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## **XTAL: A Program for Calculating Interatomic Distances and Coordination Numbers for Model Structures**

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# XTAL : A PROGRAM FOR CALCULATING INTERATOMIC DISTANCES AND COORDINATION NUMBERS FOR MODEL STRUCTURES

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A description is given of a program, XTAL, which enables the user to study the interatomic distances and atomic coordination numbers for an arrangement of atoms of given positions. It is intended primarily for use in the interpretation of diffraction results for non-crystalline samples, but has already found application in other fields as well. The approach used by the program involves a calculation of partial radial distribution functions. The program is written to be both general and flexible so that it may be used to study a wide variety of periodic structures including crystals and the results of molecular dynamics calculations, as well as non-periodic structures such as molecules and ball-and-stick models.

## 1. Introduction

The program XTAL enables the interatomic distances and atomic coordination numbers for an arrangement of atoms to be evaluated by means of a calculation of the partial radial distribution functions (RDFs). The RDF is chosen in preference to any other function because it gives coordination numbers directly. However, the output of the program is intended primarily to be used in conjunction with the GENIE data display and manipulation program [1] and provision is made for easy calculation of other functions.

In the case of periodic structures (crystals) the atomic environment of a particular atom is identical to that of an equivalent atom in any other unit cell and hence it is only necessary to calculate the partial RDFs for origin atoms in one unit cell. Thus for periodic structures the method used by the program involves constructing a model where a central 'origin' unit cell is surrounded with further layers of unit cells and then calculating the RDFs for origin atoms in the 'origin' cell only. The number of layers is chosen by the user to achieve an acceptable maximum distance for which the results are reliable. The program treats non-periodic structures by setting the number of layers to zero.

## 2. Theory

The partial pair distribution function for an arrangement of atoms may be defined by

$$g_{ir}(r) = \frac{1}{N_i} \sum_{j=1}^{N_l} \sum_{\substack{j'=1 \\ j \neq j'}}^{N_{l'}} \langle \delta(\underline{r} + \underline{R}_j - \underline{R}_{j'}) \rangle \quad (1)$$

where  $\underline{R}_j$  is the position of the  $j^{\text{th}}$  atom. The  $j, j'$  sums are over the  $N_l, N_{l'}$  atoms of element  $l, l'$  and  $j \neq j'$  means that  $j$  and  $j'$  are not allowed to refer to the same atom.  $g_{ll'}(r)$  may be interpreted as the number density of atoms of element  $l'$  at a distance  $r$  ( $=|\underline{r}|$ ) from an origin atom of element  $l$ , averaged over all possible origin atoms and directions of  $\underline{r}$ .

At high  $r$  the partial pair distribution function tends to its average value

$$\lim_{r \rightarrow \infty} g_{ll'}(r) = g_{l'}^{\circ} = \frac{N_{l'}}{V} \quad (2)$$

where  $V$  is the volume of the sample and  $g_{l'}^{\circ}$  is the macroscopic number density of  $l'$  atoms. At lower  $r$   $g_{ll'}(r)$  oscillates about this value.

A partial correlation function  $t_{ll'}(r)$  and a partial radial distribution function (RDF)  $n_{ll'}(r)$  may also be defined;

$$t_{ll'}(r) = 4\pi r g_{ll'}(r) \quad (3)$$

$$n_{ll'}(r) = 4\pi r^2 g_{ll'}(r) \quad (4)$$

$n_{ll'}(r)dr$  gives the number of atoms of element  $l'$  at distances in the range  $(r, r+dr)$  from an origin atom of element  $l$ , averaged over all possible origin atoms and directions. Integrating an RDF over a range of  $r$  gives the coordination number for that range of  $r$ .

In a neutron diffraction experiment a total function is measured which is a weighted sum of the partial functions. The total RDF  $N(r)$ , correlation function  $T(r)$  and pair distribution function  $G(r)$  measured in a neutron diffraction experiment are given respectively by

$$N(r) = \sum_{l,l'} c_l \bar{b}_l \bar{b}_{l'} n_{ll'}(r) \quad (5)$$

$$T(r) = \sum_{l,l'} c_l \bar{b}_l \bar{b}_{l'} t_{ll'}(r) \quad (6)$$

$$G(r) = \sum_{l,l'} c_l \bar{b}_l \bar{b}_{l'} g_{ll'}(r) \quad (7)$$

where  $c_l$  ( $= N_l/N$ ) is the atomic fraction for element  $l$ ,  $\bar{b}_l$  is the coherent neutron scattering length for element  $l$ , and the  $l$  and  $l'$  summations are both over the elements of the sample.

In the case where an additional weighting factor is attached to each atom (for example the occupancy of a site may be less than one) equation (1) becomes

$$g_{ll'}(r) = \frac{1}{N_l} \sum_{i=1}^{N_l} w_i \sum_{\substack{j=1 \\ j \neq j'}}^{N_l} \sum_{j'=1}^{N_{l'}} w_j w_{j'} \langle \delta(\underline{r} + \underline{R}_j - \underline{R}_{j'}) \rangle \quad (6)$$

where  $w_i$  is the weight associated with the  $i^{\text{th}}$  atom.

### 3. Input to the Program

The program is written in Fortran to run on a computer running the VMS operating system. In order to use the program the user must provide (either by editing or by writing a simple program) a free format input file with extension .XTAL which specifies the model as follows:

line	entry	parameters
1	1	Title (a line of text)
2	1	Unit cell mode (integer)
	2	Atom position mode (integer)
	3	Number of atoms in unit cell (integer)
	4	Number of atom types (integer)
	5	Distance scale factor
	(6	Weighting mode (integer))
3	1	Text line
4	-	Unit cell specification
5	-	Unit cell specification
6	-	Unit cell specification
7	1	Text line
8 etc	-	Atom specification

#### Definition of Terms

- The unit cell mode indicates how the unit cell is to be specified:

Mode 0 means that the model is non-periodic (and hence there is no unit cell to be specified).

Mode 1 means that the unit cell is specified by three Cartesian translation vectors  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$ . Each unit cell specification line of the file gives the three Cartesian components of one of these vectors.

Mode 2 means that the unit cell is specified by three lattice parameters  $a$ ,  $b$  and  $c$  and the three angles (in degrees)  $\alpha$ ,  $\beta$  and  $\gamma$  between  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$  according to the conventional definition. The first unit cell specification line of the file gives  $a$ ,  $b$  and  $c$ , whilst the second line gives  $\alpha$ ,  $\beta$  and  $\gamma$ . The third line contains no information.

- The atom position mode indicates how the atom positions are to be specified:
  - Mode 1 means that the position of each atom is given by three Cartesian coordinates.
  - Mode 2 means that the position  $\underline{r}$  of each atom is given by three components  $r_a, r_b$  and  $r_c$  where  $\underline{r} = r_a \underline{a} + r_b \underline{b} + r_c \underline{c}$ .
- The weighting mode is optional. It indicates whether or not weights for the atoms are to be used.
  - Mode 0 means that any weights are to be ignored (ie. all weights are assumed equal to one).
  - A mode other than 0 indicates that any weights given will be used in the calculation. Any weights not given are assumed equal to one.
- Each line of atom position specification gives the number of the atom (1,2,3...), the atom type (integer), and the three values (real) which specify the position of that atom. The atom types should be numbered sequentially (1,2,3...). A weight for the atom may optionally be given at the end of the line. Note that the full contents of the unit cell must be specified in the .XTAL file for a periodic structure; the program does not make use of crystallographic symmetry to generate equivalent atomic positions within the unit cell.

As an example the input file BCC.XTAL is given for a body-centred cubic unit cell with different atom types at cell corners and centres (with no weighting of atoms):

```

bcc
1      1      2      2      1.0
translation vectors...
1.0    0.0    0.0
0.0    1.0    0.0
0.0    0.0    1.0
atoms in the cell...
1      1      0.0    0.0    0.0
2      2      0.5    0.5    0.5
  
```

#### 4. Running the Program

The program XTAL is currently available at ISIS on the VAX computers running the VMS operating system. The program may be run interactively by typing `RUN G_F:XTAL` where it is assumed that the logical name G\_F has been defined (by the command `ASS LAD$DISK:[LADMGR.PROGS] G_F`) to indicate the area used to store the programs for the ATLAS suite [2,3]. It will also be necessary for the user to have LAD user rights to have access to the program. In cases where the number of atoms is large it may be preferable to run the program in batch and such a batch job may be submitted by use of the command `@G_F:XTAL_B`.

In the case of a periodic structure the number of layers  $M$  should be chosen according to the required maximum reliable distance, as described in section 5. The calculated RDFs may be chosen to be in absolute units of atoms/Å (assuming distances are given in Ångstroms in the .XTAL file) as defined by equation (4) so that the area under a histogram bin gives the number of atoms which occur in the range of distances covered by the bin. In this case coordination numbers may be obtained in GENIE by integrating the workspace which contains the RDF over a restricted range of  $r$  (eg. INT W1 0.9 1.1). Alternatively a normalisation may be selected for which the height of the histogram equals the number of atoms which occur in the range of distances covered by the bin; this may be of particular use in ascertaining quickly (without the need for integration over a range of distance) the coordination number at a particular distance in a model. The results will be output to a file of the same name as the input .XTAL file. The output file may be chosen to be either a binary file of extension .RDF which may be read into GENIE by the READ command (ie. a GENIE intermediate file), or an ASCII file of extension .RDF\_ASC. As well as the partial RDFs, the user may also choose to evaluate the total RDF, defined by equation (5), in which case the user must supply the coherent neutron scattering lengths for each element involved.

The density is an important structural parameter and hence the program calculates the atomic number density where possible (ie. for periodic structures for which a meaningful volume is clear). The relevant atomic number density  $g_v^o$  is also stored in the output file together with each partial RDF to enable a calculation of its average density component (equation (2)).

The program offers the opportunity to write the coordinates of every atom in the full model used to generate the partial RDFs to an ASCII file which is given the same name as the input .XTAL file and has extension .COORDS. There is also an option to 'analyse distances'. This option prompts the use for a distance  $r_0$  and a tolerance  $\Delta$ . The program reports any interatomic distances in the model that occur in the range  $r_0 \pm \Delta$ , giving the exact distance and the details of the two atoms involved. A list is then given of all the unique distances which occur in this range. Finally this list is written to an ASCII file of extension .DISTS.

It is generally recommended that the user chooses the option to write the results to a GENIE intermediate file of extension .RDF in which case they may be read in to GENIE workspaces by using the command @G\_F:RDF within GENIE. Alternatively a single function may be selected and read into a workspace by use of the command @G\_F:RDF1. These GENIE commands also perform conversion of RDFs to correlation functions  $t_{ij}(r)$  or pair distribution functions  $g_{ij}(r)$  if required (equations (3) and (4)). Furthermore the average density component (eg. equation (2)) is calculated where possible.

The GENIE input programs RDF and RDF1 offer the option of broadening the functions from the .RDF file. The purpose of this broadening is to simulate the broadening of experimental data due to thermal motion and finite resolution in real-space (and possibly static disorder). A simple algorithm is used to broaden the data with a Gaussian function (of unity area so as to preserve coordination numbers);

$$P(r) = \frac{I}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(r-r_0)^2}{2\sigma^2}\right) \quad (9)$$

A program is available to enable the model specified by a .XTAL file to be viewed by use of the graphics program Schakal [4]. An input file for Schakal of extension .DAT may be created from a .XTAL file by **RUN G\_F:X2SCH**. This file may be read into Schakal by the command **L D**. Another program, run by **RUN G\_F:SCH2X**, is also available to convert a .DAT file to a .XTAL file. A version of the Schakal program which produces POSTSCRIPT output files may be run by typing **RUN G\_F:SCHAKWORK**.

## 5. Details of the Calculation

For periodic structures the program will check that all of the specified atoms are contained within the specified unit cell. If they are not then it is possible for them to be shifted into the unit cell by a combination of translation vectors  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  ('re-boxing'). In the case of a crystal structure this may indicate an error in the specification of the unit cell. However, for a molecular dynamics model this is not necessarily an error since it is quite possible for atoms to pass outside the cell during the simulation.

The program builds a periodic model by surrounding a central origin cell by  $M$  layers of unit cells. There are thus  $2M+1$  cells on a side. The maximum value of  $r$  at which atoms may be found is given by  $(M+1)$  times the longest diagonal of the unit cell. However, the maximum value of  $r$  for which the result is reliable is given by  $M$  times the smallest of the three  $d$ -spacings  $d_{100}$ ,  $d_{010}$  and  $d_{001}$ , since the vector  $\mathbf{r}$  should not pass outside the model whatever its direction for the calculated RDF  $n(r)$  to be reliable. For example;

$$d_{001} = \frac{c\sqrt{\Delta}}{\sin \gamma} \quad (10)$$

where

$$\Delta = \begin{vmatrix} 1 & \cos \gamma & \cos \beta \\ \cos \gamma & 1 & \cos \alpha \\ \cos \beta & \cos \alpha & 1 \end{vmatrix} \quad (11)$$

and  $\alpha$ ,  $\beta$  and  $\gamma$  are the angles between  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$ .

The results in the output file are given in the form of histogram data (ie. each pair of values  $(x, y)$  specifies the top left hand corner of a histogram bin).

## 6. Examples

The figures show some examples of the use of the program XTAL.

Figure 1 shows the partial RDFs calculated for a body centred cubic (bcc) structure which has different elements at the cube corners and centres and which has a lattice parameter  $a=1.0\text{\AA}$  (the .XTAL file is the example given in section 3). The calculation was performed with  $M=4$  and with the normalisation option where histogram height equals number of atoms at that distance. Each atom has 8 unlike-atom nearest neighbours at a distance  $\sqrt{3}a/2$ , 6 like-atom next nearest neighbours at a distance  $a$ , 12 like-atom third nearest neighbours at a

distance  $\sqrt{2}a$  and so on, and these coordination numbers are apparent from the figure with the chosen normalisation option.

Figure 2a shows the RDF calculated for a perfect icosahedral molecule composed of 12 identical atoms (there is only one partial function) with a bond length  $r_I=1.809\text{\AA}$ . The calculation was performed with the normalisation option of absolute units and with a spacing of  $\Delta r=0.015\text{\AA}$ . The calculation results were broadened with a Gaussian of width  $\sigma=0.13\text{\AA}$ . The unbroadened function has been multiplied by  $\Delta r$  with the consequences both that it is on the same scale as the broadened function and that histogram height equals coordination number. In an icosahedral molecule, as shown in figure 3, each atom has 5 nearest neighbours at a distance corresponding to the bond length  $r_I$ , 5 second nearest neighbours at a distance  $1.618r_I$  and a single third nearest neighbour at a distance  $1.903r_I$ . Figure 2b shows the experimentally measured RDF of amorphous boron which is believed to have a structure which involves icosahedral units [5].

Figure 4 shows the partial RDFs calculated by XTAL for the reported structure of the  $\alpha$ -phase of  $\text{CF}_4$  [6]. The unbroadened RDFs are shown with the normalisation choice for which histogram height equals the number of atoms at that distance. The broadened and average density functions are both in absolute units but have been divided by a factor of 5.0 so that they are on the same scale as the unbroadened function. The XTAL calculation was performed with  $M=3$  layers and  $\Delta r=0.01\text{\AA}$ , whilst a Gaussian width  $\sigma=0.10\text{\AA}$  was used for the broadening.  $\text{CF}_4$  is a molecular crystal composed of tetrahedral  $\text{CF}_4$  molecules. The coordination numbers are apparent from the heights of the histograms of figure 4; each F has one C at  $\sim 1.32\text{\AA}$ , each C has 4 F at  $\sim 1.32\text{\AA}$ , each C has 2 nearest neighbour Cs along each axis in 3-dimensional space at distances from  $4.2\text{\AA}$  to  $4.5\text{\AA}$  etc. Figure 5 shows a plot of the unit cell for this reported structure. Figure 6a shows the calculated total neutron correlation function  $T(r)$  for the reported structure of the  $\alpha$ -phase of  $\text{CF}_4$  whilst figure 6b shows the total correlation function for  $\text{CF}_4$  in the  $\alpha$ -phase obtained from a preliminary analysis of an experimental measurement made on the LAD instrument at ISIS [7]. At low  $r$  the agreement is good, but at high  $r$  the oscillations in the experimental function have a smaller amplitude than for the calculation. The most likely cause of this is the finite resolution of the raw experimental data which were Fourier transformed to obtain the data shown in figure 6b (LAD has  $\Delta Q/Q=1.8\%$  at the scattering angle,  $35^\circ$ , appropriate to the data used here).

Figure 7a shows the total neutron correlation function  $T(r)$  for a 576 atom molecular dynamics simulation of lithium disilicate ( $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ ) glass [8] as calculated by XTAL together with the average density contribution. The molecular dynamics simulation was performed with a cell for which  $a=24.10\text{\AA}$ ,  $b=18.95\text{\AA}$ ,  $c=15.90\text{\AA}$ ,  $\alpha=90^\circ$ ,  $\beta=104.24^\circ$  and  $\gamma=90^\circ$ . Hence a single layer ( $M=1$ ) was sufficient for the XTAL calculation, which was performed with  $\Delta r=0.03\text{\AA}$ . Figure 7b shows an experimental measurement of  $T(r)$  for lithium disilicate glass [9,10]. The negative-going peak at  $2.0\text{\AA}$  is due to Li-O correlations. Even though the model function has not been broadened to simulate the effects of thermal motion and real-space resolution, the XTAL calculation shows it to be too broad in comparison to the experimental data.

The following files which relate to the examples are available:

- G\_F:BCC.XTAL - The input file for XTAL to do the calculation shown in figure 1.
- G\_F:ICOS.XTAL - The input file for XTAL to do the calculation shown in figure 2a.
- G\_F:ICOS.DAT - The input file used by Schakal to do the plot shown in figure 3.



- G\_F:CF4\_2\_X.XTAL - The input file for XTAL to do the calculation shown in figures 4 and 6a.
- G\_F:CF4\_2\_X.DAT - The input file used by Schakal to do the plot shown in figure 5.

## Appendix A. GENIE parameters stored in the output .RDF file

With each workspace  $n_{ir}(r)$  in the .RDF file the GENIE user\_par parameters are used to store the following information:

- 1 - the number of blocks in the output file.
- 15 - the relevant atomic number density  $g_r^\circ$  for calculating the high  $r$  limit.
- 19 - unit cell mode.
- 20 - normalisation option.
- 21,22... -  $\bar{b}_i$  values used to calculate the total RDF (if this has been done).

## References

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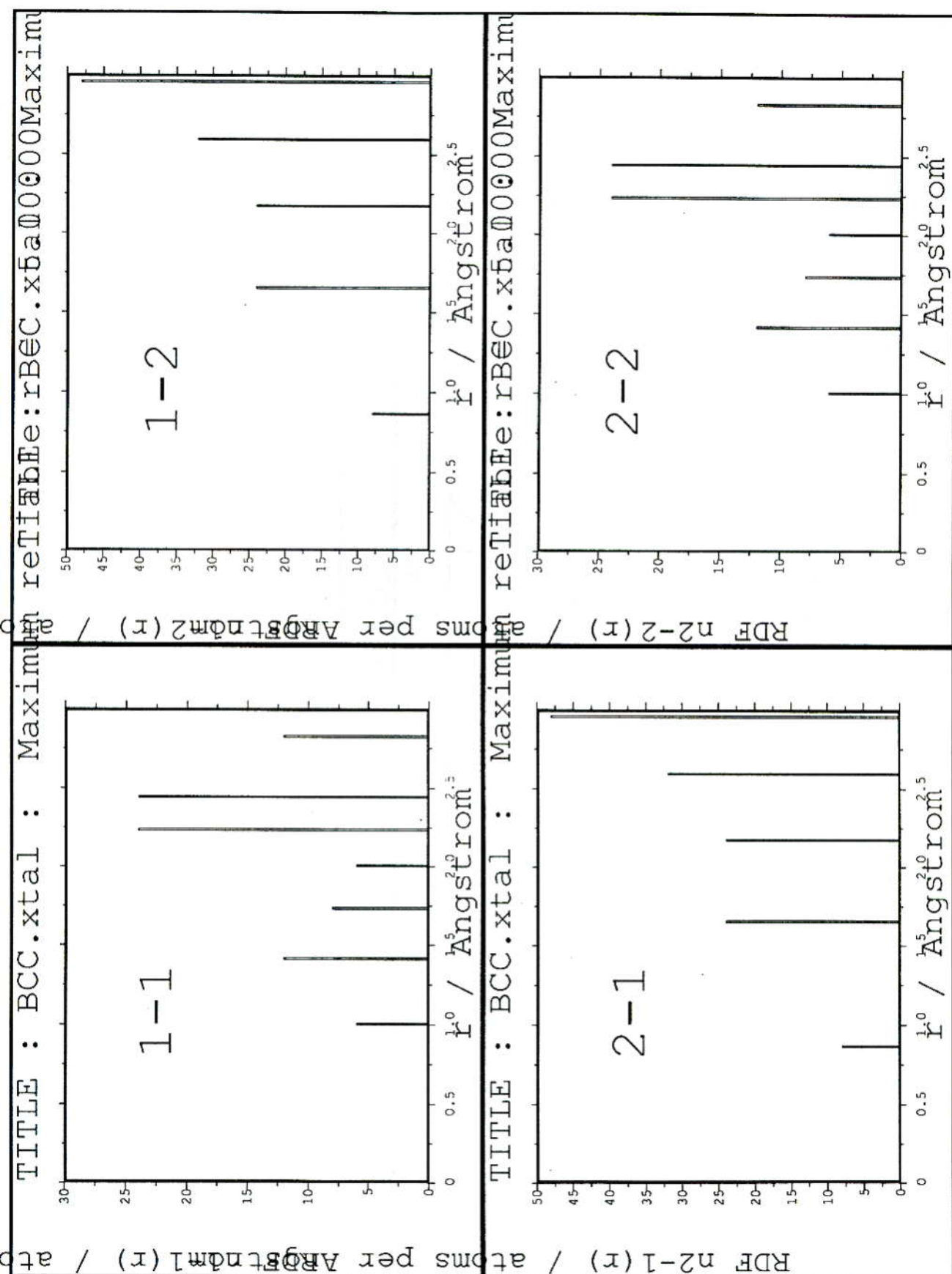


Figure 1. The partial RDFs for a BCC structure with lattice parameter 1.0Å and with different elements at the cube corners and centres.

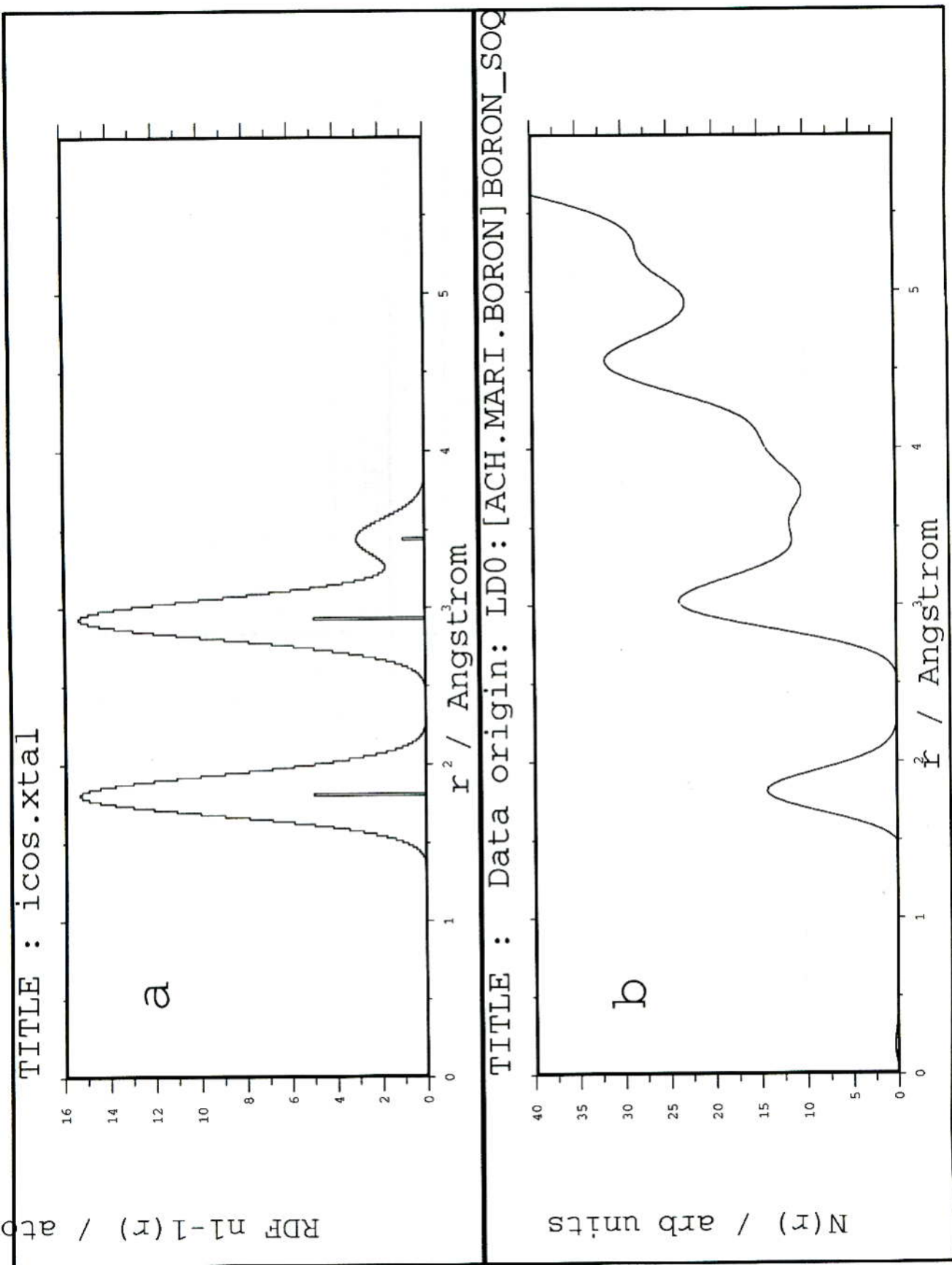


Figure 2. a) The calculated RDF for an icosahedral molecule with and without broadening. b) The experimental RDF of amorphous boron [5].

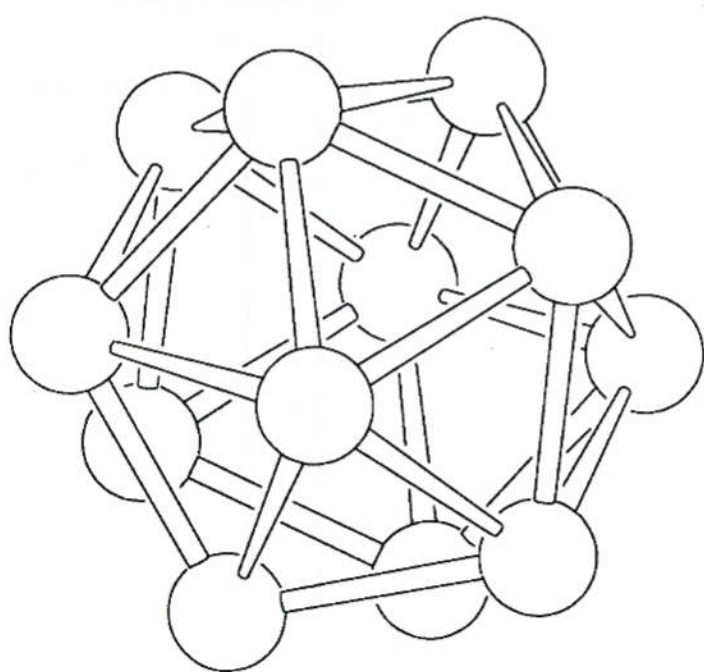


Figure 3. An icosahedral molecule.

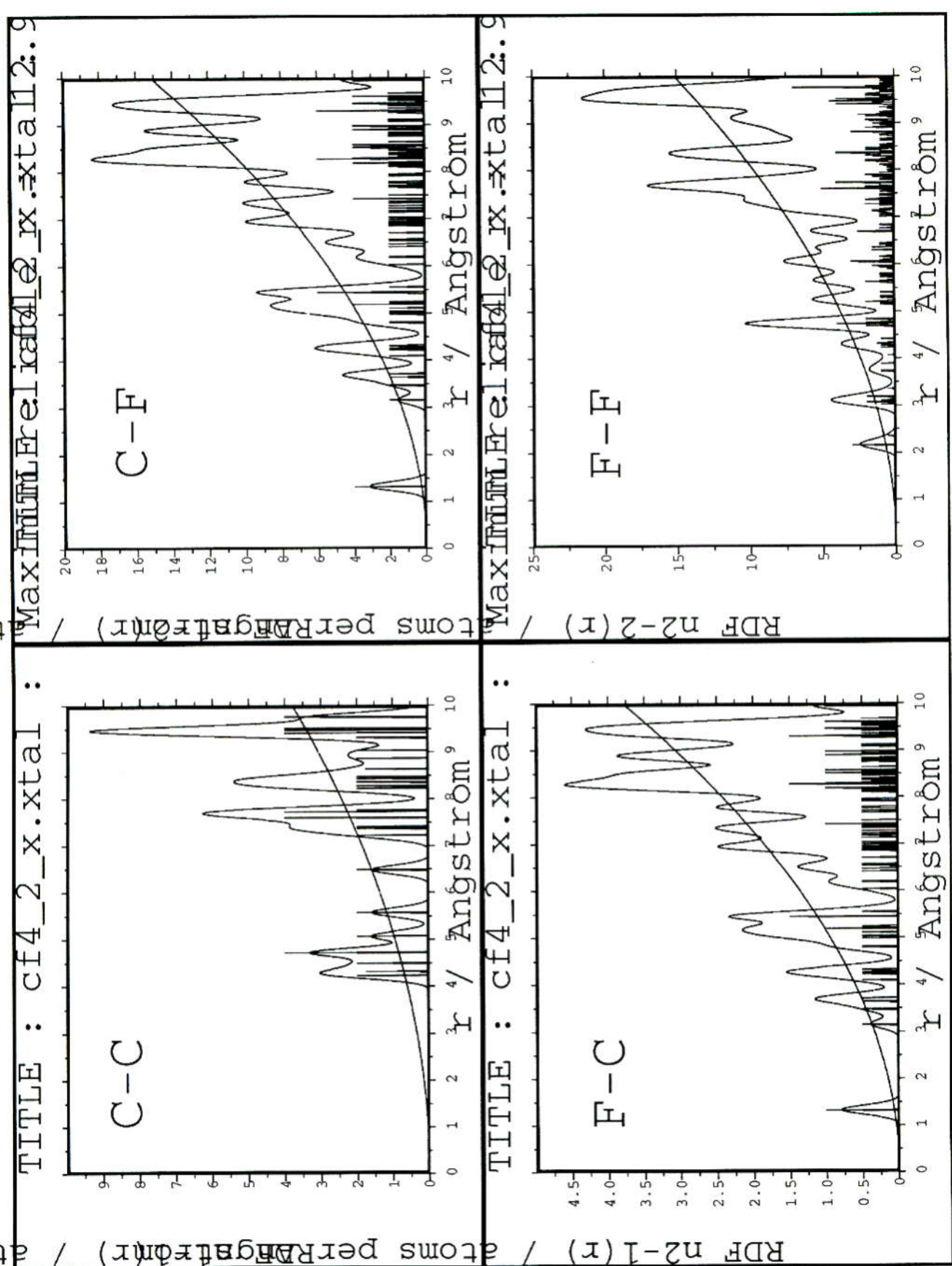
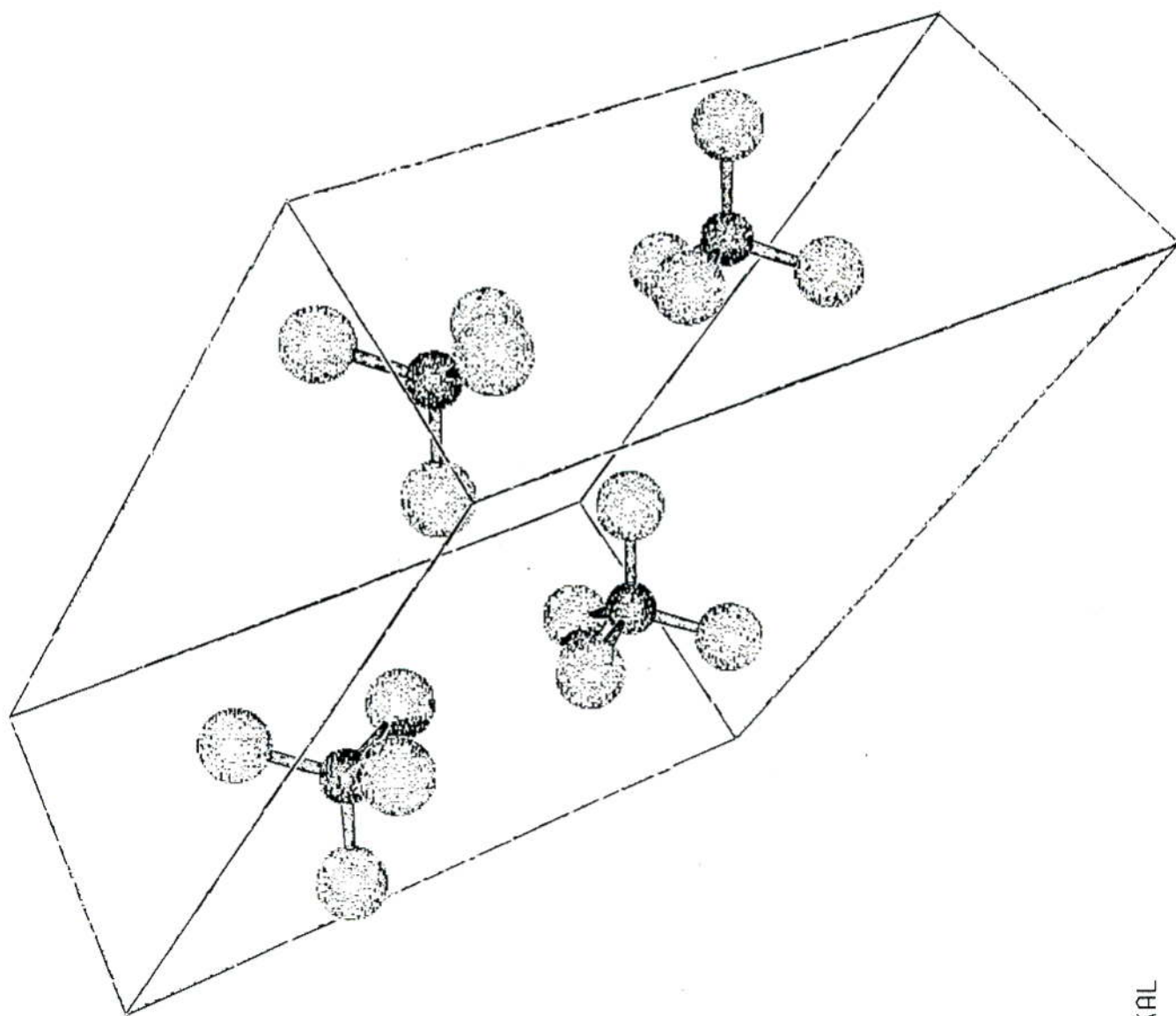


Figure 4. The partial RDFs for the reported structure of the  $\alpha$ -phase of  $\text{CF}_4$  [6], showing the unbrodened RDF (histogram), the broadened RDF (featured line) and the average density contribution (smooth line).



SCHAKAL

Figure 5. A plot of the reported unit cell of the  $\alpha$ -phase of  $\text{CF}_4$  [6] produced by the program Schakal [4].

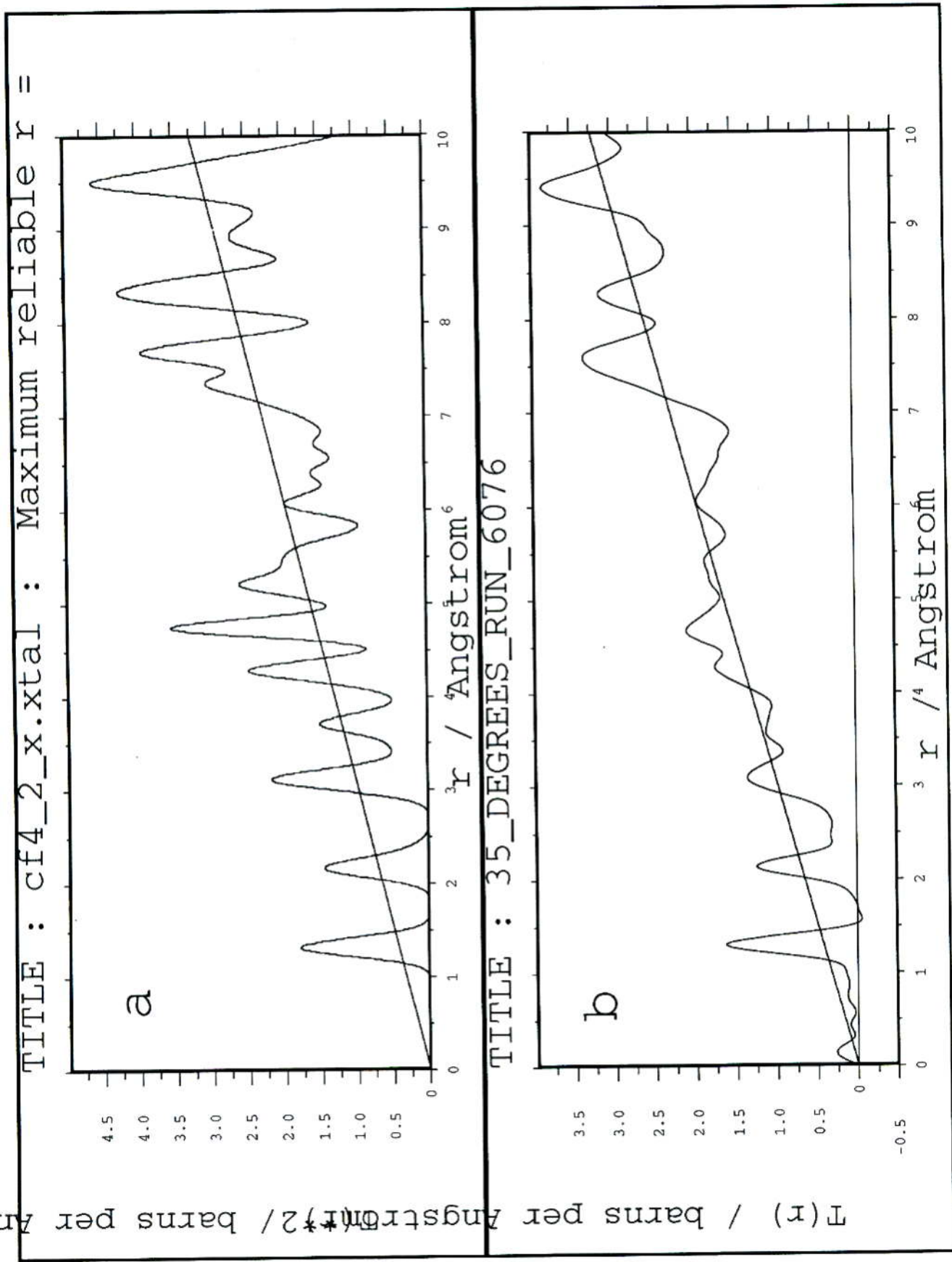


Figure 6. a) The calculated total correlation function for the reported structure of the  $\alpha$ -phase of  $\text{CF}_4$  [6].  
 b) The measured total correlation function of  $\text{CF}_4$  in the  $\alpha$ -phase [7].

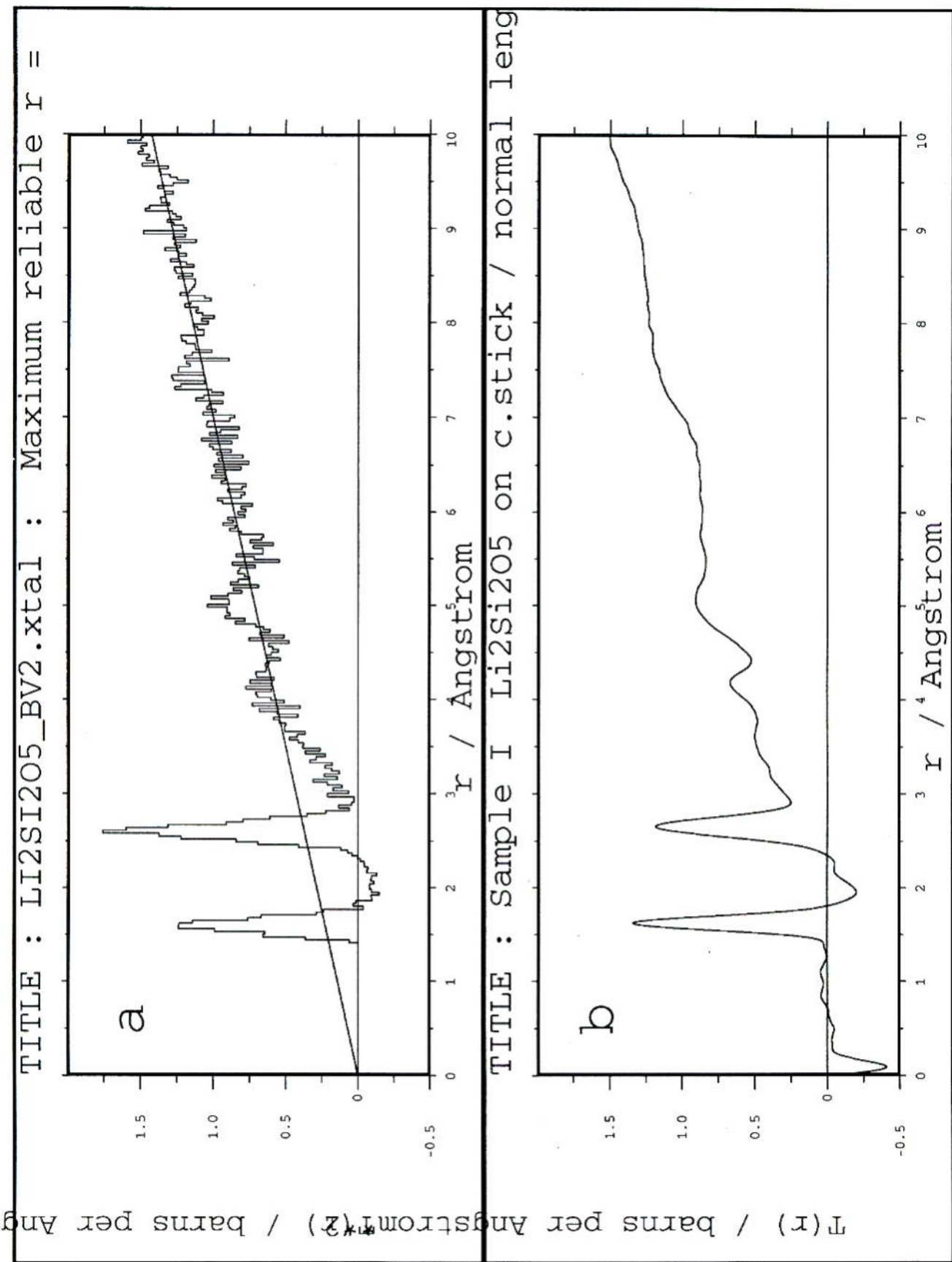


Figure 7. a) The total correlation function  $T(r)$  for a molecular dynamics simulation of lithium disilicate glass [8] as calculated by XTAL (histogram) together with the average density contribution (straight line). b) An experimental measurement of the total neutron correlation function for lithium disilicate glass [9,10].