

Magnetic interactions in cubic-, hexagonal- and trigonal barium iron oxide fluoride, BaFeO₂F

CLEMENS, Oliver, MARCO, Jose F., THOMAS, Michael F., FORDER, Sue, ZHANG, Hongbin, CARTENET, Simon, MONZE, Anais, BINGHAM, Paul A. <<http://orcid.org/0000-0001-6017-0798>>, SLATER, Peter R. and BERRY, Frank J.

Available from Sheffield Hallam University Research Archive (SHURA) at:

<http://shura.shu.ac.uk/12637/>

This document is the author deposited version. You are advised to consult the publisher's version if you wish to cite from it.

Published version

CLEMENS, Oliver, MARCO, Jose F., THOMAS, Michael F., FORDER, Sue, ZHANG, Hongbin, CARTENET, Simon, MONZE, Anais, BINGHAM, Paul A., SLATER, Peter R. and BERRY, Frank J. (2016). Magnetic interactions in cubic-, hexagonal- and trigonal barium iron oxide fluoride, BaFeO₂F. *Journal of Physics: Condensed Matter*, 28 (34).

Repository use policy

Copyright © and Moral Rights for the papers on this site are retained by the individual authors and/or other copyright owners. Users may download and/or print one copy of any article(s) in SHURA to facilitate their private study or for non-commercial research. You may not engage in further distribution of the material or use it for any profit-making activities or any commercial gain.

Magnetic interactions in cubic-, hexagonal- and trigonal- barium iron oxide fluoride, BaFeO₂F

Oliver Clemens^{a,b,c}, José F. Marco^d, Michael F. Thomas^e, Susan D. Forder^f, Hongbin Zhang^g, Simon Cartenet^f, Anais Monze^f, Paul A. Bingham^f, Peter R. Slater^a, Frank J. Berry^{a,*}

^a School of Chemistry, The University of Birmingham, Birmingham B15 2TT, United Kingdom.

^b Technical University of Darmstadt, Joint Research Laboratory Nanomaterials, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany.

^c Karlsruhe Institute of Technology, Institute of Nanotechnology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

^d Instituto de Química-Física, "Rocasolano", CSIC, Serrano 119, 28006 Madrid, Spain.

^e Department of Physics, University of Liverpool, Liverpool L69 3BX, United Kingdom.

^f Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield S1 1WB, United Kingdom.

^g Technical University of Darmstadt, Theory of Magnetic Materials, Jovanka-Bontschits-Straße 2, 64287 Darmstadt, Germany.

*: corresponding author

Fax +44 (0)121 4144403

Email f.j.berry.1@bham.ac.uk

Abstract

^{57}Fe Mössbauer spectra have been recorded from the hexagonal (6H)- and trigonal (15R)- modifications of BaFeO_2F and are compared with those previously recorded from the cubic form of BaFeO_2F . The spectra, recorded over a temperature range from 15 to 650K show that all of the iron in all the compounds is in the Fe^{3+} state. Spectra from the 6H- and 15R- modifications were successfully fitted with components that were related to the Fe(1) and Fe(2) structural sites in the 6H variant and to the Fe(1), Fe(2) and Fe(3) structural sites in the 15R form. The magnetic ordering temperatures were determined as $597\pm 3\text{K}$ for 6H- BaFeO_2F and $636\pm 3\text{K}$ for 15R- BaFeO_2F . These values are surprisingly close to the value of $645\pm 5\text{K}$ determined for the cubic form. The magnetic interactions in the three forms are compared with a view to explaining this similarity of magnetic ordering temperature.

Keywords

Mössbauer spectra, magnetic ordering temperature, superexchange.

1 Introduction

Perovskite-related oxide fluorides have attracted significant interest since the observation of superconductivity in $\text{Sr}_2\text{CuO}_2\text{F}_{2+d}$ [1-4]. We have been particularly interested in the synthesis, structural- and magnetic- characterisation of fluorinated cubic perovskite-related structures of composition MFeO_2F ($\text{M} = \text{Sr}, \text{Ba}$) [5-12] using polyvinylidenedifluoride (PVDF) as a fluorinating agent [13]. More recently, we have reported on the synthesis and structural characterisation of two structurally different modifications of BaFeO_2F : hexagonal 6H- BaFeO_2F (space group $P6_3/mmc$ [14]) and trigonal 15R- BaFeO_2F (space group $R-3m$ [15]).

The structures of the BaFeO_2F modifications can be understood in terms of the close packing of BaO_2F layers with iron occupying $\frac{1}{4}$ of the octahedral sites. If a layer “A” is surrounded by two layers with different orientation (*e.g.* BAC), it is assigned the letter *c* in the Jagodzinski notation whereas if the layer “A” is surrounded by two layers with the same orientation (*e.g.* BAB), it is assigned the letter *h* [16]. For a stapling sequence *ccc...* the simple cubic perovskite structure is formed as found, for example, in SrFeO_3 whereas the hexagonal perovskite structure is obtained for the sequence *hhh...*in, for example, BaCoO_3 . Hence the modifications of BaFeO_2F considered here differ in the stacking sequence of the BaO_2F layers. The respective stacking sequences are *ccc...* for cubic BaFeO_2F , *cchcch...* for 6H- BaFeO_2F and *hcchhcchhcch...* for 15R- BaFeO_2F . The stacking sequence also determines how the iron octahedra are connected to the neighbouring octahedra. For octahedra connecting via *c*-type layers the octahedron only shares corners with the neighbouring octahedra via this layer. For connection via an *h*-type layer the two octahedra share a common face. An overview of the structures of the three modifications is given in Figure 1. Although the type of modification formed in inorganic compounds is often influenced by the average transition metal oxidation state and the size of the A site cation (here Ba^{2+}), in this work the low temperature fluorination routes have allowed the synthesis of three different perovskite-type structures all containing Fe^{3+} with the same A site cations and identical overall anion composition.

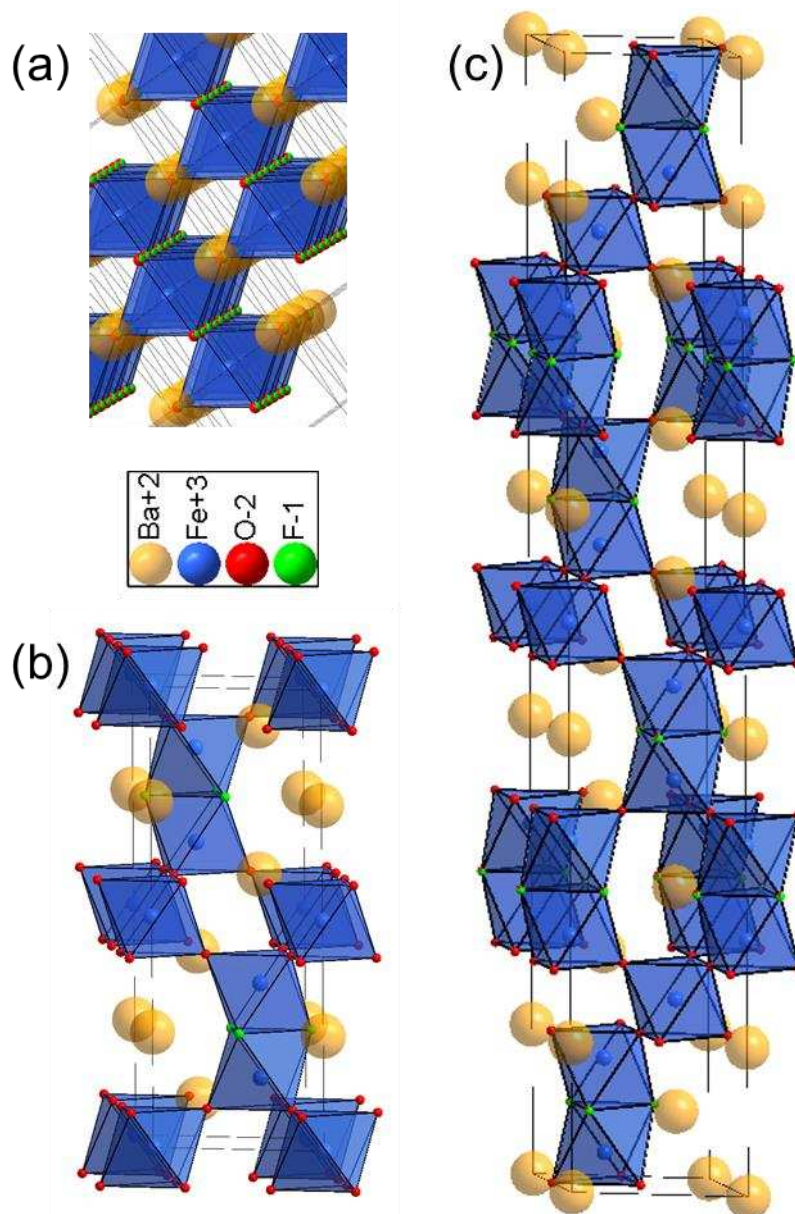


Figure 1. Crystal structures of (a) cubic-, (b) hexagonal 6H- and (c) trigonal 15R-BaFeO₂F.

Furthermore, the magnetic structures of the hexagonal- and trigonal- modifications of BaFeO₂F as revealed by neutron powder diffraction are complex [14, 15] and, as might be expected, are different from those identified by neutron powder diffraction and ⁵⁷Fe Mössbauer spectroscopy in cubic BaFeO₂F [9]. Cubic BaFeO₂F shows G-type antiferromagnetic ordering, i. e. each iron atom possesses spin direction opposite to its nearest neighbours. In 6H- and 15R- BaFeO₂F, the spins on neighbouring Fe atoms (i.e. octahedra which are connected by either corner or face) are also aligned antiparallel. In an alternative description, the iron atoms between close packed BaO₂F layers align parallel (the octahedra are not connected to other octahedra of the same layer), but align antiparallel to neighbouring layers. The

1
2
3 magnetic moments are aligned parallel to the *a/b*-plane in both cases, i.e.
4 perpendicular to the stacking direction of BaO₂F layers [14, 15].
5
6

7
8 We have now recorded ⁵⁷Fe Mössbauer spectra from both 6H-BaFeO₂F and
9 15R-BaFeO₂F at temperatures between 630K and 15 K. We report here on these
10 spectra and compare them with data recorded over a similar temperature range from
11 cubic BaFeO₂F [9]. The results are discussed in terms of the different magnetic
12 interactions between the Fe³⁺ ions which originate from the differences in crystal
13 structure.
14
15
16
17
18

20 **2 Experimental Details**

21
22 Cubic perovskite-related BaFeO_{2.5} [17] was prepared by the calcination of
23 appropriate quantities of a well ground mixture of BaCO₃ and α-Fe₂O₃ at 1100°C for
24 24 h in air with one intermediate regrinding. Fluorination was achieved by mixing this
25 compound with PVDF in a 0.60 molar ratio (precursor oxide : CH₂CF₂ unit and
26 equivalent to a 20% excess) and heating the mixture at 375°C for 24 h in air.
27
28
29
30
31

32 Hexagonal 6H-BaFeO_{3-d} was prepared by heating a stoichiometric planetary ball-
33 milled mixture of BaCO₃ and α-Fe₂O₃ at 970°C for 12 h under flowing oxygen. The
34 sample was slowly cooled to room temperature to increase the oxygen uptake and
35 the heating procedure was repeated a second time. Fluorination was achieved by
36 mixing the 6H-BaFeO_{3-d} with a 4 % excess of PVDF, grinding in n-pentane, and
37 slowly heating to 370°C (20°C/h) under air for 20 h.
38
39
40
41
42

43 Trigonal 15R-BaFeO₂F was prepared by heating a stoichiometric planetary ball-
44 milled mixture of BaF₂, BaCO₃ and α-Fe₂O₃, which had been pressed into a pellet, at
45 900°C for 12 h under air in a covered alumina crucible. The product was quenched to
46 room temperature to give a precursor oxide of composition 15R-BaFeO_{3-d}F_{0.2} (as
47 reported in [18, 19]). 15R-BaFeO₂F was prepared by grinding 15R-BaFeO_{3-d}F_{0.2} and
48 a 4 % excess of PVDF in n-pentane and slowly heating the mixture to 370°C at
49 20°C/h under air. The sample was maintained at 370°C for 20 h.
50
51
52
53
54
55
56

57 ⁵⁷Fe Mössbauer spectra were recorded with a constant acceleration spectrometer in
58 transmission geometry using a ca. 25 mCi ⁵⁷Co/Rh source and a helium closed-cycle
59 cryorefrigerator. For temperatures above room temperature a furnace sample
60 chamber was used using thermocouple temperature control. All spectra were

1
2
3 computer fitted and the chemical isomer shift data are quoted relative to that of
4 metallic iron at room temperature.
5
6

7
8 Exchange parameters were estimated using density functional theory (DFT) based
9 on calculations for the fluoride ordered structure of 6H-BaFeO₂F (*P6₃/mmc*). DFT
10 calculations were performed using the full potential linear augmented planewave
11 method as implemented in the Wien2k code [20]. The exchange-correlation
12 potentials are approximated using the local spin density functional as parameterized
13 [21]. The self-consistent calculations were carried out with RMT*KMAX of 7.0 on a k-
14 mesh of 13×13×4 to guarantee good convergence. The exchange parameters were
15 estimated using the energy mapping methods, where the total energies between
16 experimental AFM, ferromagnetic (FM) and another AFM states are compared to
17 obtain the exchange parameters between nearest neighbors of local moments on Fe
18 ions.
19
20
21
22
23
24
25
26
27
28

29 **3 Results**

30
31 The ⁵⁷Fe Mössbauer spectra and fitting parameters for cubic BaFeO₂F were reported
32 earlier [9]. The magnetic ordering temperature was determined as T_N = 645±5K.
33
34

35 **3.1 Mössbauer spectra recorded from the hexagonal (6H)- and trigonal (15R)-** 36 **phases of BaFeO₂F in the temperature range 15 to 300K.**

37
38 The ⁵⁷Fe Mössbauer spectra recorded from the hexagonal (6H) phase at 15K, 77K
39 and 300K are shown in Figure 2 and the fitting parameters are listed in Table 1. The
40 spectra recorded from the trigonal (15R) phase at 16K, 69K and 298K are shown in
41 Figure 3 with the fitting parameters listed in Table 2. All the fitted spectral
42 components from both phases showed ordered magnetic structure with values of
43 magnetic hyperfine field (B_{hf}) and isomer shift (δ) characteristic of iron in the Fe³⁺
44 oxidation state.
45
46
47
48
49
50
51
52

53
54 In both the 6H and 15R materials all the Mossbauer spectra consist of overlapping
55 sextet components in which one sextet has a significantly higher hyperfine field. This
56 sextet represents the Fe1 site in the 6H compound and the Fe3 site in the 15R
57 compound. In these octahedral sites the Fe ion interacts magnetically with 6
58 neighbouring Fe ions via the corner anions (the configuration of the 3c cubic
59 material).
60

1
2
3 In addition to the high field sextet, the spectra of the 6H material show three
4 overlapping sextets with lower hyperfine field assigned to the Fe2 site. In this site the
5 Fe ions interact with three Fe ions via corner anions and with an Fe ion on the
6 nearest Fe2 site via an octahedron face. Additional splitting of the hyperfine field
7 values of these components indicates some randomness around this site, possibly
8 due to a degree of O/F disorder on the neighbouring anion sites.
9
10
11
12
13

14
15 The occupation ratio of 1:2 for Fe1:Fe2 sites in the structure implies a relative area of
16 33% for the higher field component. The values shown in Table 1 are not far from this
17 value when account is taken of the difficulty of determining relative areas accurately
18 in spectra with overlapping components. There may, however, be some evidence for
19 a relatively smaller recoil free fraction on the high field site from the relative area of
20 this component in the 300K spectrum.
21
22
23
24
25

26 In the spectra of the 15R material, the lower field sextet components are assigned to
27 the Fe1 and Fe2 sites. The structure implies relative areas of 20%: 40%: 40% for the
28 Fe3: Fe1: Fe2 sites and the values of Table 2 show fair agreement with these values.
29
30
31

32 The values do, however, lend some additional support for a relatively smaller value of
33 recoil free fraction for the high field component.
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

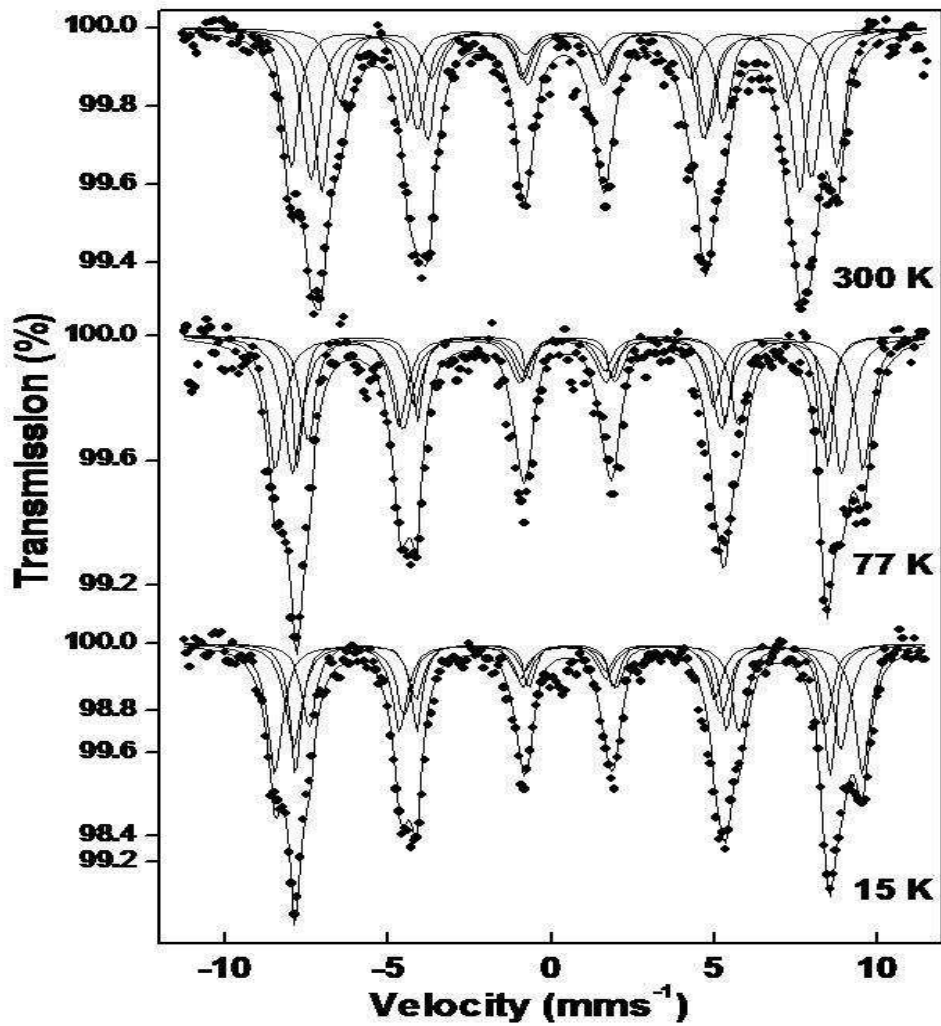


Figure 2. ^{57}Fe Mössbauer spectra recorded from $6\text{H-BaFeO}_2\text{F}$ at low temperatures

Table 1. ^{57}Fe Mössbauer parameters recorded from 6H-BaFeO₂F at low temperatures

Temperature (K)	$\delta \pm 0.02$ (mms ⁻¹)	$e^2qQ/2 \pm 0.02$ (mms ⁻¹)	$B \pm 0.5$ (T)	Relative Area ± 3 (%)
300	0.41	-0.02	51.9	25
	0.36	-0.08	45.5	30
	0.33	-0.02	47.7	29
	0.33	0.05	42.5	16
77	0.54	0.00	55.9	29
	0.48	-0.13	50.4	18
	0.41	0.07	52.3	32
	0.41	0.02	49.1	21
15	0.54	-0.01	55.8	31
	0.48	-0.13	50.8	23
	0.42	0.07	52.1	27
	0.45	0.02	49.1	19

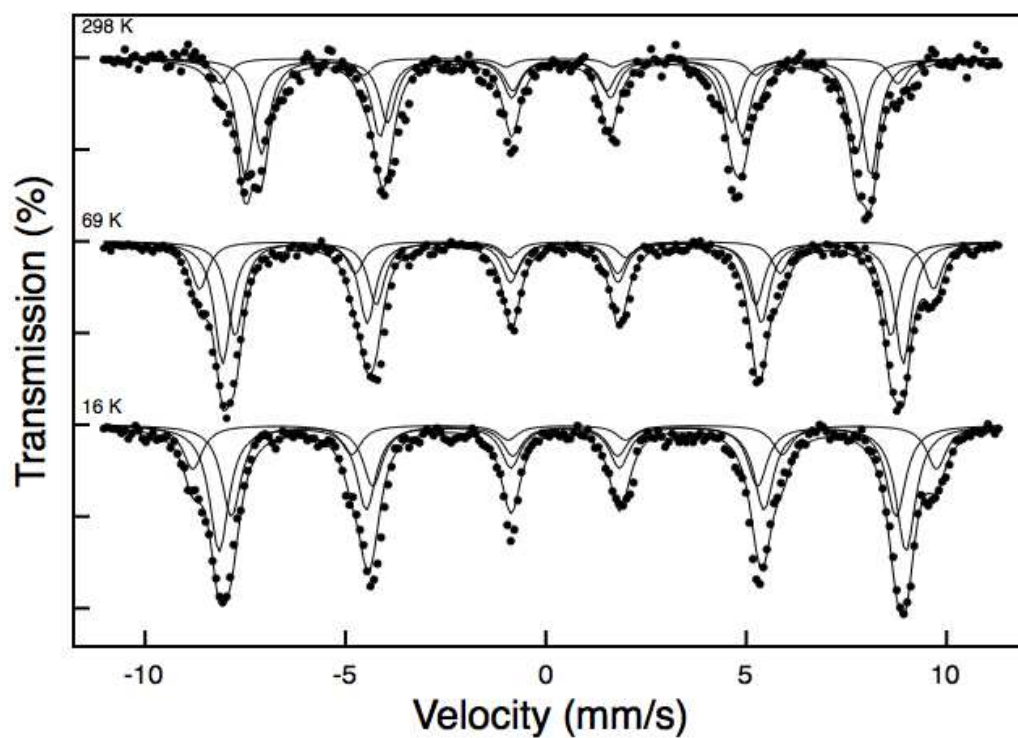
Figure 3. ^{57}Fe Mössbauer spectra recorded from 15R-BaFeO₂F at low temperatures

Table 2. ^{57}Fe Mössbauer parameters recorded from 15R-BaFeO₂F at low temperatures

Temperature (K)	$\delta \pm 0.02$ (mms ⁻¹)	$e^2qQ/2 \pm 0.02$ (mms ⁻¹)	$B \pm 0.05$ (T)	Relative Area ± 3 (%)
298	0.46	-0.08	52.4	12
	0.33	-0.06	48.4	41
	0.37	-0.02	46.1	47
77	0.53	-0.03	56.8	17
	0.47	-0.08	50.7	36
	0.44	-0.03	52.7	48
16	0.50	-0.06	57.5	18
	0.46	-0.04	51.4	35
	0.45	-0.06	53.1	48

3.2 Determination of magnetic ordering temperature for the hexagonal (6H)- and trigonal (15R)- phases of BaFeO₂F

The ^{57}Fe Mössbauer spectra of hexagonal 6H-BaFeO₂F at temperatures of 295K, 473K, 573K, 593K, 597K and 603K are shown in Figure 4 with the fitting parameters listed in Table 3. These spectra are seen to continue to high temperature those spectra shown in Figure 2. Comparison of the fits at 300K/295K in Tables 1 and 3 where the separate series of low temperature and high temperature spectra overlap shows basically the same fit although in the slightly better resolved spectrum at 295K the large intensity sextet with hyperfine field $B_{\text{hf}} = 45.7\text{T}$ replaces the sum of the slightly split components with $B_{\text{hf}} = 45.5\text{T}$ and 47.5T seen in the 300K spectrum. Overall the fits are consistent with a smooth evolution of the parameters of the spectral components with temperature up to the magnetic ordering temperature.

A graph of average magnetic hyperfine field $B_{\text{hf}}(\text{T})$ versus temperature T is shown in Figure 6. In order to extract the value of T_{N} points evaluated from the expression

$$B_{\text{hf}}(T) = B_{\text{hf}}(0)[1 - T/T_{\text{N}}]^{\beta}$$

which describes the variation of the mean hyperfine field with temperature as $T \rightarrow T_{\text{N}}$ were compared with the experimental points. This expression, valid as $T \rightarrow T_{\text{N}}$, is good for the determination of T_{N} but less reliable for the value of $B_{\text{hf}}(0)$. The best agreement between theoretical and experimental points, shown in Figure 6, was obtained with the values of $\beta = 0.30$, $B_{\text{hf}}(0) = 52.4\text{T}$ and $T_{\text{N}} = 597 \pm 3\text{K}$.

1
2
3 Spectra recorded from trigonal 15R-BaFeO₂F at temperatures of 296K, 373K, 473K,
4 573K, 628K, 635K and 638K are shown in Figure 5 with the fitting parameters listed
5 in Table 4. These spectra continue the variation of the spectra with temperature from
6 those seen in Figure 3. The fitting parameters of these spectra also show a smooth
7 evolution with temperature up to the magnetic ordering temperature. In an analysis
8 similar to that described above the best agreement between theoretical and
9 experimental points, shown in Figure 7, gave values of $\beta = 0.30$, $B_{\text{hf}}(0) = 52.4\text{T}$ and
10 $T_N = 636 \pm 3\text{K}$.
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

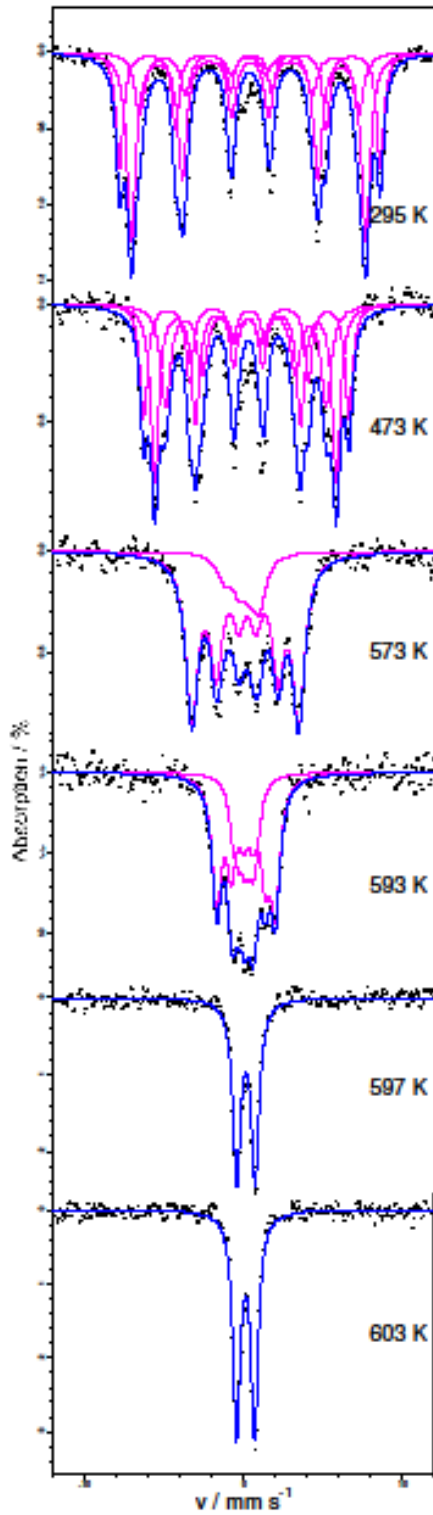


Figure 4. ^{57}Fe Mössbauer spectra recorded from 6H-BaFeO₂F at temperatures above ambient temperature.

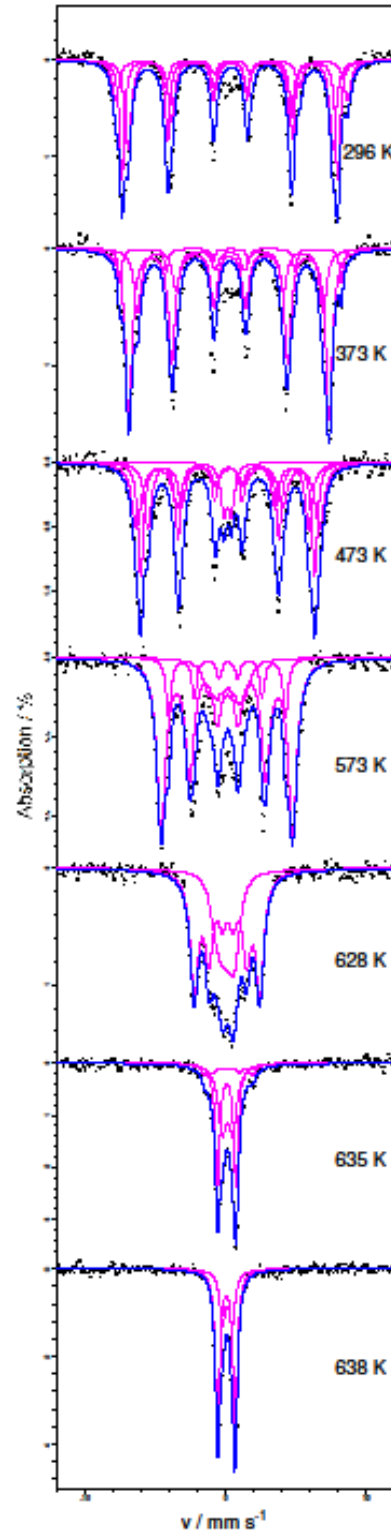


Figure 5. ^{57}Fe Mössbauer spectra recorded from 15R-BaFeO₂F at temperatures above ambient temperature.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

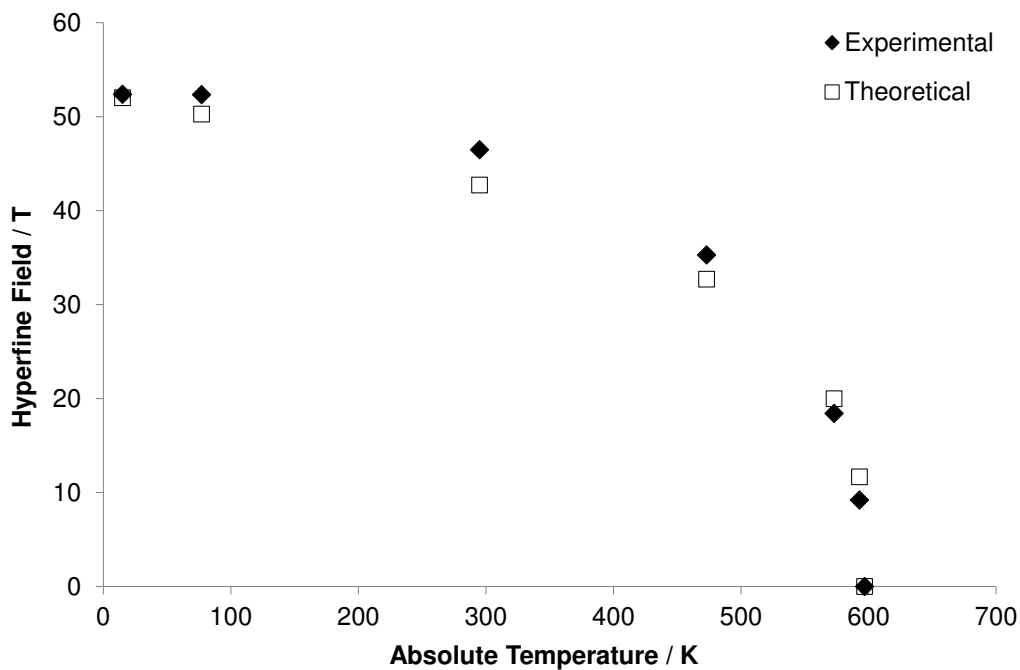


Figure 6. Plot of magnetic hyperfine field as a function of temperature for 6H-BaFeO₂F

Table 3. ⁵⁷Fe Mössbauer parameters recorded above ambient temperature for 6H-BaFeO₂F.

Temperature (K)	$\delta \pm 0.02$ (mm s ⁻¹)	$e^2Qq/2 / \Delta \pm 0.02$ (mm s ⁻¹)	$B \pm 0.05$ (T)	Relative area ± 2 (%)
295	0.42	-0.06	50.8	27
	0.35	-0.10	45.7	53
	0.33	0.02	42.7	20
473	0.24	-0.16	40.0	26
	0.19	-0.16	35.4	42
	0.22	-0.18	31.3	32
573	0.15	-0.12	20.8	83
	0.12	-0.38	6.8	17
593	0.19	-0.14	11.4	69
	0.08	-0.06	4.3	31
597	0.14	1.15	-	100
603	0.13	1.13	-	100

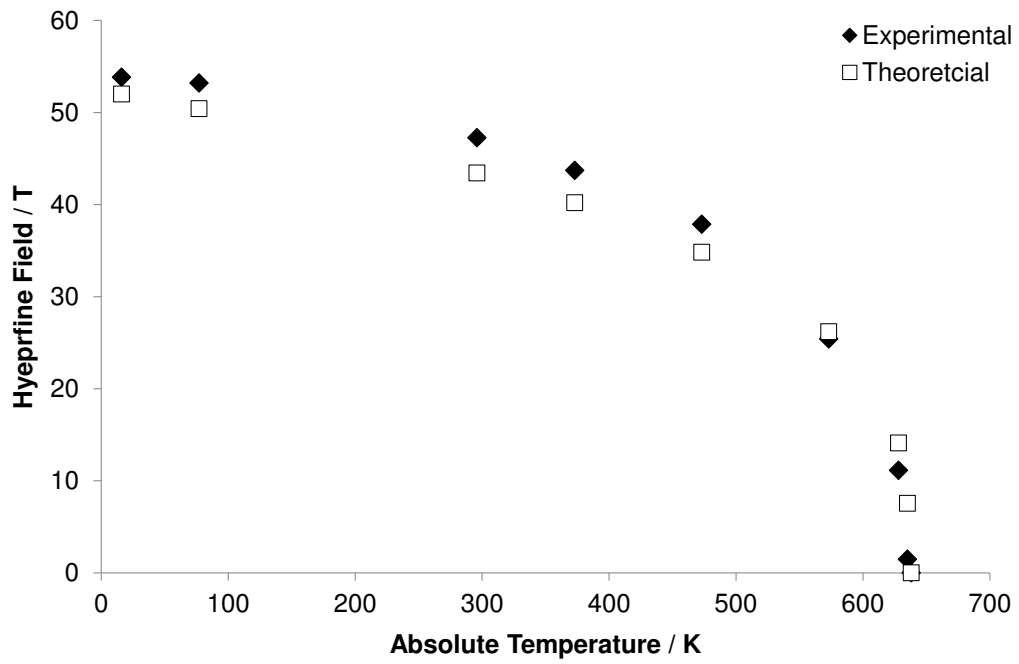


Figure 7. Plot of magnetic hyperfine field as a function of temperature for 15R-BaFeO₂F

Table 4. ^{57}Fe Mössbauer parameters recorded above ambient temperature for 15R-BaFeO₂F.

Temperature (K)	$\delta \pm 0.02$ (mm s ⁻¹)	$e^2Qq/2 / \Delta \pm 0.02$ (mm s ⁻¹)	$B \pm 0.05$ (T)	Relative area ± 2 (%)
296	0.46	-0.06	51.1	20
	0.31	-0.02	47.5	40
	0.36	-0.04	45.1	40
373	0.37	-0.02	48.8	8
	0.28	-0.06	44.2	66
	0.33	0.04	40.9	26
473	0.35	0.02	42.1	7
	0.21	-0.06	38.5	71
	0.30	0.18	34.5	22
573	0.13	-0.06	29.0	71
	0.16	-0.08	25.8	14
	0.12	-0.08	8.0	15
628	0.13	-0.04	14.4	67
	0.08	-0.10	4.5	33
635	0.15	0.18	10.5	12
	0.15	0.74	-	42
	0.09	1.31	-	46
638	0.16	0.67	-	30
	0.09	1.25	-	70

4 Discussion

The preparation of BaFeO₂F in three structural modifications (cubic, hexagonal and trigonal) enables the magnetic properties (including the magnetic ordering temperatures) to be compared as a sole function of the different structural environments and free from considerations of different iron oxidation states.

4.1 Magnetic characteristics of individual structures

In order to facilitate the structural discussion a selection of Fe-Fe bond distances and Fe-X-Fe angles are collected in Table 5. A summary of magnetic moments is contained in Table 6.

Table 5. Selected Fe-Fe bond distances and Fe-X-Fe (X = anion) angles in cubic-, 6H- and 15R-BaFeO₂F.

compound		bond distance Fe-Fe [Å]	bond angle Fe-X-Fe [°]
cubic BaFeO ₂ F [9]	Fe-Fe	4.06	180.0
6H-BaFeO ₂ F [14]	Fe1 connected to 6 Fe2 via corners (O ²⁻)	3.93	173.9
	Fe2 connected to 3 Fe1 via corners (O ²⁻)	3.93	173.9
	Fe2 connected to 1 Fe2 via face (F ⁻)	2.92	85.8
15R-BaFeO ₂ F [15]	Fe3 connected to 6 Fe1 via corners (O ²⁻)	3.93	173.0
	Fe2 connected to 3 Fe2 via corners (O ²⁻)	3.80	180.0
	Fe1 connected to 3 Fe3 via corners (O ²⁻)	3.93	173.0
	Fe1 connected to 1 Fe2 via face (83% F ⁻ / 17% O ²⁻)	2.96	86.3

Table 6. Summary of magnetic moments on Fe³⁺ in cubic-, 6H- and 15R-BaFeO₂F from neutron diffraction data.

compound	site	μ _B
cubic BaFeO ₂ F [9] at 4.2 K	Fe	3.94
6H-BaFeO ₂ F [14] at 298 K	Fe1	3.65
	Fe2	3.32
15R-BaFeO ₂ F [15] at 298 K	Fe1	3.55
	Fe2	3.47
	Fe3	3.97

4.1.1 Cubic BaFeO₂F (*Pm-3m*)

It can be seen in Figure 1a that each Fe³⁺ ion in cubic BaFeO₂F is surrounded by an octahedron of anions. The octahedra are connected via corner sharing of anions. The ⁵⁷Fe Mössbauer spectra recorded in the magnetically ordered temperature range

1
2
3 consist of a single magnetic sextet with broadened lines [9]. The single sextet arises
4 from the single crystallographic site of the Fe^{3+} ions and the broadening is attributed
5 to the effect of different quadrupole interactions where different configurations of O^{2-}
6 and F^- ions in the surrounding anion sites result in different angles between the
7 principal axis of the electric field gradient (EFG) and the magnetic hyperfine field
8 direction. This model gave good fits to the spectra with hyperfine values
9 characteristic of Fe^{3+} ions [9].
10
11
12
13
14
15

16 **4.1.2 Hexagonal 6H-BaFeO₂F (*P6₃/mmc*)**

17 From Figure 1b the Fe^{3+} ions in this hexagonal structure can be seen to occupy two
18 crystallographically different sites Fe1 and Fe2 with a relative multiplicity ratio of 1:2.
19 The Mössbauer spectra in the magnetically ordered temperature range show
20 magnetic sextet components in which the sextet with the largest value of hyperfine
21 field is partially separated from the other magnetic components. The fitting values of
22 this partially separated sextet (for example at 15K, $B_{\text{hf}} = 55.8\text{T}$, $\delta = 0.54\text{mm/s}$ and
23 relative area = 31%) clearly indicate that this component arises from iron on the Fe1
24 site which has similar coordination to iron in the cubic compound. The other sextet
25 components, accounting for 69% of the spectral area, arise from the Fe2 site and are
26 characterised by smaller values of B_{hf} and δ . A possible explanation for these smaller
27 values of hyperfine parameters stems from the structural observation that in the Fe2
28 sites the iron ions are displaced from the centres of their octahedra in the sense of a
29 mutual repulsion between the iron ions. This brings each iron ion closer to the three
30 O^{2-} anions of the octahedron than to the three F^- ions which define the common face.
31 Proximity to the O^{2-} ions can lead to a more covalent interaction which will result in
32 the observed smaller values of B_{hf} and δ for these sextet components. This is also in
33 line with the value of the iron magnetic moments for the iron ions in the Fe1 and Fe2
34 sites determined by room temperature neutron diffraction [14] (Table 6) are $3.65 \mu_{\text{B}}$
35 and $3.32 \mu_{\text{B}}$ respectively. The relatively short distance ($d = 2.92 \text{ \AA}$) between Fe ions
36 on the Fe2 sites gives rise to the possibility of direct exchange interaction along the z
37 axis which is discussed below in Section 4.2. Such direct interaction can also result in
38 the formation of partially covalent bonds, which again could be used to explain the
39 lower B_{hf} .
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

4.1.3 Trigonal 15R-BaFeO₂F (*R-3m*)

In Figure 1c it is seen that the Fe³⁺ ions in this trigonal structure occupy three distinct sites Fe1, Fe2 and Fe3 with relative populations 2:2:1. The Mössbauer spectra in the temperature range of magnetic order show a profile which is well fitted by three sextet components. The component with the largest value of hyperfine field (at 16K $B_{\text{hf}} = 57.3$ T, $\delta = 0,50$ mm/s) has a fitted relative area of 18% - close to the 20% expected by identifying this component with the Fe3 site which is connected with six neighbour octahedra via corner sharing O²⁻ ions. The other two sextet components are identified with the Fe1 and Fe2 sites. The areas of these components (which are difficult to determine precisely in the fitting due to the degree of overlap) are consistent with the 40% areas expected from the structure. The smaller values of hyperfine field and isomer shift (at 16K $B_{\text{hf}} = 51.4$ T and $\delta = 0.46$ mm/s) are consistent with the greater degree of covalency of the iron ions in the Fe1 and Fe2 sites as discussed above.

4.2 Magnetic ordering temperatures of cubic, hexagonal and trigonal BaFeO₂F

The magnetic ordering temperatures of the cubic, hexagonal and trigonal forms of BaFeO₂F have been found to be 645 ± 5 K [9], 597 ± 3 K and 636 ± 3 K respectively.

The striking feature of these values is their similarity. In these different structures the iron is always present as Fe³⁺ but the differences in crystal structure lead to an expectation of 3D magnetic structure in the cubic phase but a degree of 1D nature in the hexagonal- and trigonal- forms where the magnetic coupling along the z axis is strong but that in the crystallographic a-b plane is weak. In addition the magnetic coupling in the cubic phase is by six 180⁰ superexchange pathways via corner sharing O²⁻ anions (as shown in Figure 8a) which is known to give strong antiferromagnetic interaction.

In the hexagonal phase the Fe1 sites interact via six 180⁰ superexchange paths (as in the cubic phase) but the Fe2 sites interact with three 180⁰ superexchange paths and three 90⁰ superexchange paths via the three F⁻ ions that define the shared face of the adjacent octahedron.

In the trigonal phase the Fe3 site couples via six 180⁰ superexchange paths (as in the cubic phase and in the Fe1 site of the hexagonal compound) but the Fe1 and Fe2

1
2
3 sites interact via three 180° superexchange paths and three 90° superexchange
4 paths.
5
6

7
8 It is expected that the 90° superexchange coupling across the shared face of the
9 adjacent octahedron would be different from the 180° coupling of the cubic phase.
10 This should lead to weaker links in the chain of magnetic interactions along the z axis
11 and in appreciable lowering of the magnetic ordering in the hexagonal and trigonal
12 phases from that of the cubic phase.
13
14
15

16
17 The experimental result, where only a modest reduction in the magnetic ordering
18 temperatures in the hexagonal and trigonal phases is observed, focusses attention
19 on
20
21
22

23
24 (1) the magnetic interaction of the Fe ions across the common face of the adjacent
25 octahedra
26

27
28 (2) the geometrical configuration of the interacting Fe ions in the hexagonal- and
29 trigonal- structures
30
31

32 We consider these aspects in turn.
33

34
35 (1) Magnetic interaction between the Fe sites across a common octahedral face
36 can have two parts (i) 90° superexchange proceeding via the three anions that
37 define this face and (ii) direct exchange [22] between the Fe ions
38
39

40 (i) The 90° superexchange interaction between $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ can occur via
41 charge transfer between $\text{Fe}(d\varepsilon) \leftrightarrow \text{O}(p_\pi)$ and non-orthogonal
42 (antiferromagnetic) exchange ($p_\sigma - d\gamma'$) as sketched in Figure 8c. Such
43 interactions occur in MnCl_2 [23].
44
45
46

47 (ii) Direct exchange [22] may also occur – arising from the proximity of the Fe
48 ions on Fe2 sites in the 6H phase or the Fe1 and Fe2 sites in the 15R
49 phase. This interaction is sketched in Figure 8b.
50
51
52
53
54
55
56
57
58
59
60

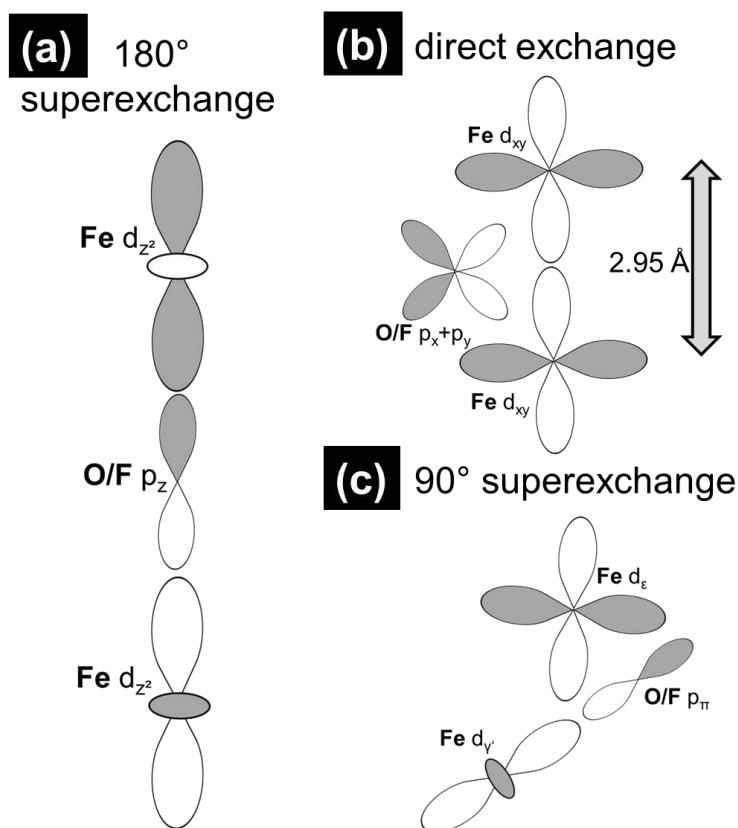


Figure 8. Exchange interactions for (a) corner sharing Fe octahedra and (b) and (c) face sharing octahedra

Accounts of the above mechanisms (i) and (ii) are given in references [23] and [22, 24] respectively. These accounts lead to the expectation of antiferromagnetic coupling by each mechanism for the case where both ions have $3d^5$ high spin configuration. This is in agreement with the observed magnetic structure. An evaluation has been made of the combined strength of these interactions using DFT based calculations (see later in this section), and the experimental result of the similar ordering temperatures indicates that this combined antiferromagnetic interaction must be strong.

(2) In the 6H- structure each Fe2 ion has three strong 180° superexchange interactions with Fe1 ions of the neighbouring layer as well as the Fe2 – Fe2 interaction discussed above. The combined effect of these interactions will stabilise the antiferromagnetic structure and limit the reduction in ordering temperature as compared with the cubic phase.

1
2
3 Similar combinations of strong 180° superexchange and the 90° superexchange and
4 direct exchange interactions occur for the Fe1 and Fe2 site Fe^{3+} ions in the trigonal
5 form which similarly lead to a limited reduction in the magnetic ordering temperature
6 compared to the cubic form.
7
8
9

10
11 DFT based calculations can help to understand the distinct magnitudes of exchange
12 interactions arising between face shared- (exchange parameter J_1) and corner
13 shared- octahedra (exchange parameter J_2). In contrast to our expectation, we found
14 that J_1 (0.143 eV) is significantly larger than J_2 (0.046 eV). However, it is important to
15 keep in mind that for c-type layers, one iron atom shares its polyhedron with three
16 neighbouring octahedra via corners. Therefore, the interlayer exchange couplings for
17 octahedra connected via c-type and h-type layers can be calculated to be $J_c = 3 J_2 =$
18 0.138 eV and $J_h = J_1 = 0.143$ eV respectively. Therefore, J_c and J_h must be regarded
19 to be in the same order of magnitude, and this can serve to explain why the magnetic
20 ordering temperatures are similar for the three modifications (cubic-, 6H- and 15R-
21 BaFeO_2F).
22
23
24
25
26
27
28
29
30

31 Robust antiferromagnetism in some fluorinated hexagonal perovskites has been
32 reported [19] but in these compounds, 6H- $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{FeF}_x\text{O}_{3-\delta}$ and 15R- $\text{BaFeF}_x\text{O}_{3-\delta}$,
33 the high magnetic ordering temperatures are associated with fluorination causing
34 major structural changes that enhance the magnetic coupling, e. g. ordering of anion
35 vacancies within the hexagonal- type layers resulting in corner sharing of tetrahedra
36 connecting the iron ions between those hexagonal- type layers. In the phases of
37 BaFeO_2F examined here fluorination gives completely filled anion sublattices with
38 octahedral coordination, while additionally assuring an oxidation state of +3 for all the
39 Fe ions. In these present systems it is the effect of the different interconnection of
40 octahedra (face-sharing vs. corner-sharing) that define the magnetic coupling
41 mechanisms that are responsible for the differences in magnetic ordering
42 temperatures in the different forms of BaFeO_2F .
43
44
45
46
47
48
49
50
51
52

53 It is noted that the magnetic ordering temperatures of the 6H- BaFeO_2F (597 ± 3 K)
54 and the 15R – BaFeO_2F (636 ± 3 K) are significantly different. A major difference
55 between those two phases lies in the fact that for the 15R phase the hexagonal
56 layers cannot only contain fluoride ions, but also must contain some oxide ions at
57 least partially regarding a simple consideration of stoichiometry ($12k$ (c-type) and $6h$
58 (h-type) anion sites for the 6H compound vs. $18h$ and $9e$ (both c-type) as well as $18h$
59
60

(h-type) anion sites for the 15R compound). Although this structure is too large to be calculated by means of DFT methods, we assume that a partial composition of the h-type layers by oxide ions might result in slightly more robust exchange interactions between cations connected via such layers and therefore an increased ordering temperature by about 40 K.

5 Conclusions

The ^{57}Fe Mössbauer spectra recorded from the cubic-, hexagonal- and trigonal modifications of BaFeO_2F can be related to the structural characteristics surrounding the Fe^{3+} sites in these materials. The similarity in the magnetic ordering temperatures of the three modifications can be explained by the details of the magnetic interactions between the Fe^{3+} sites in the three materials.

6 Acknowledgements

Oliver Clemens thanks the German Academic Exchange Service (DAAD) for being given a Postdoctoral Research Fellowship and the German Science Foundation for providing an Emmy Noether Research Fellowship (Grant No. CL 551/2-1). We acknowledge financial support from Spanish MINECO (Project MAT2015-64110-C2-1-P).

7 References

- [1] Francesconi M G and Greaves C 1997 Anion substitutions and insertions in copper oxide superconductors *Supercond. Sci. Technol.* **10** A29
- [2] Greaves C and Francesconi M G 1998 Fluorine insertion in inorganic materials *Curr. Opin. Solid State Mater. Sci.* **3** 132-6
- [3] McCabe E E and Greaves C 2007 Review: Fluorine insertion reactions into pre-formed metal oxides *J. Fluorine Chem.* **128** 448-58
- [4] Clemens O and Slater P R 2013 Topochemical modifications of mixed metal oxide compounds by low-temperature fluorination routes *Rev. Inorg. Chem.* **33** 105-17
- [5] Berry F J, Ren X, Heap R, Slater P and Thomas M F 2005 Fluorination of perovskite-related SrFeO_{3-d} *Solid State Commun.* **134** 621-4
- [6] Berry F J, Heap R, Helgason Ö, Moore E A, Shim S, Slater P R and Thomas M F 2008 Magnetic order in perovskite-related SrFeO_2F *J. Phys.: Condens. Matter* **20** 215207
- [7] Clemens O, Haberkorn R, Slater P R and Beck H P 2010 Synthesis and characterisation of the $\text{Sr}_x\text{Ba}_{1-x}\text{FeO}_{3-y}$ -system and the fluorinated phases $\text{Sr}_x\text{Ba}_{1-x}\text{FeO}_2\text{F}$ *Solid State Sci.* **12** 1455-63

- 1
2
3 [8] Heap R, Slater P R, Berry F J, Helgason O and Wright A J 2007 Synthesis
4 and structural determination of the new oxide fluoride BaFeO_2F *Solid State*
5 *Commun.* **141** 467-70
6
7 [9] Berry F J, Coomer F C, Hancock C, Helgason Ö, Moore E A, Slater P R,
8 Wright A J and Thomas M F 2011 Structure and magnetic properties of the
9 cubic oxide fluoride BaFeO_2F *J. Solid State Chem.* **184** 1361-6
10
11 [10] Clemens O, Haberkorn R, Slater P R and Beck H P 2010 Synthesis and
12 characterisation of the $\text{Sr}_x\text{Ba}_{1-x}\text{FeO}_{3-y}$ -system and the fluorinated phases
13 $\text{Sr}_x\text{Ba}_{1-x}\text{FeO}_2\text{F}$ *Solid State Sci.* **12** 1455-63
14
15 [11] Clemens O, Berry F J, Wright A J, Knight K S, Perez-Mato J M, Igartua J M
16 and Slater P R 2013 A neutron diffraction study and mode analysis of
17 compounds of the system $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-x}\text{F}_x$ ($x=1, 0.8, 0.5, 0.2$) and an
18 investigation of their magnetic properties *J. Solid State Chem.* **206** 158-69
19
20 [12] Clemens O, Berry F J, Wright A J, Knight K S, Perez-Mato J M, Igartua J M
21 and Slater P R 2015 Reply to "Structural and magnetic behavior of the cubic
22 oxyfluoride SrFeO_2F studied by neutron diffraction" *J. Solid State Chem.* **226**
23 326-31
24
25 [13] Slater P R 2002 PVDF as a reagent for the synthesis of K_2NiF_4 -related
26 inorganic oxide fluorides *J. Fluorine Chem.* **117** 43-5
27
28 [14] Clemens O, Wright A J, Berry F J, Smith R I and Slater P R 2013 Synthesis,
29 structural and magnetic characterisation of the fully fluorinated compound 6H-
30 BaFeO_2F *J. Solid State Chem.* **198** 262-9
31
32 [15] Clemens O, Berry F J, Bauer J, Wright A J, Knight K S and Slater P R 2013
33 Synthesis, structural and magnetic characterisation of the fluorinated
34 compound $15\text{R-BaFeO}_2\text{F}$ *J. Solid State Chem.* **203** 218-26
35
36 [16] Müller U 2004 *Anorganische Strukturchemie* (Wiesbaden: B. G. Teubner
37 Verlag)
38
39 [17] Clemens O, Groeting M, Witte R, Manuel Perez-Mato J, Loho C, Berry F J,
40 Kruk R, Knight K S, Wright A J, Hahn H and Slater P R 2014 Crystallographic
41 and Magnetic Structure of the Perovskite-Type Compound $\text{BaFeO}_{2.5}$:
42 Unrivaled Complexity in Oxygen Vacancy Ordering *Inorg. Chem.* **53** 5911-21
43
44 [18] Sturza M, Daviero-Minaud S, Kabbour H, Gardoll O and Mentré O 2010
45 Fluorination of Iron Hexagonal Perovskites Promoting Low Temperature
46 Oxygen Mobility *Chem. Mater.* **22** 6726-35
47
48 [19] Sturza M, Kabbour H, Daviero-Minaud S, Filimonov D, Pokholok K, Tiercelin
49 N, Porcher F, Aldon L and Mentré O 2011 Unprecedented Robust
50 Antiferromagnetism in Fluorinated Hexagonal Perovskites *J. Am. Chem. Soc.*
51 **133** 10901-9
52
53 [20] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D and Luitz J 2001 *WIEN2k,*
54 *An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal*
55 *Properties* (Techn. Universität Wien, Austria)
56
57 [21] Perdew J P and Wang Y 1992 Accurate and simple analytic representation of
58 the electron-gas correlation system *Phys. Rev. B* **45** 13244-9
59
60 [22] Goodenough J B 1960 Direct Cation- -Cation Interactions in Several Oxides
Physical Review **117** 1442-51
[23] Suzuki M and Suzuki I 2009 *Lecture on Superexchange* (Binghamton: State
University of New York)
[24] Goodenough J B 1963 *Magnetism and the Chemical Bond* (New York:
Interscience Publisher)