MIXSCAT

Users Guide

Version 1.0

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Preface

Disclaimer

The MIXSCAT software described in this guide is provided without warranty of any kind. No liability is taken for any loss or damages, direct or indirect, that may result through the use of MIXSCAT. No warranty is made with respect to this manual, or the program and functions therein. There are no warranties that the programs are free of error, or that they are consistent with any standard, or that they will meet the requirement for a particular application. The programs and the manual have been thoroughly checked. Nevertheless, it can not be guaranteed that the manual is correct and up-to-date in every detail. This manual and the MIXSCAT program may be changed without notice.
MIXSCAT is intended as a public domain program. It may be used free of charge. Any commercial use is, however, not allowed without the explicit written permission of the authors.

Acknowledgments

The list of structure factors was adapted from the program Lazy-Pulverix written by K. Yvon, W. Jeitschko & E. Parthe.

Using MIXSCAT

Publication of results totally or partially obtained using the program MIXSCAT should state that MIXSCAT was used and contain the following reference:

> WURDEN, C., PAGE, K.L., LLOBET, A. & PROFFEN, TH. (2010) "Extracting Differential Pair Distribution Functions using MIXSCAT" *J. Appl. Cryst.*, **xx**, xxx–xxx

Contents

Chapter 1

Introduction

So what is MIXSCAT all about ? Essentially one can combine total total scattering data with different weights to extract partial or in our case differential PDFs. A partial PDF contains only information from pairs of a particular atom type. For example G_{AB} would contain only contributions from AB pairs. For a N component system, one would need $N(N+1)/2$ independent measurements. A differential PDF, $G_{\overline{AB}}$ on the other hand contains all atom-atom contributions *except* the ones from AB pairs. Here only two data sets are needed.
The different data sets can either be neutron data from samples containing different isotopes of the same element or x-ray data taken close to one elements absorption edge or, as in our case, a combination of x-ray and neutron data. This has been done, and is by no means new. What makes MIXSCAT new, is our attempt to create a simple to use tool to combine neutron and x- ray data. More discussion about other methods and plenty of references can be found in our MIXSCAT paper (Wurden et al., 2010). A more detailed discussion and summary of the equations behind this approach are given in Appendix A.
In principle MIXSCAT can be used to process real space data, $G(r)$, as well as reciprocal space data, $S(Q)$. However, we find working with real space data is more straight forward, as for example differences in instrument resolution manifest themselves at higher distances r whereas they effect $S(Q)$ over the complete range. Also in many cases, a differential PDF is extracted to aid model building and focussed on the low r region where PDF peaks are well separated. Once a useable structural model might is determined, it can be refined against all available data sets yielding partials extracted from the model.

Chapter 2

Example: CeF_3

In this chapter we will illustrate the use of MIXSCAT using the example of CeF_3. The neutron data were collected on the NPDF neutron powder diffractometer NPDF at the Lujan Neutron Scattering Center. The x-ray data were collected at beamline ID11-B at the Advanced Photon Source. The data are shown in Fig. 2.1. All input and macro files used in this example are included in the program distribution and can be found in the directory `examples/mixscat` in the installation directory.

2.1 Preparing the data

As we discussed in the introduction, MIXSCAT used the real space pair distribution function, $G(r)$ and calculates the desired differential PDF, $G_{\overline{AB}}(r)$. For details on the related notation and equations, refer to Appendix A. MIXSCAT can read files produced by PDFGETN (Peterson et al., 2000) and PDFGETX2 (Qiu et al., 2004) directly and extract some information such as $Q_{\max}$ from the header. Alternatively data files are simple multi column ASCII files containing r, $G(r)$ and an optional $\sigma(G(r))$.
Since we are taking a difference of $G(r)$ data, it is important to process the PDFs as similar as possible. In particular the truncation value $Q_{\max}$ should be the same for both data sets.

2.2 Extracting differential PDFs

As the other programs of the DISCUS package, MIXSCAT is controlled by a command language which is described in more detail in the DISCUS reference guide included in the package. Let us go through the CeF_3 example in detail. The resulting differential PDFs as well as model calculations are shown in Fig. 2.2.

```
reset
read dat,x,CeF3_bulk_binned.gr
read dat,n,CeF3_Bulk_npdf_03902.gr
```

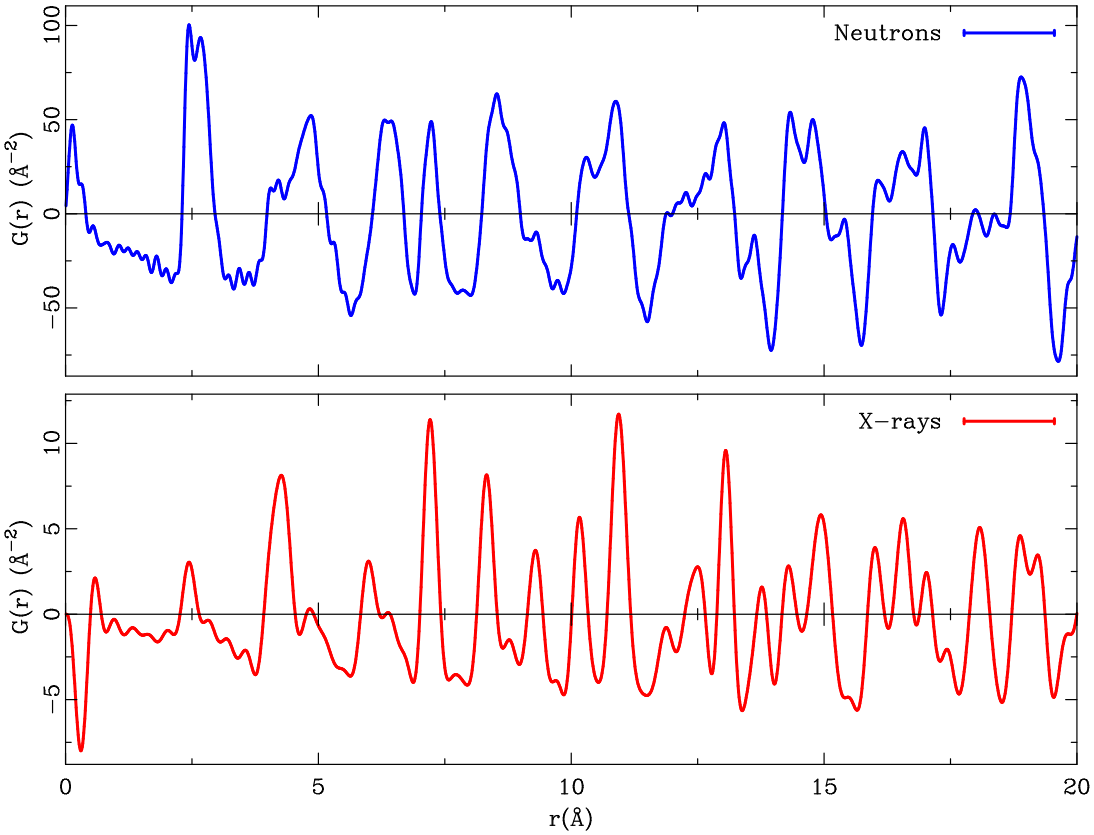

Figure 2.1: The top panel shows the experimental neutron PDF of CeF_3 collected on the instrument NPDF at the Lujan Center. The bottom panel shows the x-ray data of the same sample collected at beamline 11ID-B at the Advanced Photon Source.

First we use the command `reset` to put MIXSCAT in its initial state. Next the x-ray and neutron data files are imported using the command `read`. Note the first parameter specifying the type of data.

```
match 0.5,2.0,24./320.864
elem Ce,1,F,3
remove Ce,Ce
show
calc
```

The section above contains the setup. The command `match` allows to automatically scale the data, so the slopes $-4\pi r\rho_0$ match. The first two parameters specify the range, here $0.5 < r < 2.0$Å. The last value is the number density ρ_0 calculated as the number of atoms in the unit cell divided by the unit cell volume. As an alternative individual scale factors for each data set can be specified using the command `scal`. In a perfect world, of course, non of this is needed. The command `elem` specifies the elements and their abundance (CeF_3). Next we specify the contribution `Ce-Ce` to be removed. Finally `show` will list the current settings and `calc` execute the calculation.

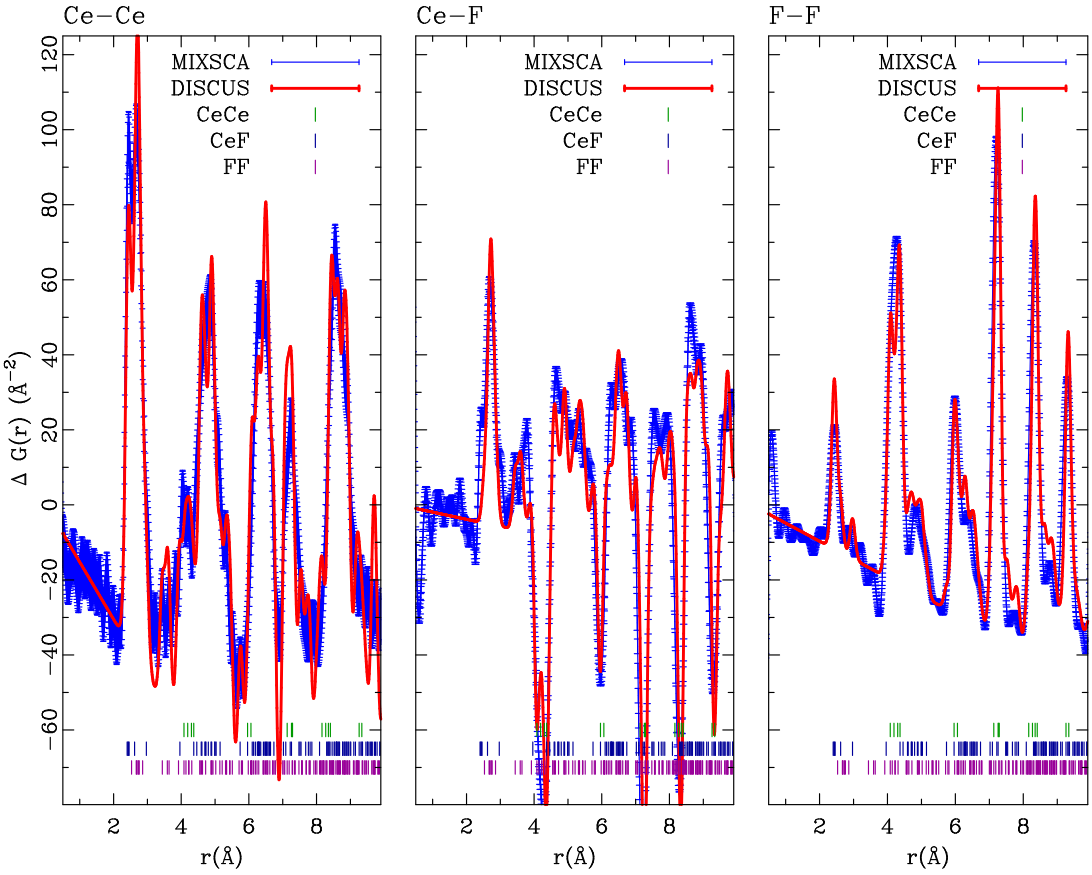

Figure 2.2: The plot shows the three extracted differential $G_{\overline{mn}}$ for CeF_3. The line with error bars is the extracted differential PDF form the neutron and x-ray data. The solid thick line is calculated from a model using DISCUS (see next section).

```
save pdf,CeCe_new_diff.gr
save wei,w_CeCe.mac
save res,CeCe.res
```

This section saves different data and results. The command `save pdf` saves the extracted differential PDF, $G_{\overline{CeCe}}(r)$. Next `save wei` saves a macro file for the program DISCUS containing the weights for the remaining pairs. This way DISCUS can calculate the corresponding differential PDF from a structural model. The output in our example is shown below.

```
set partial,CE  ,CE  ,       0.0000000
set partial,CE  ,F   ,       16.266106
set partial,F   ,F   ,       21.585993
set rden,       18.241911
```

Finally the command `save res` will save a text file with the setup similar to the information shown on the screen by the command `show`. The output for our example is shown below.

```
------------------------------------------------------------------------------
Program MIXSCAT - Version 1.0.0
------------------------------------------------------------------------------
Build date : Tue Jan  5 21:02:52 JST 2010
Save date  : Tue Jan  5 21:06:04 2010
Homepage   : http://discus.sourceforge.net
------------------------------------------------------------------------------

------------------------------------------------------------------------------
DATA SETS
------------------------------------------------------------------------------
Data set    :                          1                              2
Filename    :       CeF3_bulk_binned.gr     CeF3_Bulk_npdf_03902.gr
Radiation   :       x-rays (  0.0 A^-1)                    Neutrons
Rmin (A)    :                     0.010                        0.010
Rmax (A)    :                    99.990                       20.000
Dr (A)      :                     0.010                        0.010
Qmax (A^-1) :                     0.000                       35.000
Scale       :                1.42648721                   0.05844205
------------------------------------------------------------------------------
SETUP - Removing contribution : CE - CE
------------------------------------------------------------------------------
Data set    :                          1                              2
Weight w_mn :               0.46553183                   0.04904367
<b>^2       :              451.33862305                   0.29729757
b(CE  )     :               57.98102951                   0.48300001    c=0.250
b(F   )     :                8.99930000                   0.56599998    c=0.750
------------------------------------------------------------------------------
DIFFERENTIAL WEIGHTS
------------------------------------------------------------------------------
w(CE  -CE  ):               0.00000000
w(CE  -F   ):               3.04989457
w(F   -F   ):              12.14212132
w(rho_0)    :              18.24191093
------------------------------------------------------------------------------
```

The output contains information about the data sets and the respective weights for each atom and atom pair. The bottom of the output file shows the result from a simple error estimate of the differential PDF (see below).

```
------------------------------------------------------------------------------
ERROR ANALYSIS - Removed contribution :   CE -   CE        Difference:  2 -  1
------------------------------------------------------------------------------
Data                       File      Average data      Average sigma  Relative
   1        CeF3_bulk_binned.gr        2.75641990         0.00012269     0.00%
   2    CeF3_Bulk_npdf_03902.gr       29.27724457         5.72750998    19.56%
------------------------------------------------------------------------------
         Extracted differential       30.33419609         6.82508755    22.50%
------------------------------------------------------------------------------
```

The other differential PDFs, $G_{\overline{CeF}}(r)$ and $G_{\overline{FF}}(r)$ can be calculated in a similar way.

2.3 Calculating differential PDFs from a model

As shown in Fig. 2.2 one can calculate the corresponding differential PDF from a structural model. The program DISCUS allows to read custom weights to be used in the PDF calculation. These weights are set using the macro file `w_CeCe.mac` we saved earlier. Simply add the line below in the `pdf` module of DISCUS.

```
@w_CeCe.mac
```

Details about the underlying equations as well as information how to calculate differential PDFs with other programs such as PDFGUI are given in Appendix A.2.

Appendix A

Equations

In this appendix, we will derive the equations used in the program to extract the differential $G(r)$ functions. It is important to recognize the difference between a partial and a differential PDF. We us the following notation: The *partial* PDF, $G_{AB}(r)$ contains only contributions from atoms pairs of type AB, for example the OO partial of water would only contain oxygen-oxygen contributions. The *differential* PDF, $G_{\overline{AB}}(r)$, on the other hand will contain contributions from all atom-atom pairs *except* AB. Similarly we define the partial structure factor as $S_{AB}(Q)$ and the differential structure factor as $S_{\overline{AB}}(Q)$.

A.1 Calculating the difference

We will discuss the way how the difference is calculated using the PDF, $G(r)$. Differences in $S(Q)$ are calculated exactly the same way. The PDF can be written as

$$G(r) = \frac{1}{r}\sum_{ij}\left(\frac{c_i c_j b_i b_j}{\langle b\rangle^2}\,\delta(r - r_{ij})\right) - 4\pi r\rho_0. \tag{A.1}$$

Here the sums go over all atoms within the model crystal and r_{ij} is the separation distance between atoms i and j. The value b_i is the scattering length for atom i and $\langle b\rangle$ is the average scattering length of the model crystal. The concentration for each atom site is given by c_i and c_j. Finally ρ_0 is the number density.
The goal is to calculate a difference of two measurements and make one of the atom-atom correlations cancel each other. We will illustrate this using the case of a neutron and x-ray measurement. We write the PDFs for the two measurements as follows:

$$G^n(r) = \frac{1}{r}\sum_{ij} w_{ij}^n\, g_{ij}(r) - 4\pi r\rho_0 \tag{A.2}$$

$$G^x(r) = \frac{1}{r}\sum_{ij} w_{ij}^x\, g_{ij}(r) - 4\pi r\rho_0. \tag{A.3}$$

Here the superscript n stands for neutron data and x stands for x-ray data. $g_{ij}(r)$ describes the atom-atom correlations in the structure and it is independent of the type of measurement. The difference in measurement is contained in the weights,

$$w_{ij}^n = \frac{c_i c_j b_i bj}{\langle b \rangle^2} \tag{A.4}$$

$$w_{ij}^x = \frac{c_i c_j f_i(Q) f_j(Q)}{\langle f(Q) \rangle^2}. \tag{A.5}$$

Note that in the case of x-rays the weights are given by the atomic formfactor, $f(Q)$. When using the program on $S(Q)$ the Q dependence is actually used in the calculation. However, for calculations using $G(r)$, the weights are calculated as $f(Q = 0)$. Next we will assume that we want to remove the correlations between atoms m and n. Rewriting equations A.2 and A.3 will give us

$$G^n(r) = \frac{1}{r} w_{mn}^n \, g_{mn}(r) + \frac{1}{r} \sum_{ij \neq mn} w_{ij}^n \, g_{ij}(r) - 4\pi r \rho_0 \tag{A.6}$$

$$G^x(r) = \frac{1}{r} w_{mn}^x \, g_{mn}(r) + \frac{1}{r} \sum_{ij \neq mn} w_{ij}^x \, g_{ij}(r) - 4\pi r \rho_0. \tag{A.7}$$

Finally the differential PDF without atom pairs m, n is calculated from the experimental data $G^n(r)$ and $G^x(r)$ as

$$G_{\overline{mn}}(r) = \frac{G^n(r)}{w_{mn}^n} - \frac{G^x(r)}{w_{mn}^x}. \tag{A.8}$$

A.2 Using a model

The program calculates the desired differential PDF, $G_{\overline{mn}}(r)$, as defined in equation A.8. Unfortunately this difference has messed up the weights of the other contributions as well. First we need to derive the correct weights. Starting with equation A.8 and using the definitions in equations A.6 and A.7, one finds

$$G_{\overline{mn}}(r) = \frac{1}{r} \sum_{ij \neq mn} \left(\frac{w_{ij}^n}{w_{mn}^n} - \frac{w_{ij}^x}{w_{mn}^x} \right) g_{ij}(r) - 4\pi r \rho_0 \left(\frac{1}{w_{mn}^n} - \frac{1}{w_{mn}^x} \right). \tag{A.9}$$

The most recent version of the program DISCUS (Proffen and Neder, 1997) allows the user to specify the weights for each partial g_{ij}^c. The required commands to be used in DISCUS can be exported in MIXSCAT. A note that the concentrations c_i account for the number of pairs of a particular combination of atom types. When calculating the differential PDF, these are required to obtain the correct weights. Most modeling programs (e.g. DISCUS), however, will loop over all atom pairs. In that case the factor $c_i c_j$ needs to be divided out again. These weights can be saved and used in DISCUS to calculate the correctly weighted differential PDFs from a model.
At this time many programs such as PDFgui (Farrow et al., 2007) do not allow the user to enter specific weights for the different calculated partials and direct calculation of the differential from a model is not possible. However, once can calculate all the individual partials and 'mix' them with the correct weights. We can for example use PDFgui and calculate the neutron weighted partials, $G_{ij}^{n,c}(r)$, as

$$G_{ij}^{n,c}(r) = \frac{1}{r} w_{ij}^n g_{ij}^c(r) - 4\pi r \rho_0, \tag{A.10}$$

and we extract g_{ij}^c from this expression and use equation A.9 to calculate the correct differential PDF, $G_{\overline{mn}}^c(r)$ using e.g. a spreadsheet.

Appendix B

MIXSCAT commands

B.1 Summary

Here is a short summary of the MIXSCAT specific commands currently available:

```
calc    : Starts the calculation of the differential function
elem    : Sets sample composition
match   : Scales data by fitting low r slope
read    : Reads data and model files
remo    : Sets the partial to be removed
save    : Save commands
scal    : Sets scale factor for dataset
scat    : Overwrite internal scattering powers
show    : Display various settings
xray    : Specifies Q-value for calculating X-ray form factors
var     : Shows the available variables
```

B.2 calc

calc

This command starts the actual calculation of the differential function.

B.3 elem

elem <**a1**>,<**c1**>,<**a2**>,<**c2**>,..

This command sets the composition of the sample. For each element, the name <a1> and concentration <c1> is given. For example, CeF3 would be given as elem Ce,1.0,F,3.0.

B.4 match

match <**rmin**>,<**rmax**>,<**rho0**>

This command fits the low r region of each data set between <rmin> and <rmax>. The respective scale factors for the data sets are then determined by scaling the refined slope to the specified number density <rho0>. It is important to use a good guess of the value of <rho0>, e.g. derived from the average structure.
The resulting slope and corresponding sigma are stored in the variables res[i]. As usual res[0] contains the number of parameters available. The slope of data set 1 is in res[1], the error in res[2]. The next set is in res[3] and res[4] and so on.

B.5 read

This command reads various information from a specified file. The following formats are currently supported:

data

read "data",{**"n"**|**"x"**}**,**<**file**>
The command 'read data' reads the observed PDF. The file format is ASCII and contains 'r G(r) dummy dG(r)' in each line. The value of 'r' is in A, G(r) is the reduced PDF. The third column is ignored (needed for KUPLOT) and the last value 'dG' is the error of the PDF used to calculate the weight (w=1/dg**2) for this point to be used for the refinement. Alternative formats are 'r G(r) dG(r)' in each line or simple 'r G(r)'. In the later case, the weights are set to unity. This is also done in case the value of dG(r) is found as zero. Additional to the filename <file> the commands needs the following parameters: First the type of radiation is specified, "n" stands for neutrons and "x" for X-rays. To read multiple data sets just repeat the 'read' command.
If the data file contains a history part created by PDFgetN, some of the information is returned in the res[n] variables. Currently the following information is available after the 'read data' command:

```
res[1]   : Temperature where the data were collected (in K)
res[2]   : Qmax (only AFTER the data were read !)
```

B.6 remove

remove <**a1**>,<**a2**>
This commands sets the partial to be removed to <a1>-<a2>. For example in the case of CeF3, the command remove Ce,Ce would generate a differential function containing only Ce-F and F-F contributions.

B.7 save

This command allows one to save various data or settings. The following formats are currently supported:

pdf

save "pdf",<**name**>
This commands allows one to save the differential PDF, G(r), to the file called <name>.

results

save "results",<**name**>
This command save information about the setup and error analysis of the last calculation to the file named <name>.

weights

save "weights",<**name**>
In order to calculate the corresponding differential PDF from a structural mode, the modified weights for each remaining partial g_ij(r) is needed. This command saves the weights to a DISCUS macro file called <name>.

B.8 scat

scat {<**name**>|<**number**>},<**a1**>,<**b1**>,<**a2**>,<**b2**>,<**a3**>,<**b3**>,<**a4**>,<**b4**>,<**c**>
scat {<**name**>|<**number**>|**"all"**}, **"internal"**
The first command form defines for the element <name> or the scattering curve number <number> a new scattering factor in the exponential form. For neutron scattering lengths, set a(i) and b(i) to zero.

B.9 scal

scal <**is**>,<**factor**>
This command sets the scale factor <factor> for data set <is>. This is used in cases where the data need scaling due to systematic errors.

B.10 show

show
show "config"
show "error"
show "scat",<**is**>**,**{<**a**>|**"all"**>

This command displays all current settings. The command show "config" will show current limits such as maximum number of data points. The command show "error" will display results of an error analysis on the screen. The subcommand "scat" shows the current scattering lengths to be used for data set <is> for atom <a> or "all" atoms.

B.11 variables

The program MIXSCAT recognizes various variables. The contents of a variable can be displayed using the 'eval' command. Some variables are READONLY (RO) and can not be changed.

```
i[<n>]      : Integer variables
r[<n>]      : Real variables
res[<n>]    : Results of MIXSCAT commands (RO)
n[1]        : Number of loaded data sets (RO)
```

B.12 xray

xray [<**xq**>]

This command sets the Q-value used to calculate the scattering length used in the PDF calculation. The default value is xq=0 which results in a weight corresponding to the number of electrons of the contributing atoms. Other settings could be the Q value of the first Bragg peak or the average Q value of the data set. Calling the command without parameters prints the current setting on the screen.

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