11.480	3.9400E+02	3.7400E+02	
-10.850	5.1000E+02	5.2715E+02	
-10.220	7.4700E+02	7.3415E+02	
-9.590	9.9900E+02	9.9301E+02	
-8.960	1.3210E+03	1.3310E+03	
-8.340	1.7480E+03	1.7301E+03	
-7.710	2.3000E+03	2.1949E+03	
-7.330	2.7230E+03	2.6391E+03	
-7.080	3.1060E+03	3.2167E+03	
-6.820	3.7690E+03	3.7250E+03	
-6.570	4.1200E+03	4.0545E+03	
-6.320	4.2340E+03	4.1094E+03	
-6.070	4.0450E+03	4.1716E+03	
-5.820	4.2790E+03	4.2869E+03	
-5.560	4.5880E+03	4.5553E+03	
-5.190	5.0100E+03	4.9699E+03	
-4.810	5.4430E+03	5.4538E+03	
-4.430	5.7930E+03	5.9123E+03	
-4.180	6.2890E+03	6.3109E+03	
-3.930	6.7730E+03	6.7153E+03	
-3.670	7.1420E+03	7.1651E+03	
-3.420	7.6120E+03	7.5767E+03	
-3.170	7.7910E+03	7.8642E+03	
-2.920	7.9670E+03	8.0419E+03	
-2.670	8.1800E+03	8.2300E+03	
-2.410	8.4190E+03	8.3951E+03	
-2.160	8.5730E+03	8.6140E+03	
-1.910	8.7480E+03	8.8162E+03	
-1.720	8.8100E+03	8.9809E+03	
-1.530	9.2140E+03	9.1233E+03	
-1.340	9.4770E+03	9.2740E+03	
-1.150	9.5700E+03	9.5102E+03	
-0.970	1.0900E+04	1.0138E+04	
-0.780	1.2100E+04	1.1810E+04	
-0.590	1.5700E+04	1.5400E+04	
-0.400	2.0866E+04	2.1212E+04	
-0.210	2.6039E+04	2.7193E+04	
-0.020	3.0302E+04	3.0300E+04	
0.170	2.8204E+04	2.7074E+04	
0.360	2.2563E+04	2.2131E+04	
0.550	1.5051E+04	1.6239E+04	
0.730	1.2141E+04	1.2104E+04	
0.920	1.0376E+04	1.0345E+04	
1.110	9.6920E+03	9.5017E+03	
1.300	9.3080E+03	9.2999E+03	
1.490	9.1980E+03	9.1325E+03	
1.740	8.9270E+03	8.9552E+03	
1.990	8.7620E+03	8.7683E+03	
2.250	8.4080E+03	8.5260E+03	
2.500	8.3730E+03	8.3148E+03	
2.750	8.1760E+03	8.1376E+03	
3.000	7.9170E+03	7.9536E+03	
3.250	7.6020E+03	7.7707E+03	
3.510	7.3500E+03	7.4242E+03	
3.760	6.8340E+03	6.9867E+03	
4.010	6.4850E+03	6.5353E+03	
4.390	6.0370E+03	5.8946E+03	
4.770	5.5810E+03	5.4926E+03	
5.140	5.0130E+03	5.0484E+03	
5.400	4.7460E+03	4.6952E+03	
5.650	4.4790E+03	4.4180E+03	
5.900	4.0970E+03	4.2279E+03	
6.150	4.0890E+03	4.1508E+03	
6.400	4.0410E+03	4.1330E+03	
6.660	3.9930E+03	3.9540E+03	
6.910	3.5850E+03	3.4663E+03	
7.290	2.7010E+03	2.6985E+03	
7.920	2.0380E+03	2.0554E+03	
8.540	1.6800E+03	1.5871E+03	
9.170	1.1510E+03	1.2361E+03	
9.800	8.7100E+02	8.9764E+02	
10.430	6.4300E+02	6.5539E+02	
11.060	4.6000E+02	4.6912E+02	
11.690	3.1900E+02	3.2928E+02	
12.320	1.9400E+02	2.2604E+02	
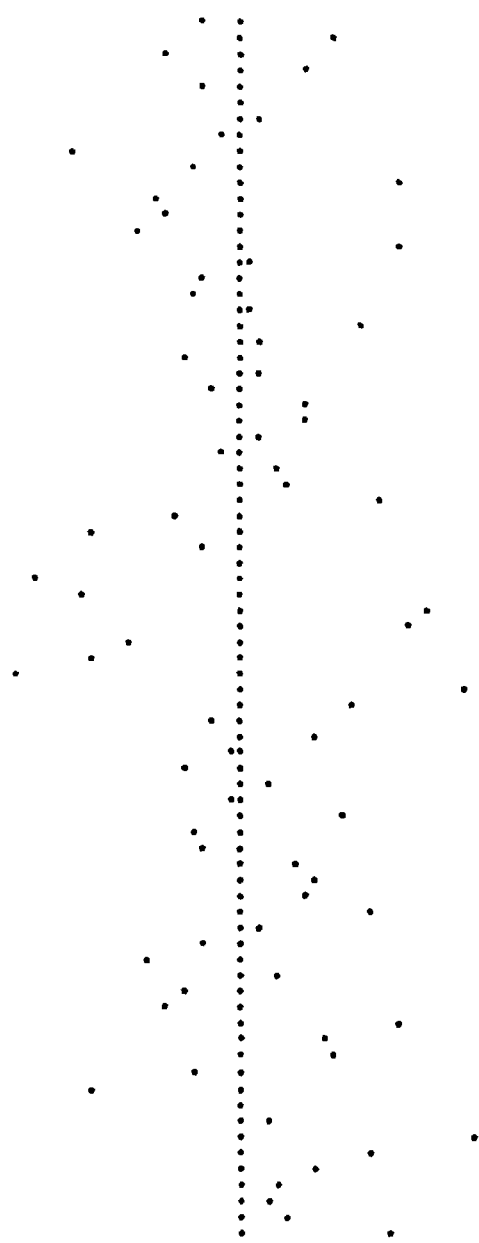
CPU TIME = 8.65 SEC.   I/O TIME = 1.44 SEC.   REAL TIME = 10.92 SEC.   REAL/CPU RATIO = 1.26

Curve No.	Substance	i_1 (%)	i_2 (%)	i_3 (%)	i_4 (%)	i_5 (%)	$FWHM_1$ (mrad)	$FWHM_2$ (mrad)	$FWHM_3$ (mrad)	$FWHM_4$ (mrad)	$FWHM_5$ (mrad)	Symmetry angle (mrad)	Variance of the Fit	Remarks
1	ice c-axis	14.559 ±0.089	0.054 ±0.097	83.66 f	0.559 f	1.167 ±0.038	0.861 ±0.005	3.700 f	10.590 f	0.950 f	0.950 f	-0.0063 ±0.0018	2.053	-181° C pure
2	ice a-axis	13.813 ±0.077	0.007 ±0.088	-1.013 f	84.676 f	2.517 ±0.039	0.849 ±0.004	3.940 f	5.870 f	10.394 f	0.950 f	-0.0082 ±0.0016	5.164	-182° C pure
3	ice c-axis	10.569 ±0.074	5.060 ±0.080	83.333 f	0.316 f	0.722 ±0.027	1.105 ±0.006	3.700 f	10.59 f	1.081 f	1.081 f	-0.0135 ±0.0019	4.023	-49° C pure
4	ice a-axis	6.430 ±0.065	9.367 ±0.074	-1.005 f	83.987 f	1.221 ±0.029	0.883 ±0.008	3.64 f	5.870 f	10.394 f	0.960 f	-0.000 ±0.023	6.325	-177° C 23 ppm HF
5	ice a-axis	5.88 ±0.192	10.474 ±0.209	-1.004 f	83.949 f	0.698 ±0.068	1.251 ±0.034	3.940 f	5.870 f	10.394 f	1.112 f	0.0815 ±0.0067	1.602	-4° C pure
6	ice a-axis	5.223 ±0.131	11.203 ±0.145	-1.004 f	83.912 f	0.666 ±0.044	1.224 ±0.024	3.94 f	5.87 f	10.394 f	1.115 f	-0.0053 ±0.0045	1.745	-1° C pure
7	cystine polycr.	-16.402 ±5.979	110.393 ±4.002	6.009 ±2.326	- -	- -	5.564 ±0.386	8.830 ±0.216	20.566 ±5.630	- -	- -	0.9167 ±0.0049	1.104	20° C non-irr
8	acetylm. polycr.	14.982 ±0.305	-13.945 ±0.050	93.854 ±0.337	5.109 ±0.018	-	4.128 ±0.064	5.564 f	8.830 f	20.566 f	-	0.7826 ±0.0069	1.820	20° C non-irr
9	acetylm. polycr	8.947 ±0.266	-14.935 ±0.044	100.516 ±0.294	5.472 ±0.016	- -	3.832 ±0.091	5.564 f	8.830 f	20.566 f	- -	2.1035 ± 0.0068	1.255	20° C γ-irr

Table 1   The fitting parameters and their uncertainties as determined by the PAACFIT analyses for all the curves shown in figures 1 and 2. The letter f indicates that the parameter has been fixed.
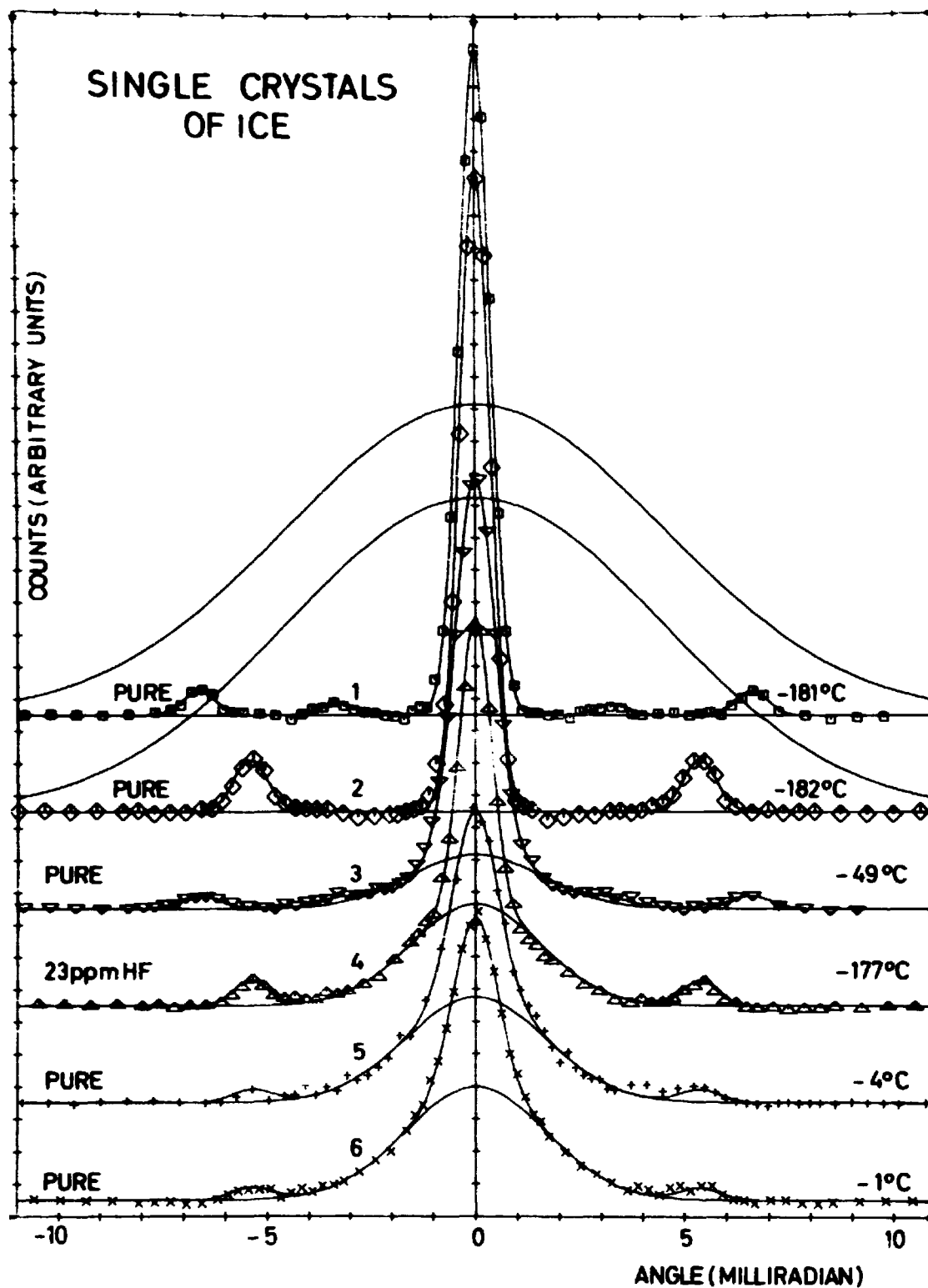
Figure 1. Positron annihilation angular correlation curves
for ice single crystals plotted by use of the PAACDRAW-
program. The curves are the best fits to the measured points
calculated by use of the PAACFIT-program. The points and the
fitting curves have been plotted after the subtraction of
the broad components, which have been plotted for the a-axis
and c-axis low temperature curves. The statistical counting
uncertainties are all smaller than roughly the size of the
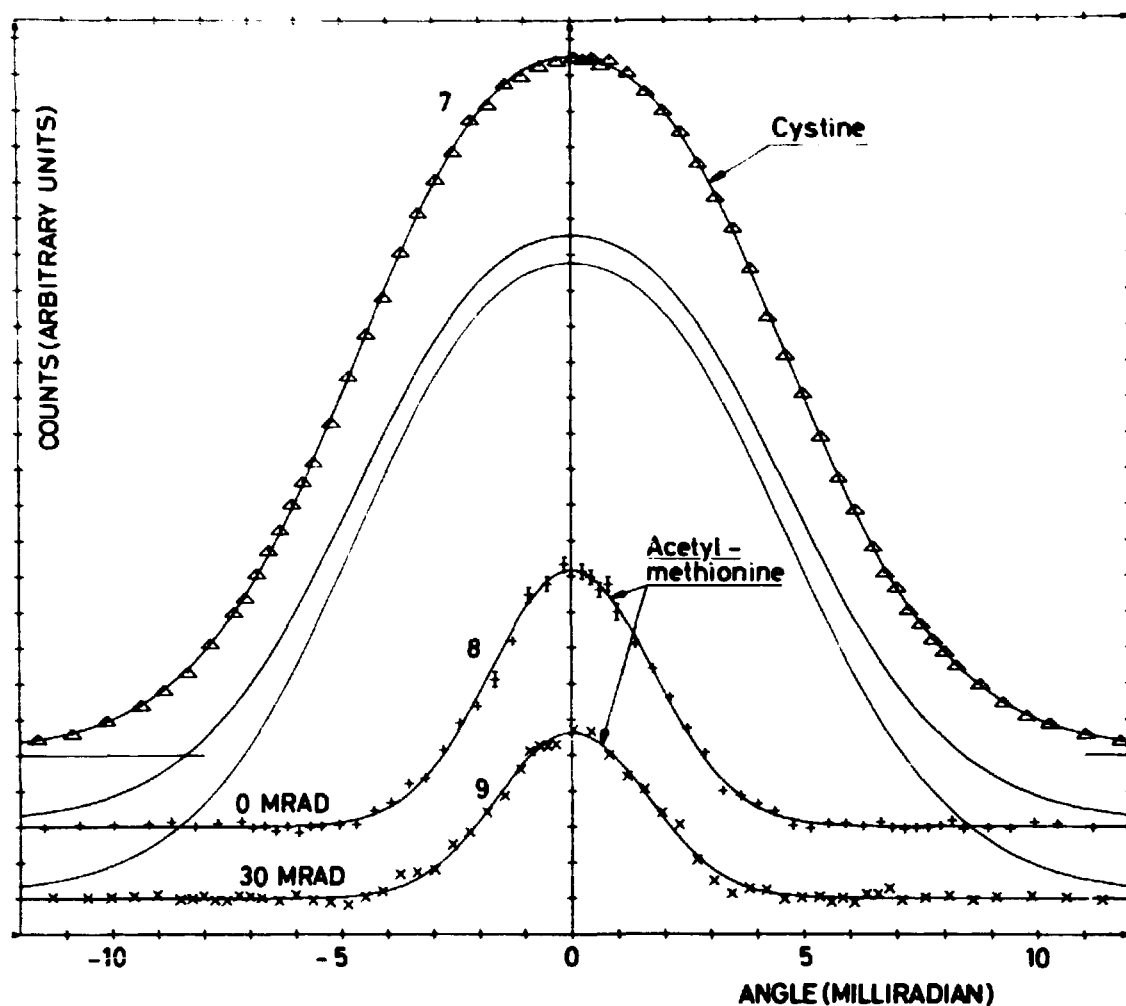marks. The parameters of the curves are shown in table 1.

Figure 2. Positron annihilation angular correlation curves
for cystine (7), acetylmethionine (8), and γ-irradiated (^{60}Co)
acetylmethionine (9) plotted by use of the PAACDRAW-program.
The curves are the best fits to the measured points calculated
by use of the PAACFIT-program. The two acetylmethionine curves
are shown after the subtraction of the broad components (shown
in the figure), whose shapes have been fixed to the shape of
the cystine curve by use of constraints in the fitting analysis.
The statistical counting uncertainties are only shown if they
are larger than roughly the size of the marks. The parameters
of the curves are shown in table 1.