Local order of deuterium in metal deuterides

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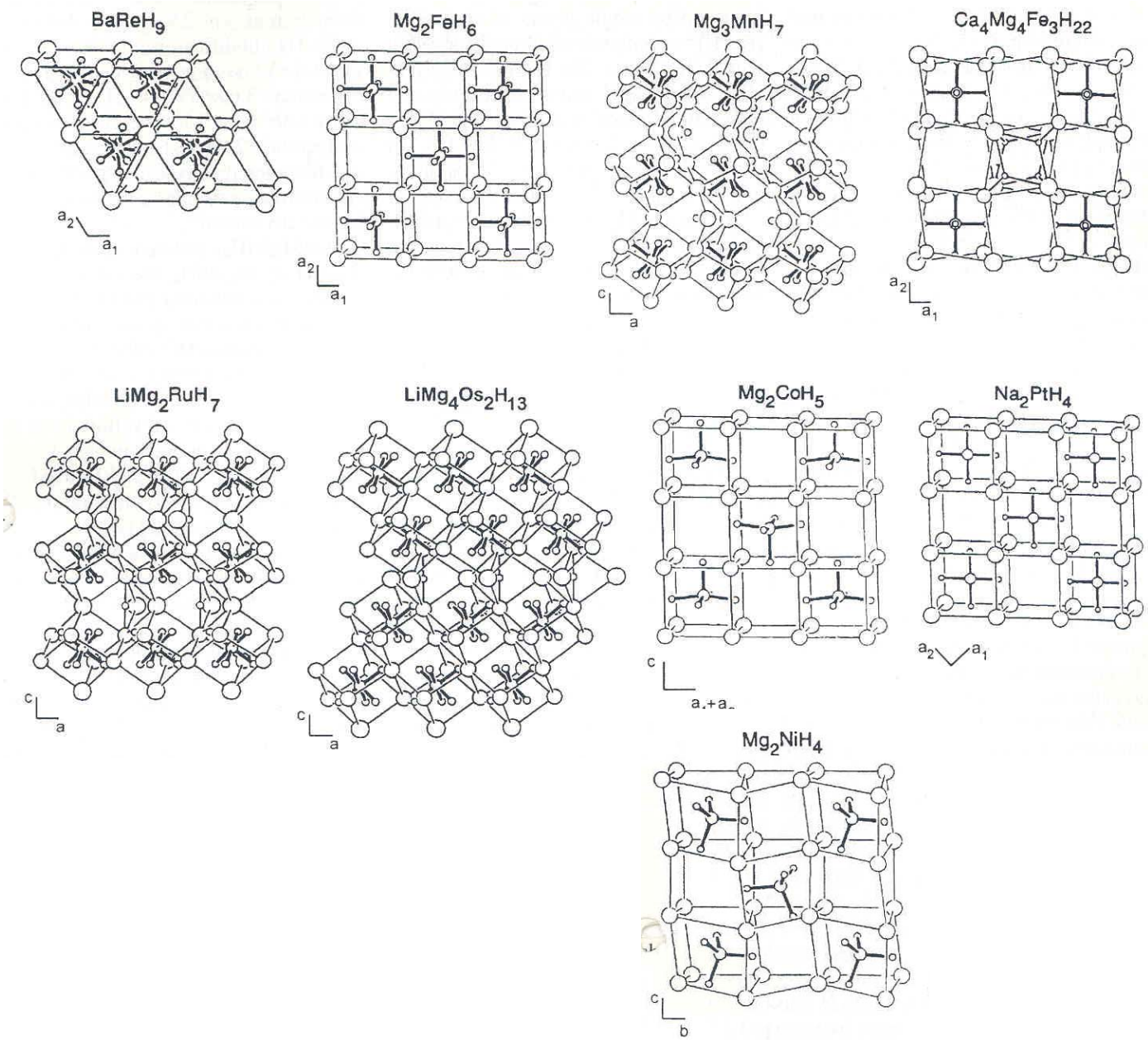
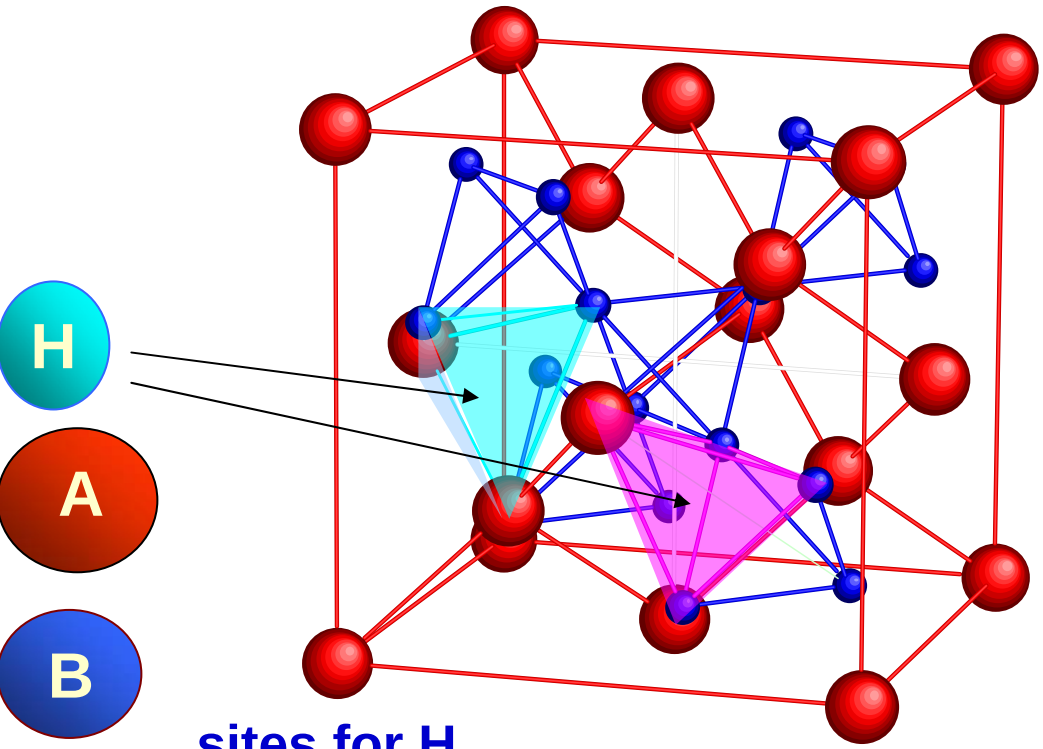
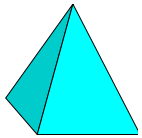
Complex transition metal hydrides



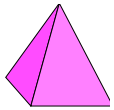
Interstitial hydrides



sites for H



A2B2 96g



AB3 32e

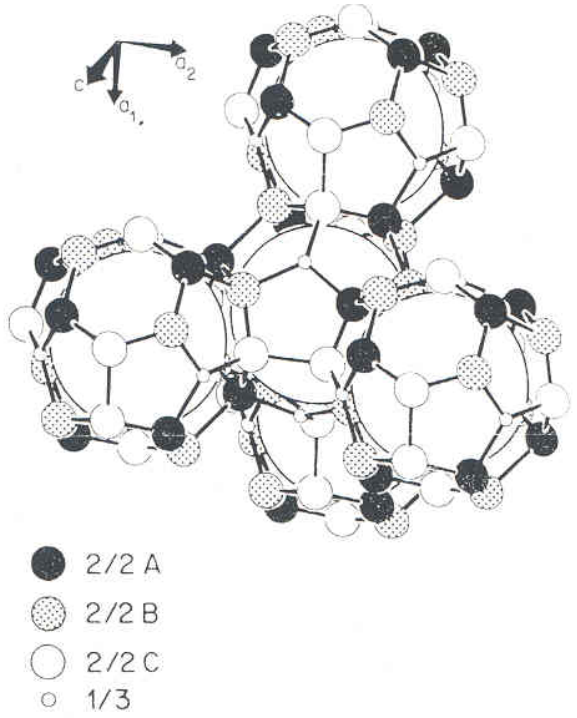
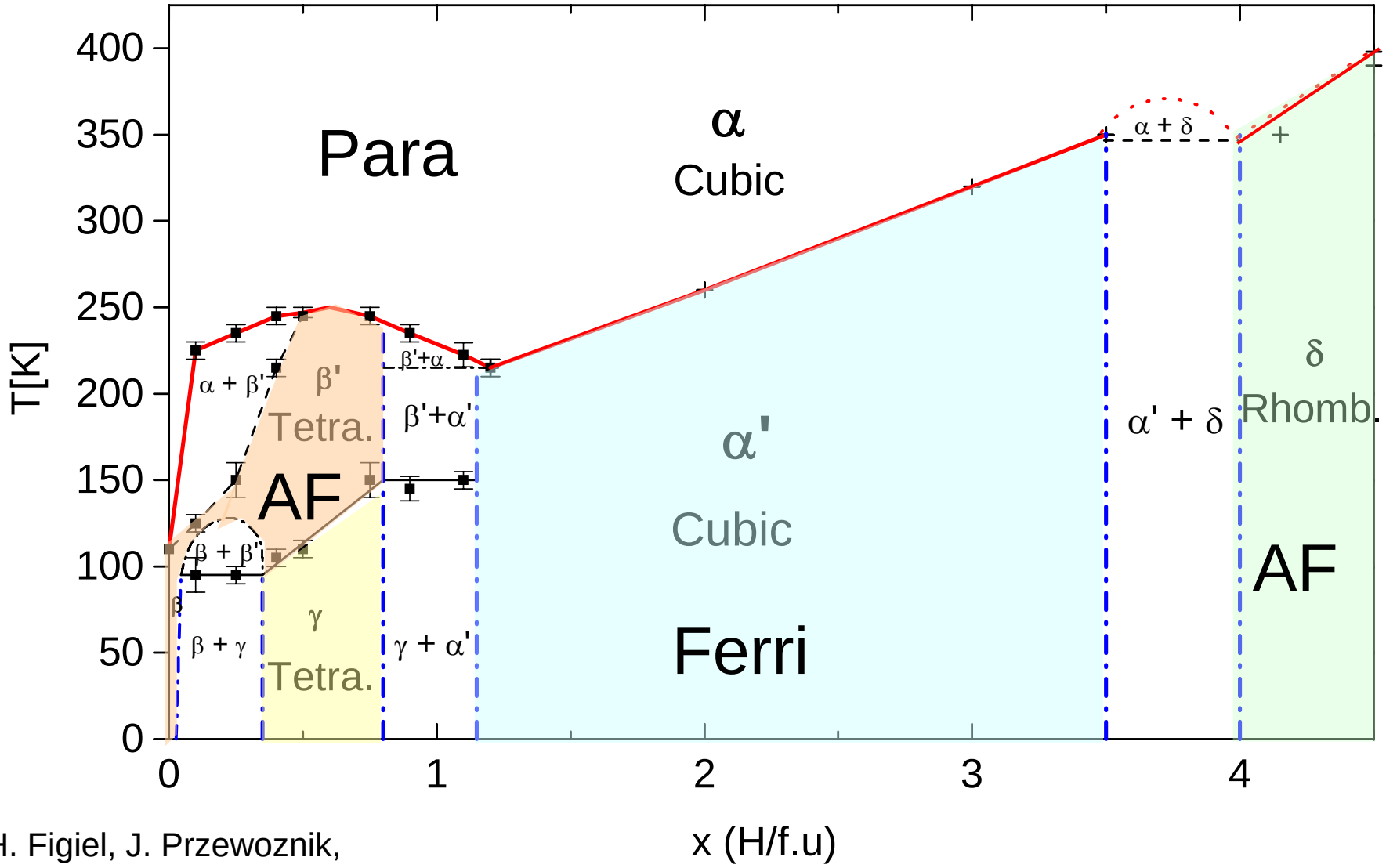


Fig. 5. The structural arrangement of the deuterium atom sites around the Zr atoms. The V atoms have been omitted for clarity. The sites which are connected by lines are about 1.3 Å apart. The distance between nearest sites 2/2A or nearest sites 2/2B is about 2.1 Å. In the disordered high temperature phase the deuterium atoms are distributed over all sites, whereas in the fully ordered low temperature phase they occupy only sites 2/2A. The tetragonal axes $a_1 = a_2$ and c vary with temperature as shown in Fig. 3.

Hydrides of Laves phases: YFe_2D_x, YMn_2D_x

Long range order (XRD + Magn.)

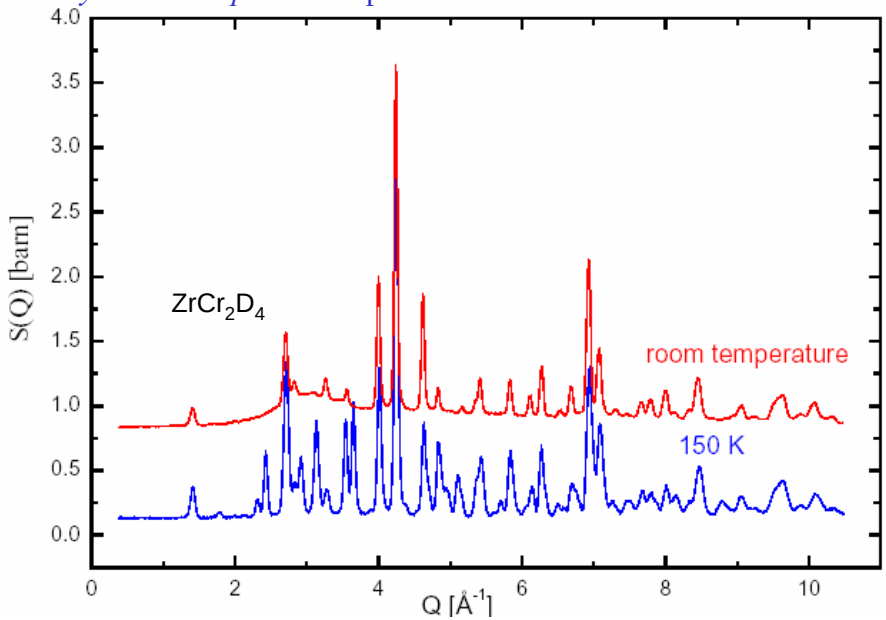


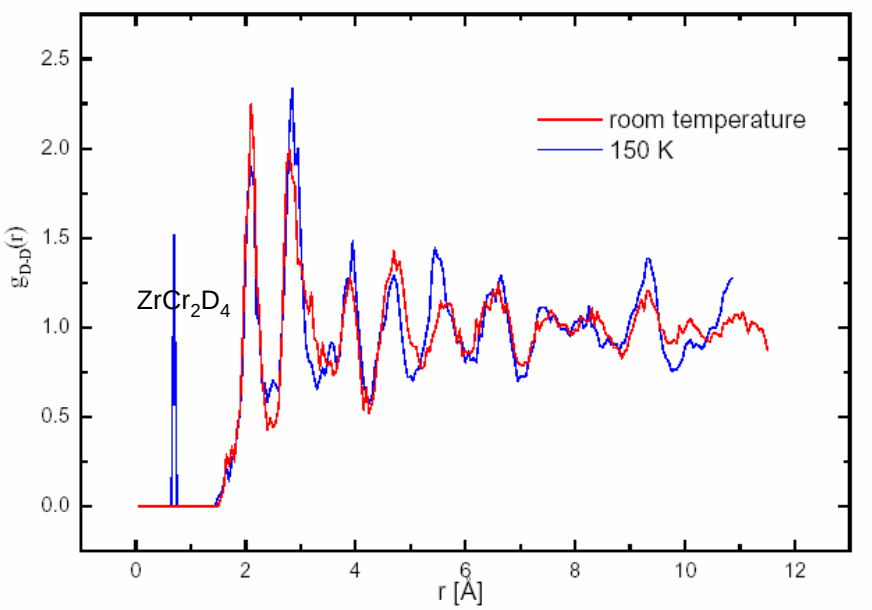
H. Figiel, J. Przewoznik,
V. Paul-Boncour, et al.
J. Alloys Compds, 274 (1998)

Phase diagram of YMn_2H_x

Long range order survives locally ?

J. Alloys and Compounds in press





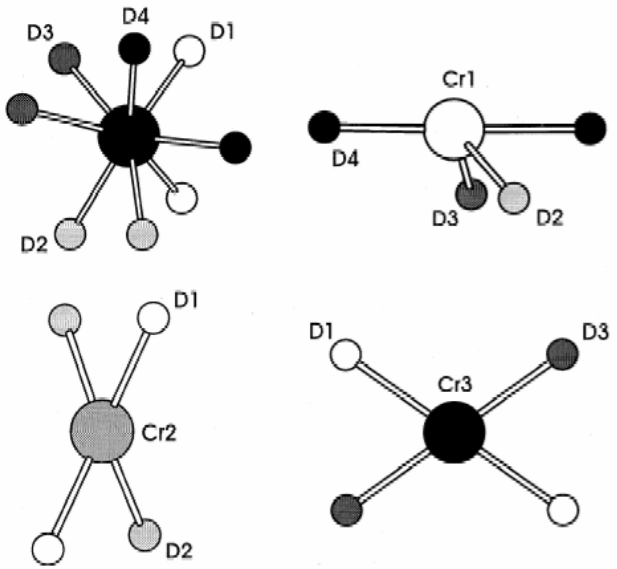


Fig. 5. Deuterium configuration around zirconium and chromium sites in monoclinic $ZrCr_2D_{3.8}$ at 1.6 K.

J. Alloys and Compounds 285 (1999) 204–211

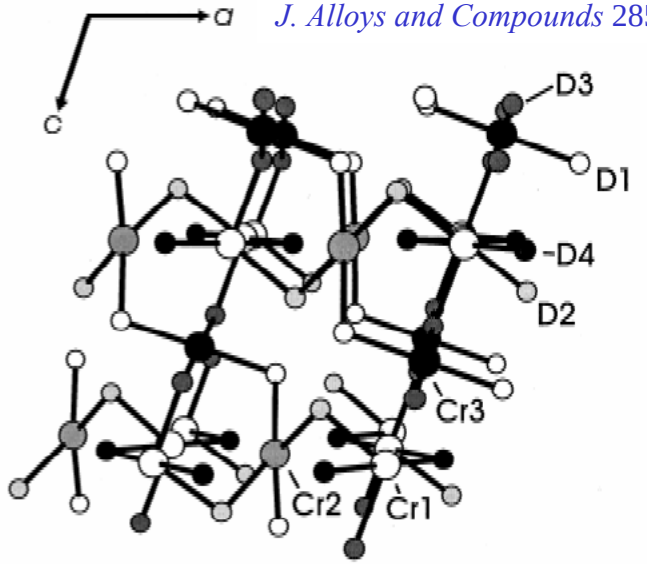
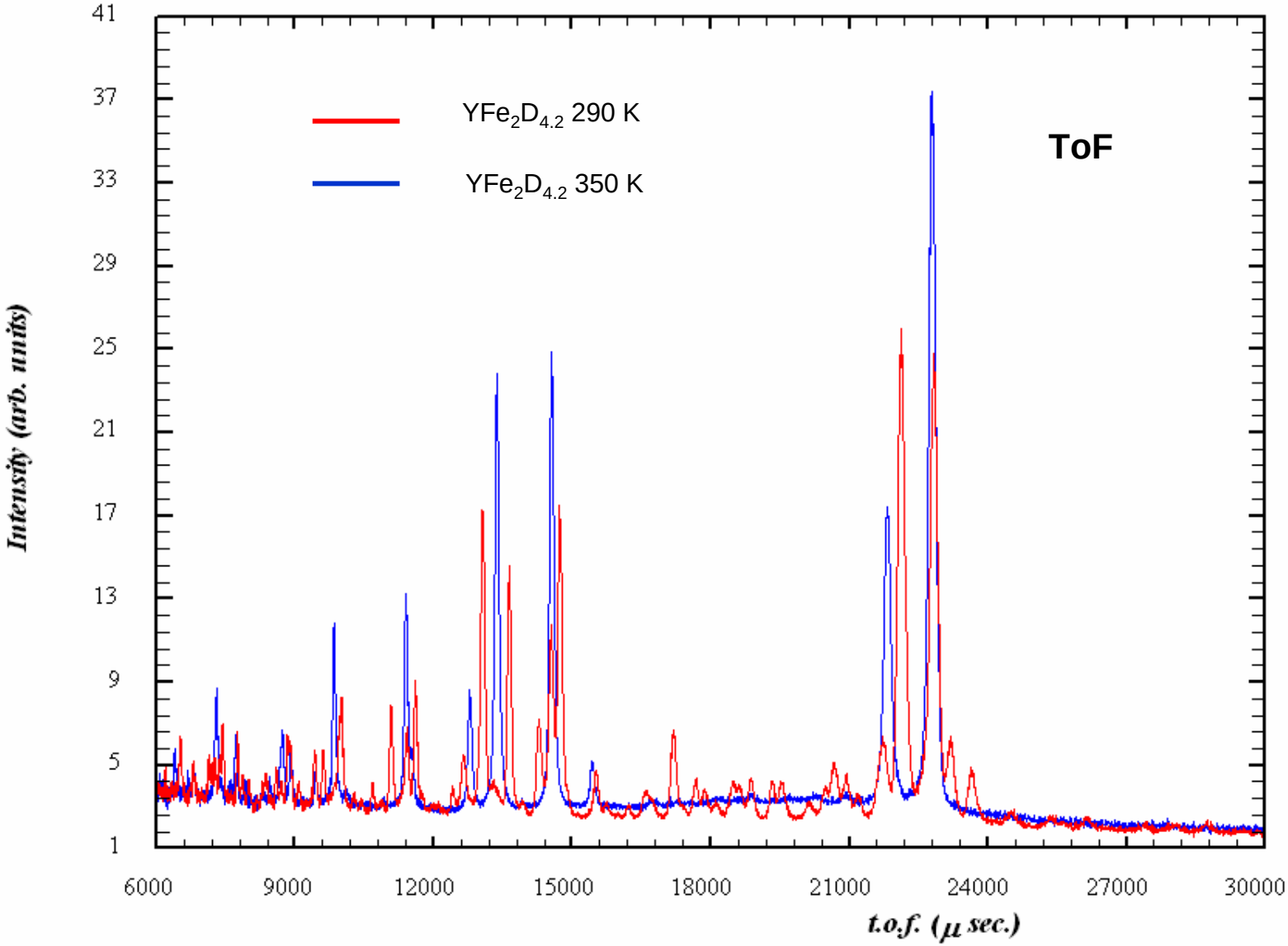


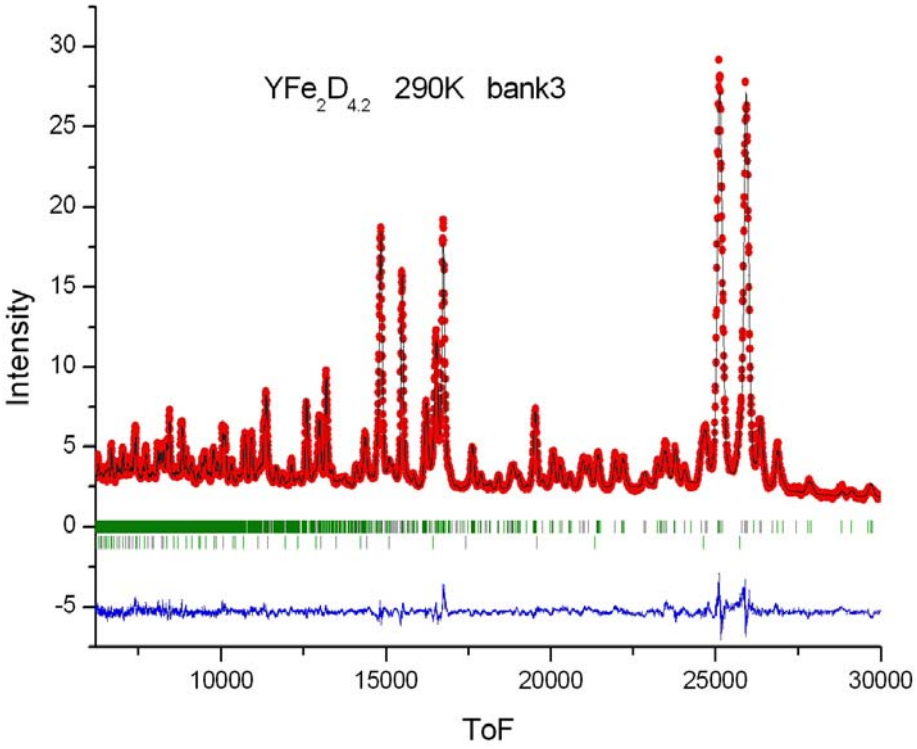
Fig. 6. Connectivity of chromium by deuterium in monoclinic $ZrCr_2D_{3.8}$ at 1.6 K as viewed along b (zirconium atoms omitted for clarity).

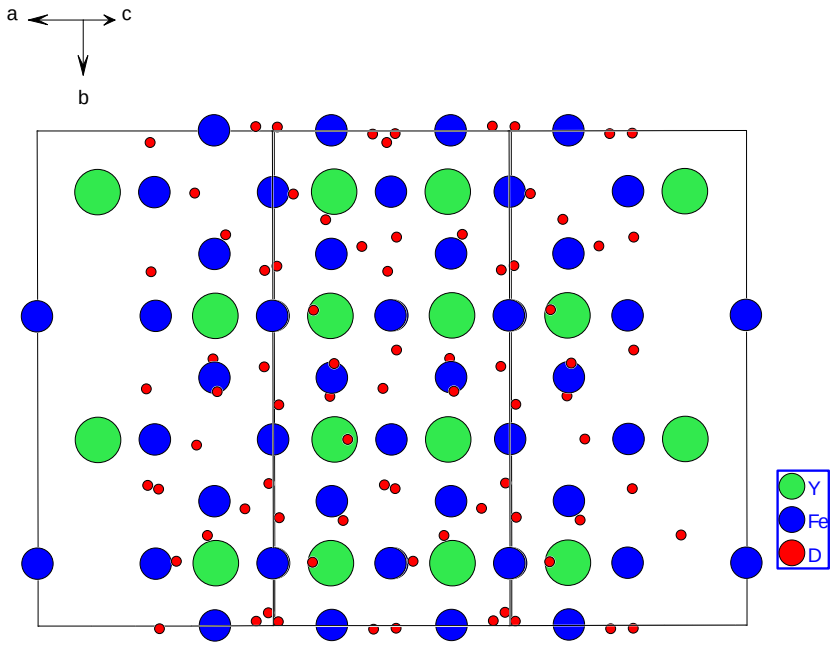
$YFe_2D_{4.2}$


YFe2D4.2 290 K
YFe2D4.2 350 K
ToF
Intensity (arb. units)
t.o.f. (μ sec.)
41
37
33
29
25
21
17
13
9
5
1
6000
9000
12000
15000
18000
21000
24000
27000
30000

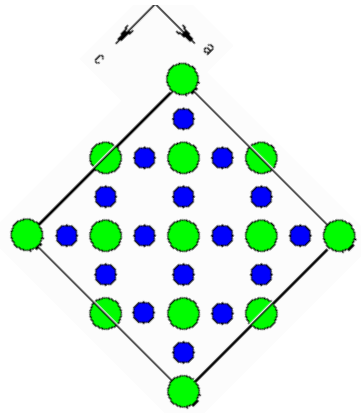
$YFe_2D_{4.2}$

Pc, 12 metal and 18 deuterium atoms
a=5.494(3), *b*=11.480(6), *c*=9.399(3) Å, *β*=122.22 (3)





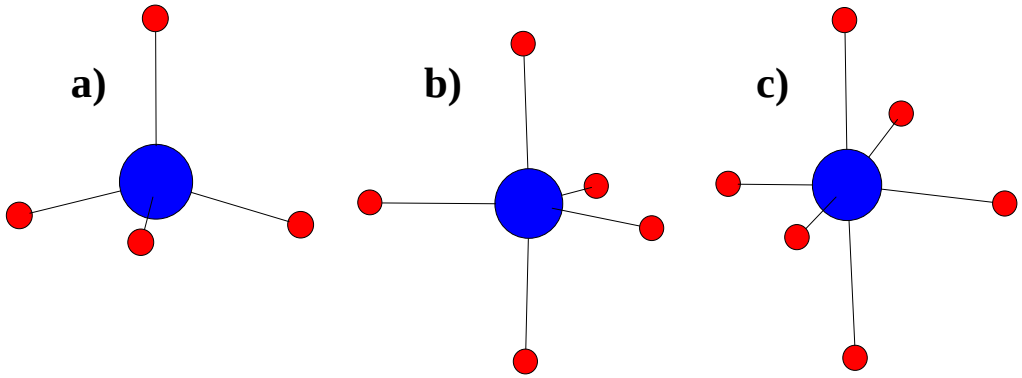
$YFe_2D_{4.2}$ LT-structure along [3 0 76] direction.

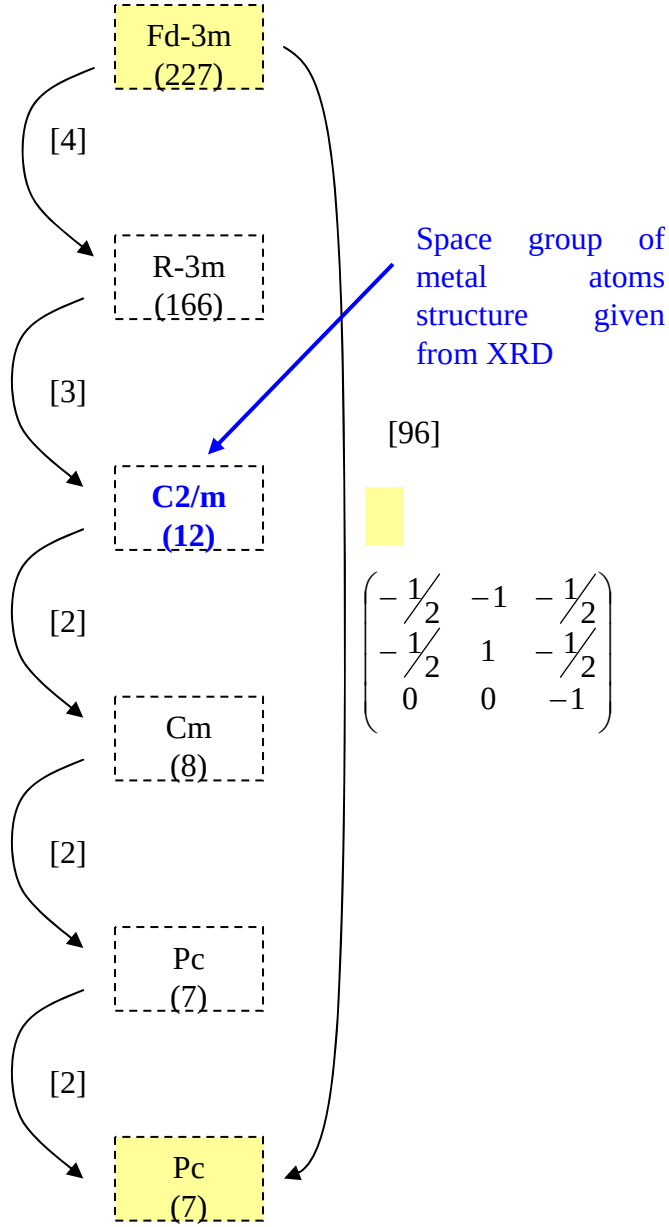


YFe_2 structure along *b*-axis.

$YFe_2D_{4.2}$

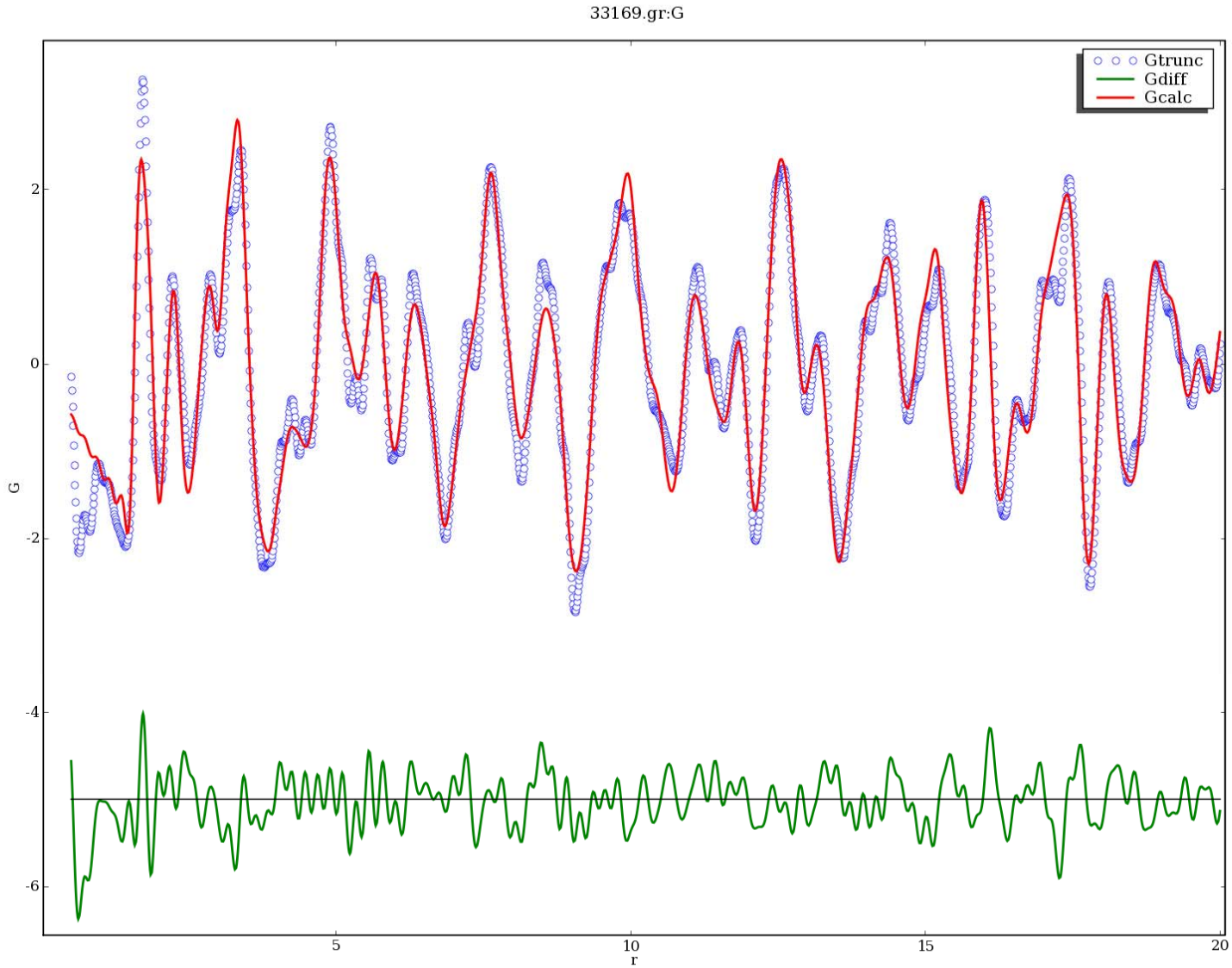
$YFe_2D_{4.2}$ LT-structure: Coordination polyhedra around Fe atoms.



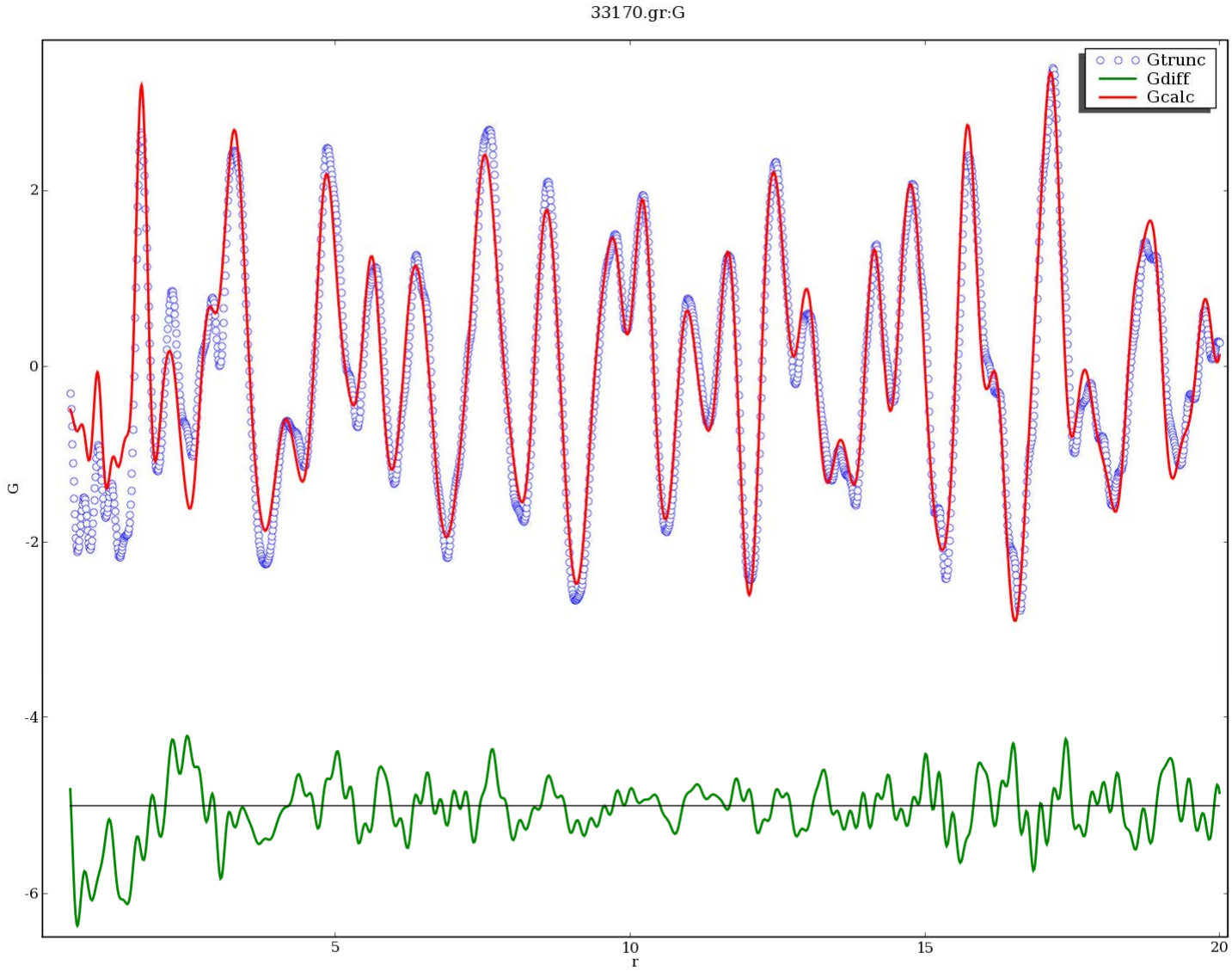


$YFe_2D_{4.2}$ LT-structure: Chain of subgroups for transformation from *Fd-3m* to *Pc* with index [96]

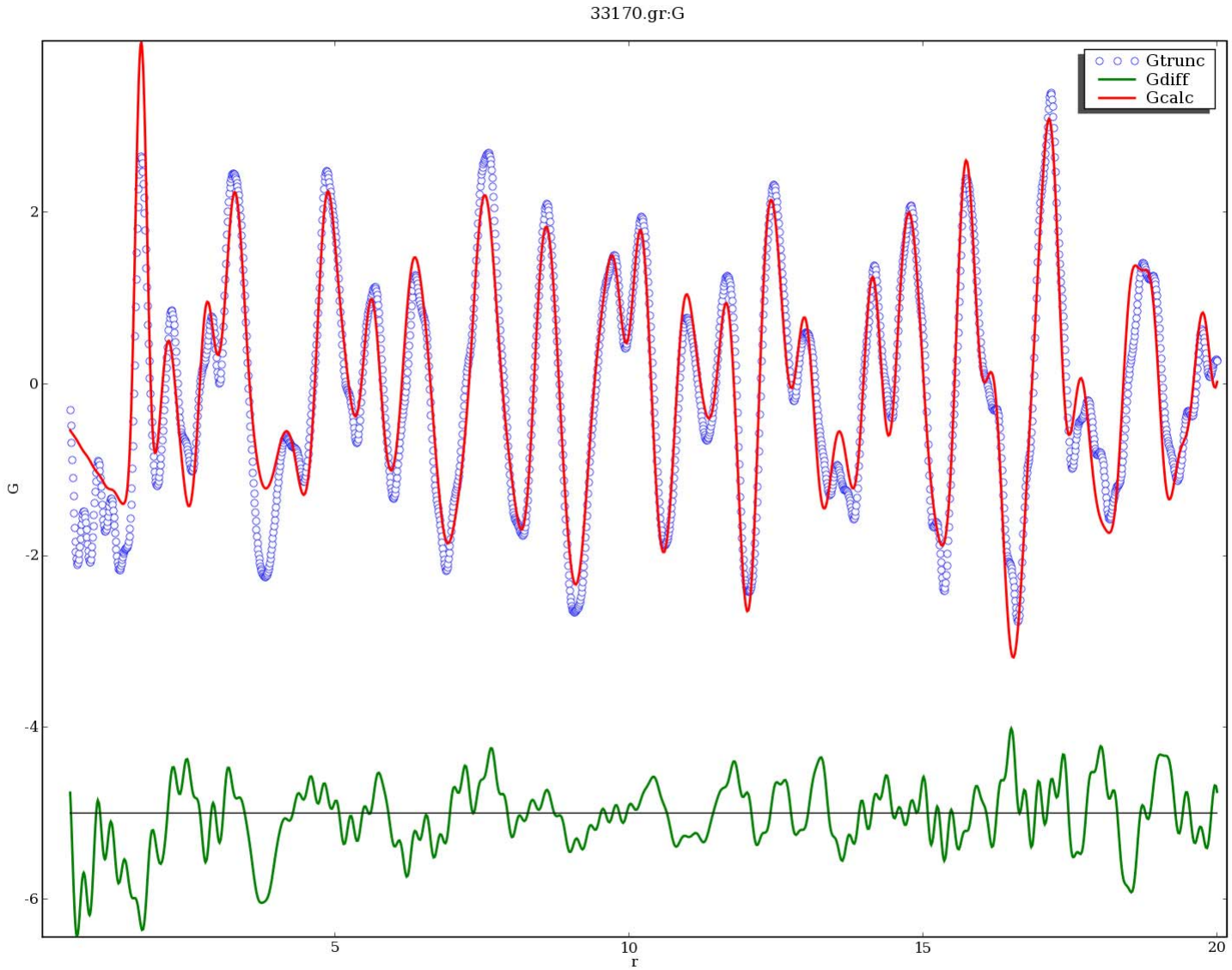
$YFe_2D_{4.2}$ - ordered

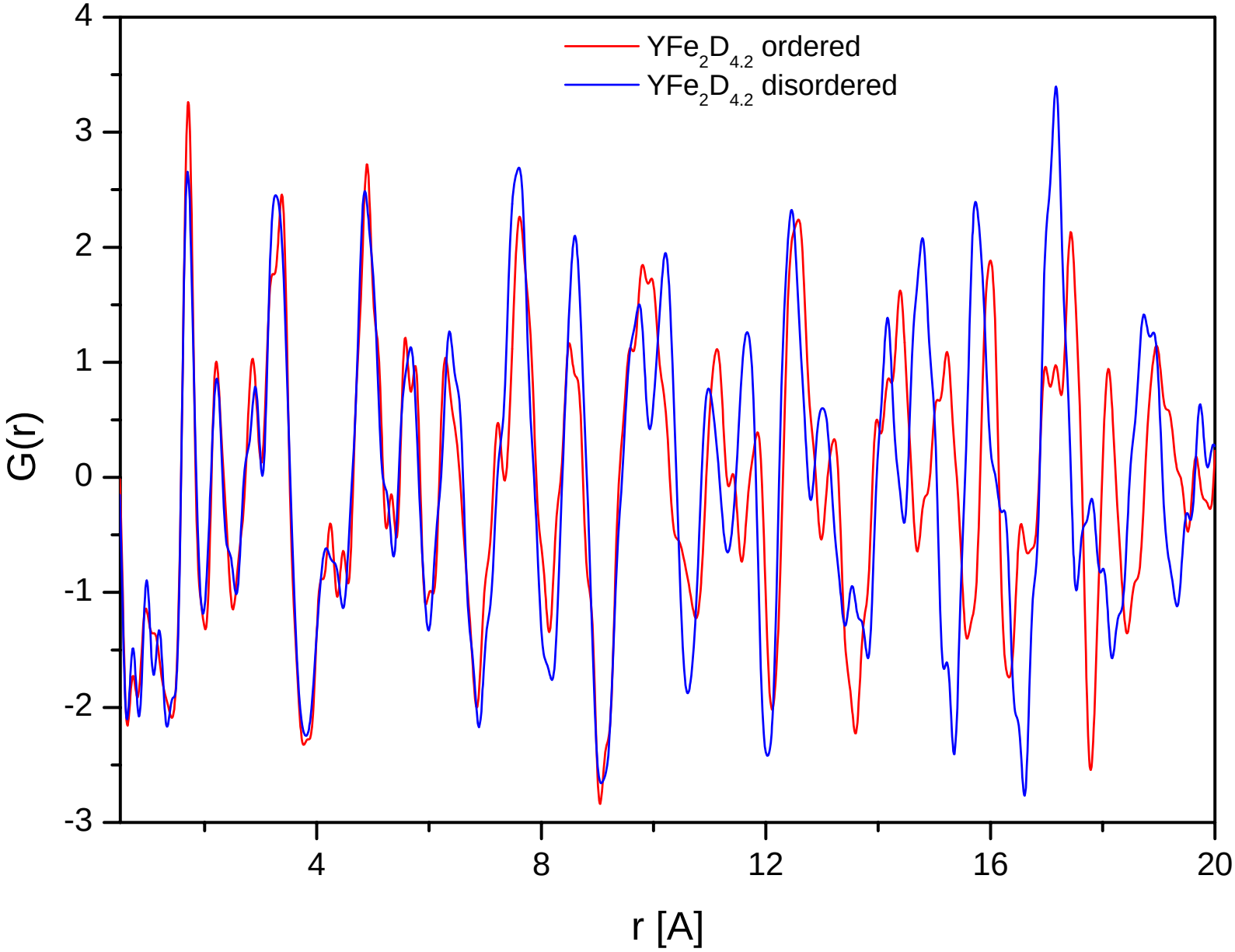


$YFe_2D_{4.2}$ - disordered

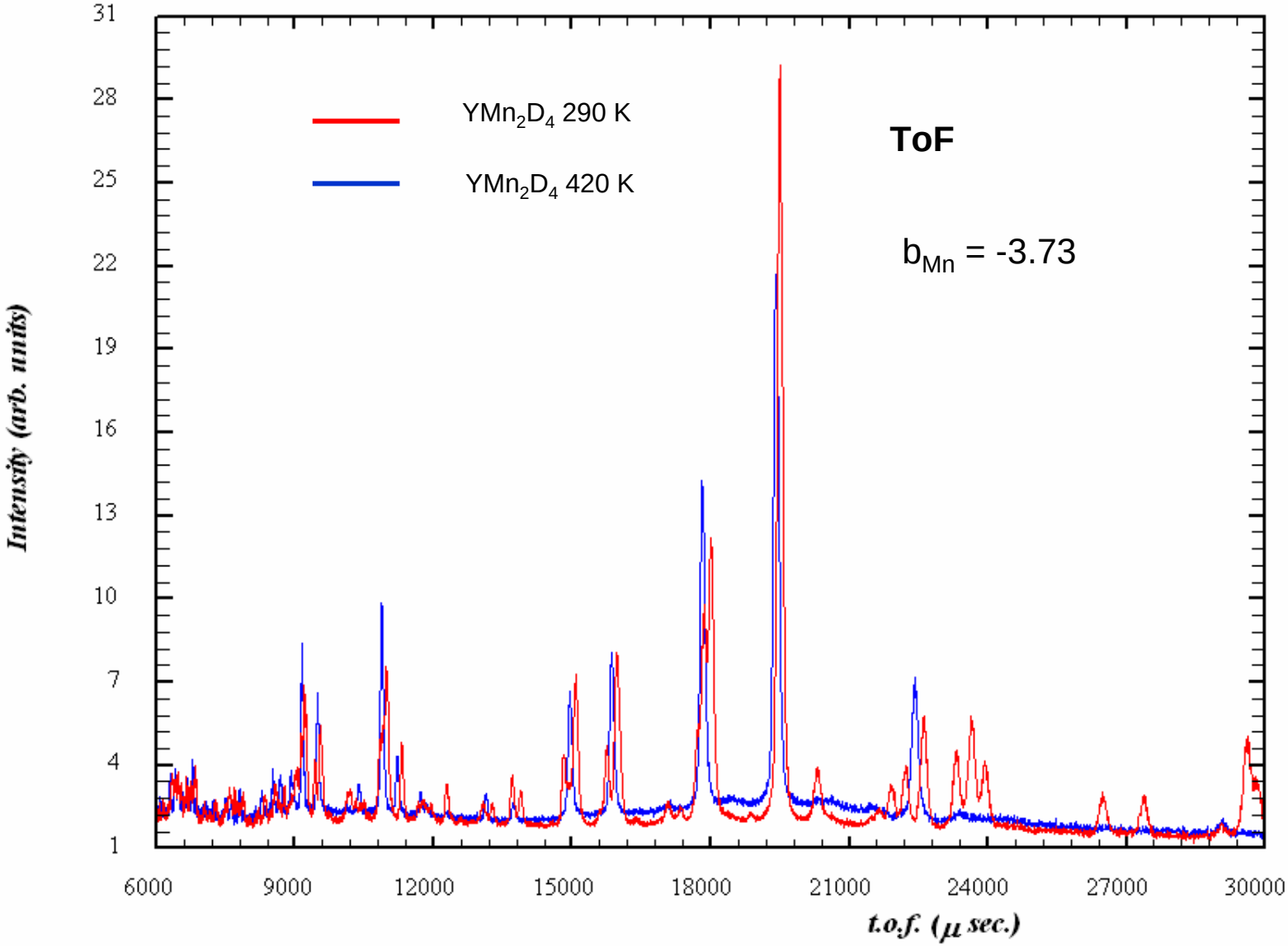


$YFe_2D_{4.2}$ – locally ordered, D-D > 2.1 Å

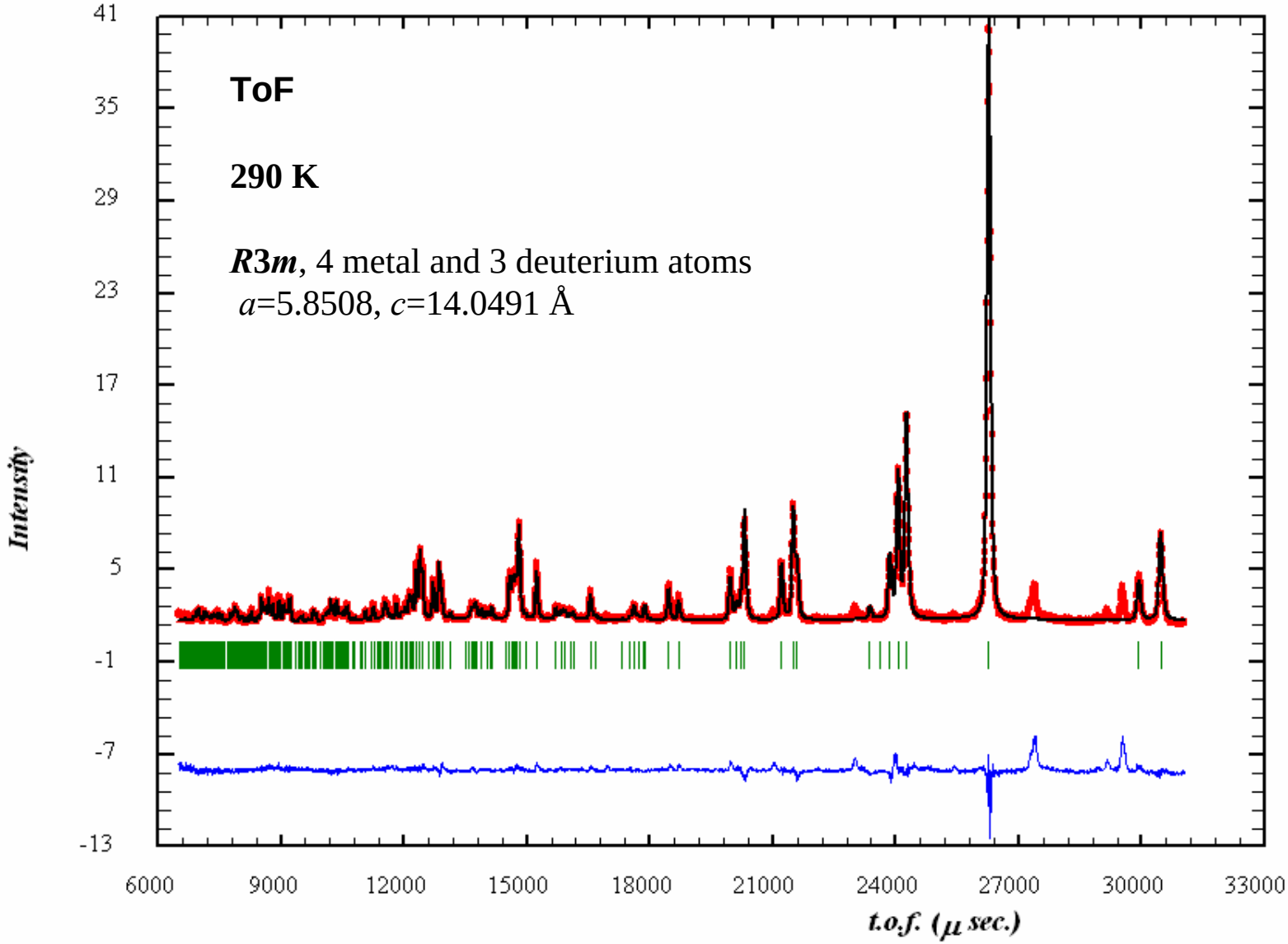



YFe2D4.2 ordered
YFe2D4.2 disordered
G(r)
r [A]
4
3
2
1
0
-1
-2
-3
4
8
12
16
20

YMn_2D_4


YMn2D4 290 K
YMn2D4 420 K
ToF
bMn = -3.73
Intensity (arb. units)
t.o.f. (μ sec.)
31
28
25
22
19
16
13
10
7
4
1
6000
9000
12000
15000
18000
21000
24000
27000
30000

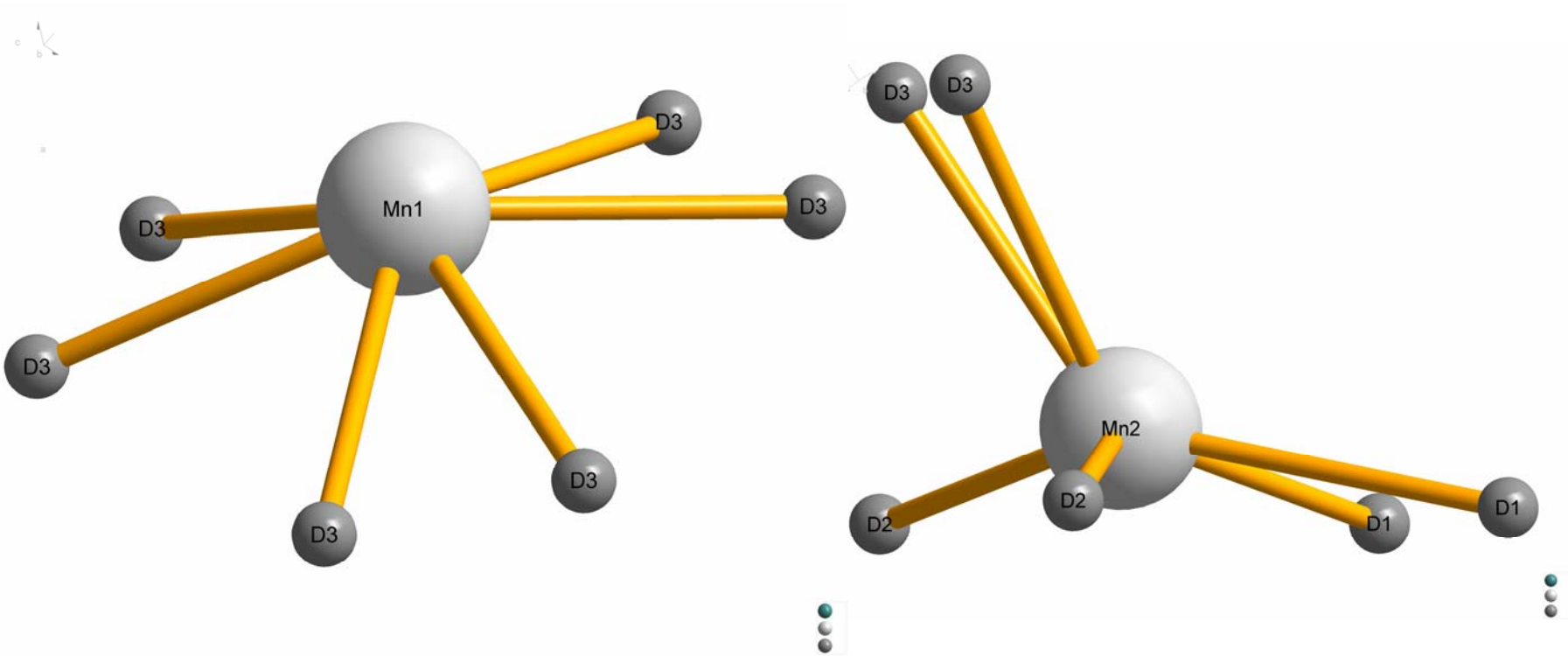
YMn_2D_4

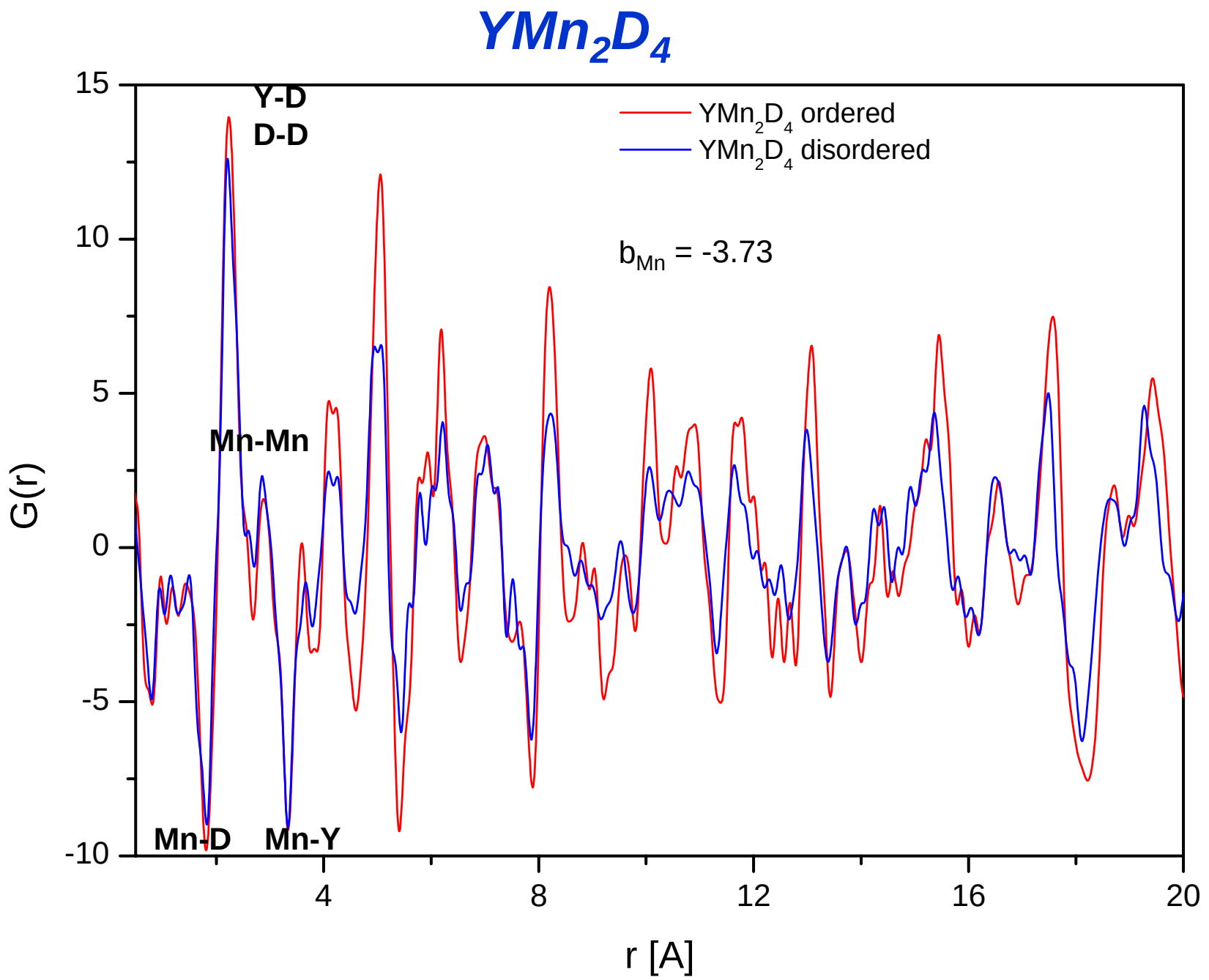

ToF
290 K
R3m, 4 metal and 3 deuterium atoms
a=5.8508, c=14.0491 Å
Intensity
41
35
29
23
17
11
5
-1
-7
-13
6000
9000
12000
15000
18000
21000
24000
27000
30000
33000
t.o.f. (μ sec.)

YMn_2D_4

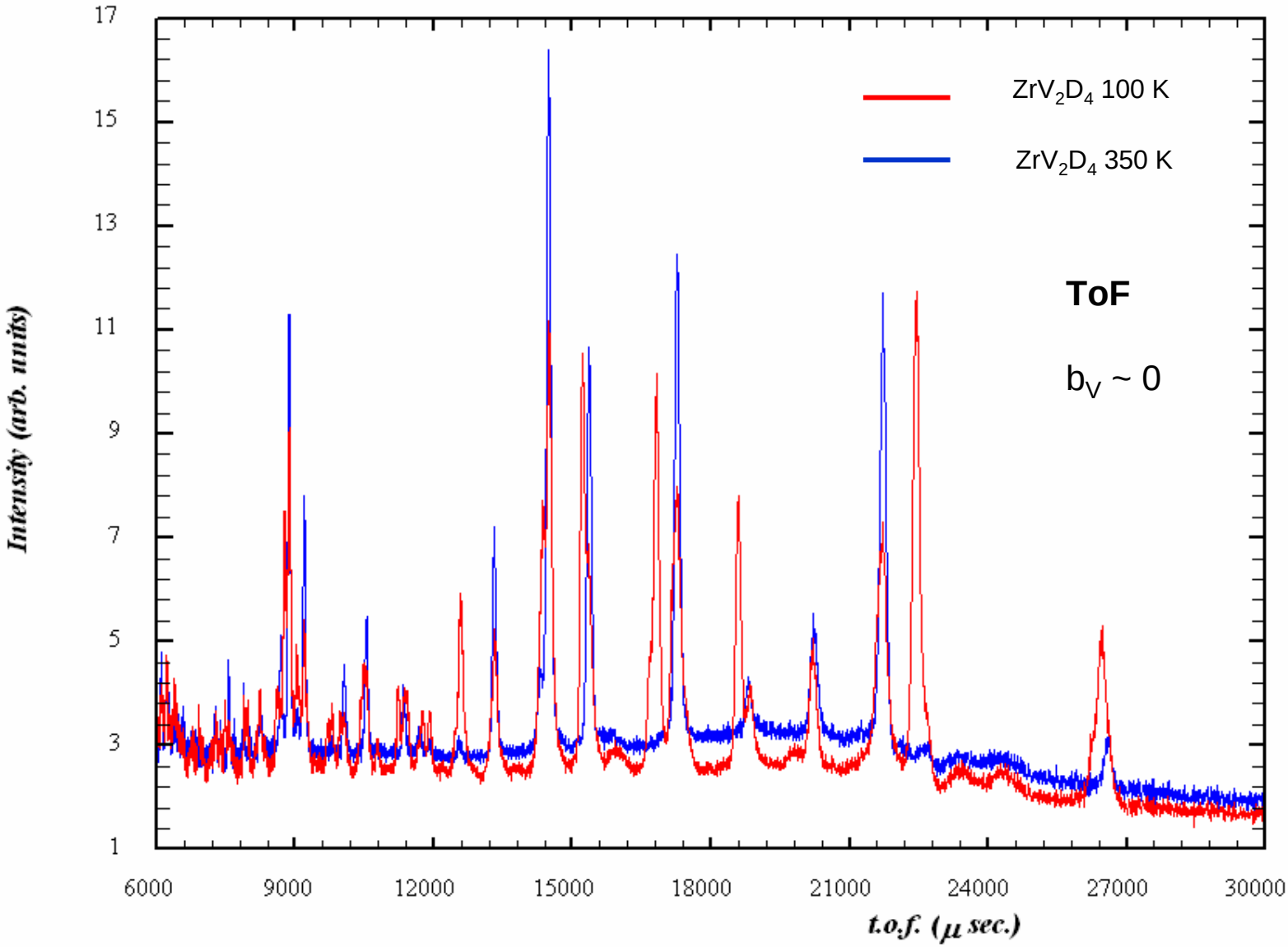
290 K

R*3*m, 4 metal and 3 deuterium atoms, D1 and D2 fully occupied, D3 half occupied
a=5.8508, *c*=14.0491 Å

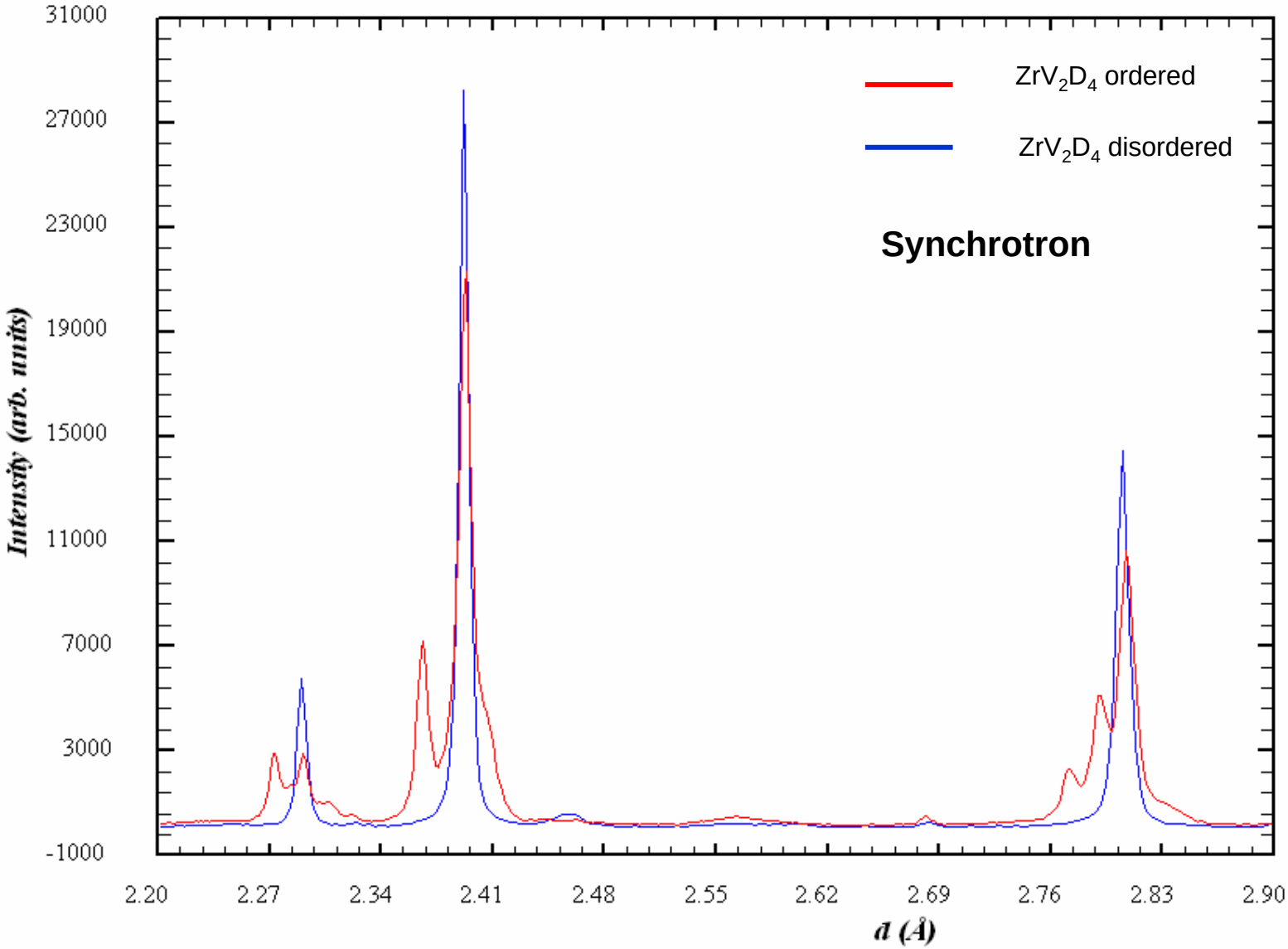



YMn2D4
Y-D
D-D
Mn-Mn
Mn-D
Mn-Y
YMn2D4 ordered
YMn2D4 disordered
bMn = -3.73
G(r)
r [A]
15
10
5
0
-5
-10
4
8
12
16
20

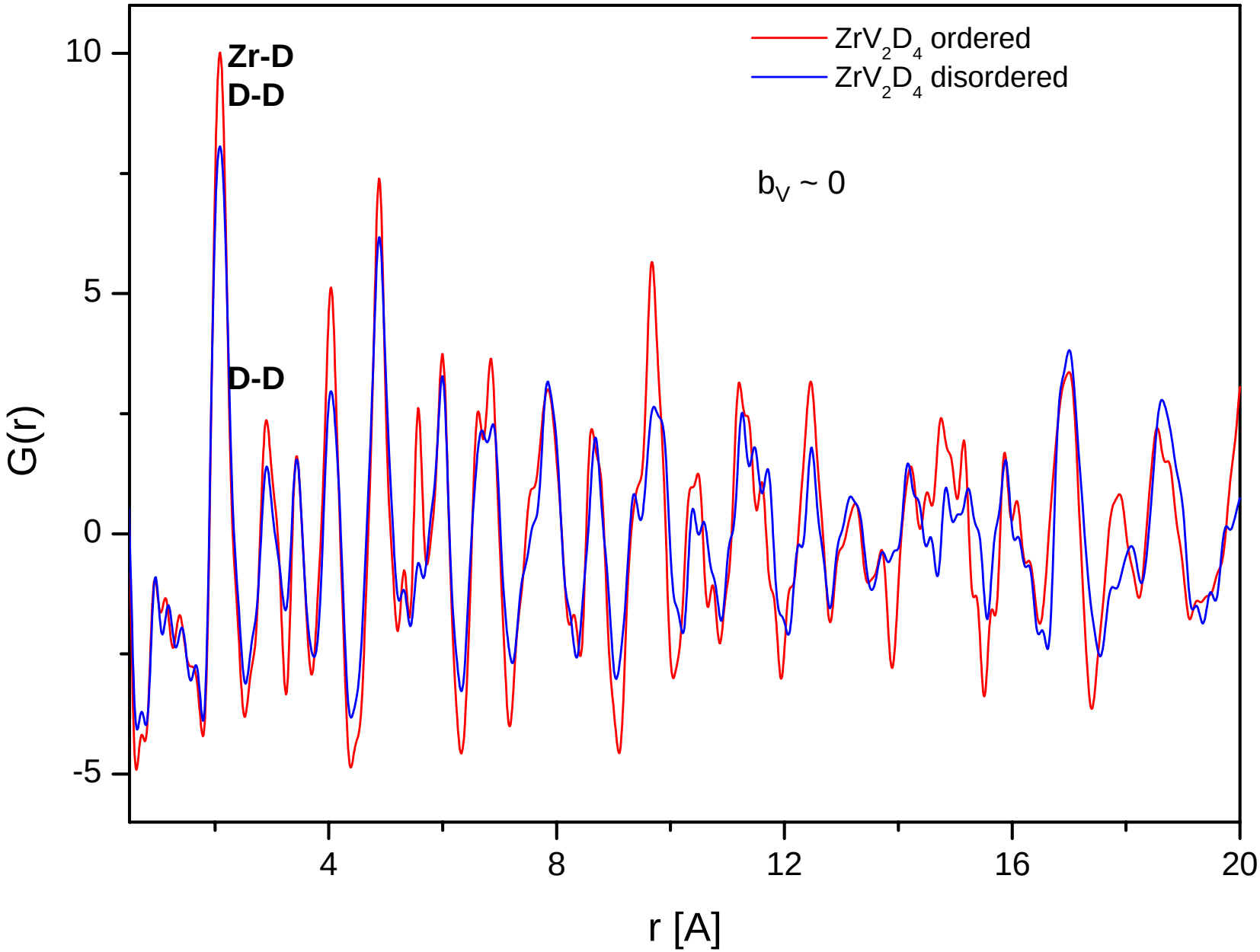
ZrV_2D_4


17
15
13
11
9
7
5
3
1
Intensity (arb. units)
6000
9000
12000
15000
18000
21000
24000
27000
30000
t.o.f. (μ sec.)
ZrV2D4 100 K
ZrV2D4 350 K
ToF
bV ~ 0

ZrV_2D_4


ZrV_2D_4 ordered
ZrV_2D_4 disordered
Synchrotron
Intensity (arb. units)
31000
27000
23000
19000
15000
11000
7000
3000
-1000
2.20
2.27
2.34
2.41
2.48
2.55
2.62
2.69
2.76
2.83
2.90
d (Å)

ZrV_2D_4

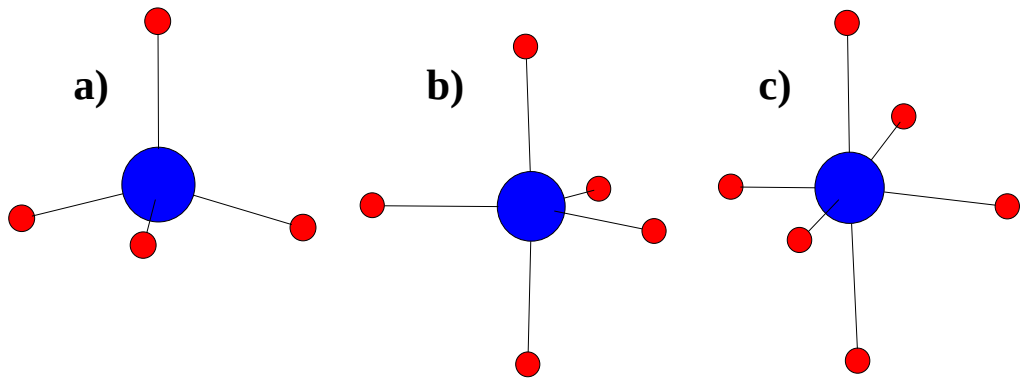

ZrV2D4 ordered
ZrV2D4 disordered
bV ~ 0
Zr-D
D-D
D-D
G(r)
r [A]
10
5
0
-5
4
8
12
16
20

Observations:

- PDFs of disordered and ordered structures look similarly up to alloy lattice parameter (~ 8Å), and then they start to differ

- PDF of disordered state cannot be well explained on short distances (transition metal – deuterium) by random occupation of available sites by deuterium, even not if deuterium atoms are kept 2.1 Å apart

Can be PDF of disordered state explained by the local existence of the same transition metal – deuterium complexes like in ordered state?



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