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# Magnetic interactions in cubic-, hexagonal- and trigonal- barium iron oxide fluoride, BaFeO<sub>2</sub>F

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## Abstract

$^{57}\text{Fe}$  Mössbauer spectra have been recorded from the hexagonal (6H)- and trigonal (15R)- modifications of  $\text{BaFeO}_2\text{F}$  and are compared with those previously recorded from the cubic form of  $\text{BaFeO}_2\text{F}$ . The spectra, recorded over a temperature range from 15 to 650K show that all of the iron in all the compounds is in the  $\text{Fe}^{3+}$  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- $\text{BaFeO}_2\text{F}$  and  $636\pm 3\text{K}$  for 15R- $\text{BaFeO}_2\text{F}$ . 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  $\text{MFeO}_2\text{F}$  ( $\text{M} = \text{Sr}, \text{Ba}$ ) [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  $\text{BaFeO}_2\text{F}$ : hexagonal 6H- $\text{BaFeO}_2\text{F}$  (space group  $P6_3/mmc$  [14]) and trigonal 15R- $\text{BaFeO}_2\text{F}$  (space group  $R-3m$  [15]).

The structures of the  $\text{BaFeO}_2\text{F}$  modifications can be understood in terms of the close packing of  $\text{BaO}_2\text{F}$  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  $\text{SrFeO}_3$  whereas the hexagonal perovskite structure is obtained for the sequence *hhh...*in, for example,  $\text{BaCoO}_3$ . Hence the modifications of  $\text{BaFeO}_2\text{F}$  considered here differ in the stacking sequence of the  $\text{BaO}_2\text{F}$  layers. The respective stacking sequences are *ccc...* for cubic  $\text{BaFeO}_2\text{F}$ , *cchcch...* for 6H- $\text{BaFeO}_2\text{F}$  and *hcchhcchhcch...* for 15R- $\text{BaFeO}_2\text{F}$ . 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  $\text{Ba}^{2+}$ ), in this work the low temperature fluorination routes have allowed the synthesis of three different perovskite-type structures all containing  $\text{Fe}^{3+}$  with the same A site cations and identical overall anion composition.

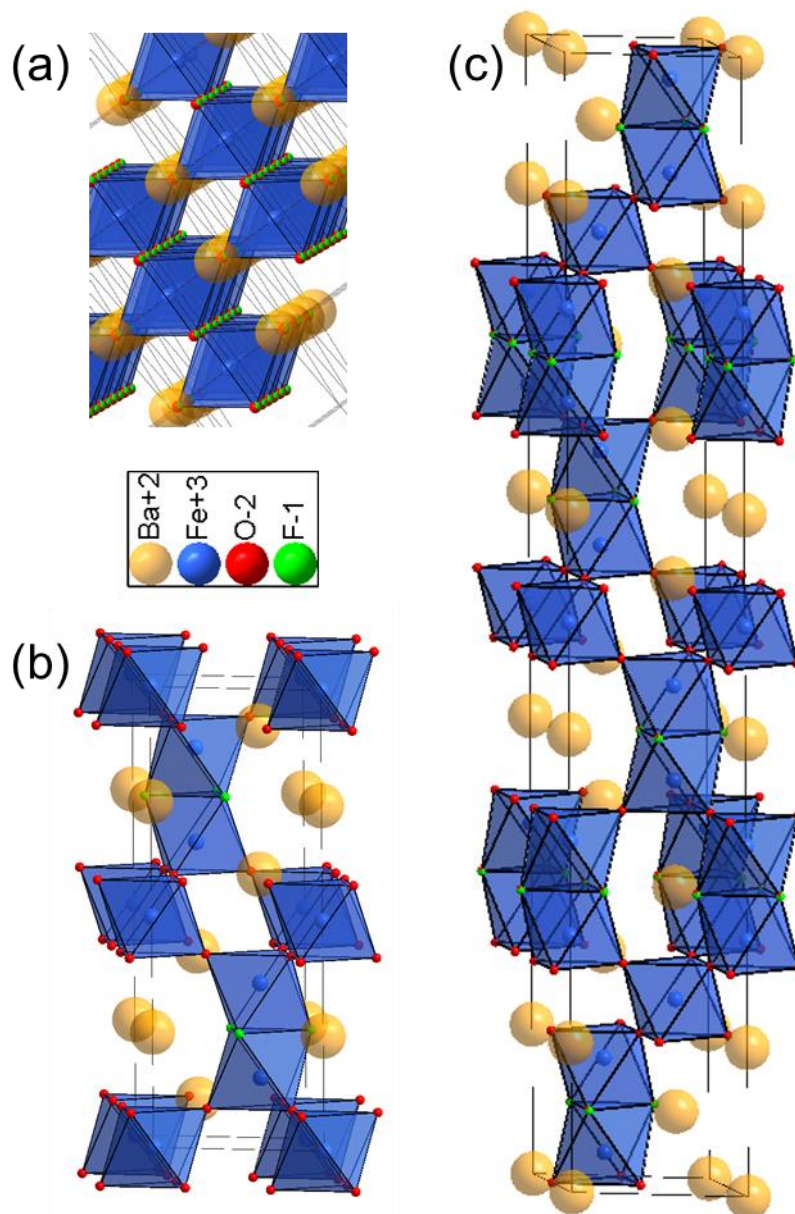


Figure 1. Crystal structures of (a) cubic-, (b) hexagonal 6H- and (c) trigonal 15R-BaFeO<sub>2</sub>F.

Furthermore, the magnetic structures of the hexagonal- and trigonal- modifications of BaFeO<sub>2</sub>F 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 <sup>57</sup>Fe Mössbauer spectroscopy in cubic BaFeO<sub>2</sub>F [9]. Cubic BaFeO<sub>2</sub>F shows G-type antiferromagnetic ordering, i. e. each iron atom possesses spin direction opposite to its nearest neighbours. In 6H- and 15R- BaFeO<sub>2</sub>F, 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 BaO<sub>2</sub>F layers align parallel (the octahedra are not connected to other octahedra of the same layer), but align antiparallel to neighbouring layers. The

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3 magnetic moments are aligned parallel to the *a/b*-plane in both cases, i.e.  
4 perpendicular to the stacking direction of BaO<sub>2</sub>F layers [14, 15].  
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8 We have now recorded <sup>57</sup>Fe Mössbauer spectra from both 6H-BaFeO<sub>2</sub>F and  
9 15R-BaFeO<sub>2</sub>F 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 BaFeO<sub>2</sub>F [9]. The results are discussed in terms of the different magnetic  
12 interactions between the Fe<sup>3+</sup> ions which originate from the differences in crystal  
13 structure.  
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## 20 **2 Experimental Details**

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22 Cubic perovskite-related BaFeO<sub>2.5</sub> [17] was prepared by the calcination of  
23 appropriate quantities of a well ground mixture of BaCO<sub>3</sub> and α-Fe<sub>2</sub>O<sub>3</sub> 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 : CH<sub>2</sub>CF<sub>2</sub> unit and  
26 equivalent to a 20% excess) and heating the mixture at 375°C for 24 h in air.  
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32 Hexagonal 6H-BaFeO<sub>3-d</sub> was prepared by heating a stoichiometric planetary ball-  
33 milled mixture of BaCO<sub>3</sub> and α-Fe<sub>2</sub>O<sub>3</sub> 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<sub>3-d</sub> 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.  
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43 Trigonal 15R-BaFeO<sub>2</sub>F was prepared by heating a stoichiometric planetary ball-  
44 milled mixture of BaF<sub>2</sub>, BaCO<sub>3</sub> and α-Fe<sub>2</sub>O<sub>3</sub>, 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<sub>3-d</sub>F<sub>0.2</sub> (as  
47 reported in [18, 19]). 15R-BaFeO<sub>2</sub>F was prepared by grinding 15R-BaFeO<sub>3-d</sub>F<sub>0.2</sub> 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.  
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57 <sup>57</sup>Fe Mössbauer spectra were recorded with a constant acceleration spectrometer in  
58 transmission geometry using a ca. 25 mCi <sup>57</sup>Co/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

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3 computer fitted and the chemical isomer shift data are quoted relative to that of  
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5 metallic iron at room temperature.  
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8 Exchange parameters were estimated using density functional theory (DFT) based  
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10 on calculations for the fluoride ordered structure of 6H-BaFeO<sub>2</sub>F (*P6<sub>3</sub>/mmc*). DFT  
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12 calculations were performed using the full potential linear augmented plane wave  
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14 method as implemented in the Wien2k code [20]. The exchange-correlation  
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16 potentials are approximated using the local spin density functional as parameterized  
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18 [21]. The self-consistent calculations were carried out with RMT\*KMAX of 7.0 on a k-  
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20 mesh of 13×13×4 to guarantee good convergence. The exchange parameters were  
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22 estimated using the energy mapping methods, where the total energies between  
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24 experimental AFM, ferromagnetic (FM) and another AFM states are compared to  
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26 obtain the exchange parameters between nearest neighbors of local moments on Fe  
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28 ions.  
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### 30 **3 Results**

31 The <sup>57</sup>Fe Mössbauer spectra and fitting parameters for cubic BaFeO<sub>2</sub>F were reported  
32  
33 earlier [9]. The magnetic ordering temperature was determined as T<sub>N</sub> = 645±5K.  
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#### 35 **3.1 Mössbauer spectra recorded from the hexagonal (6H)- and trigonal (15R)-** 36 37 **phases of BaFeO<sub>2</sub>F in the temperature range 15 to 300K.**

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39 The <sup>57</sup>Fe Mössbauer spectra recorded from the hexagonal (6H) phase at 15K, 77K  
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41 and 300K are shown in Figure 2 and the fitting parameters are listed in Table 1. The  
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43 spectra recorded from the trigonal (15R) phase at 16K, 69K and 298K are shown in  
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45 Figure 3 with the fitting parameters listed in Table 2. All the fitted spectral  
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47 components from both phases showed ordered magnetic structure with values of  
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49 magnetic hyperfine field (B<sub>hf</sub>) and isomer shift (δ) characteristic of iron in the Fe<sup>3+</sup>  
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51 oxidation state.  
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54 In both the 6H and 15R materials all the Mossbauer spectra consist of overlapping  
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56 sextet components in which one sextet has a significantly higher hyperfine field. This  
57  
58 sextet represents the Fe1 site in the 6H compound and the Fe3 site in the 15R  
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60 compound. In these octahedral sites the Fe ion interacts magnetically with 6  
neighbouring Fe ions via the corner anions ( the configuration of the 3c cubic  
material).

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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.  
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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.  
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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.  
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32 The values do, however, lend some additional support for a relatively smaller value of  
33 recoil free fraction for the high field component.  
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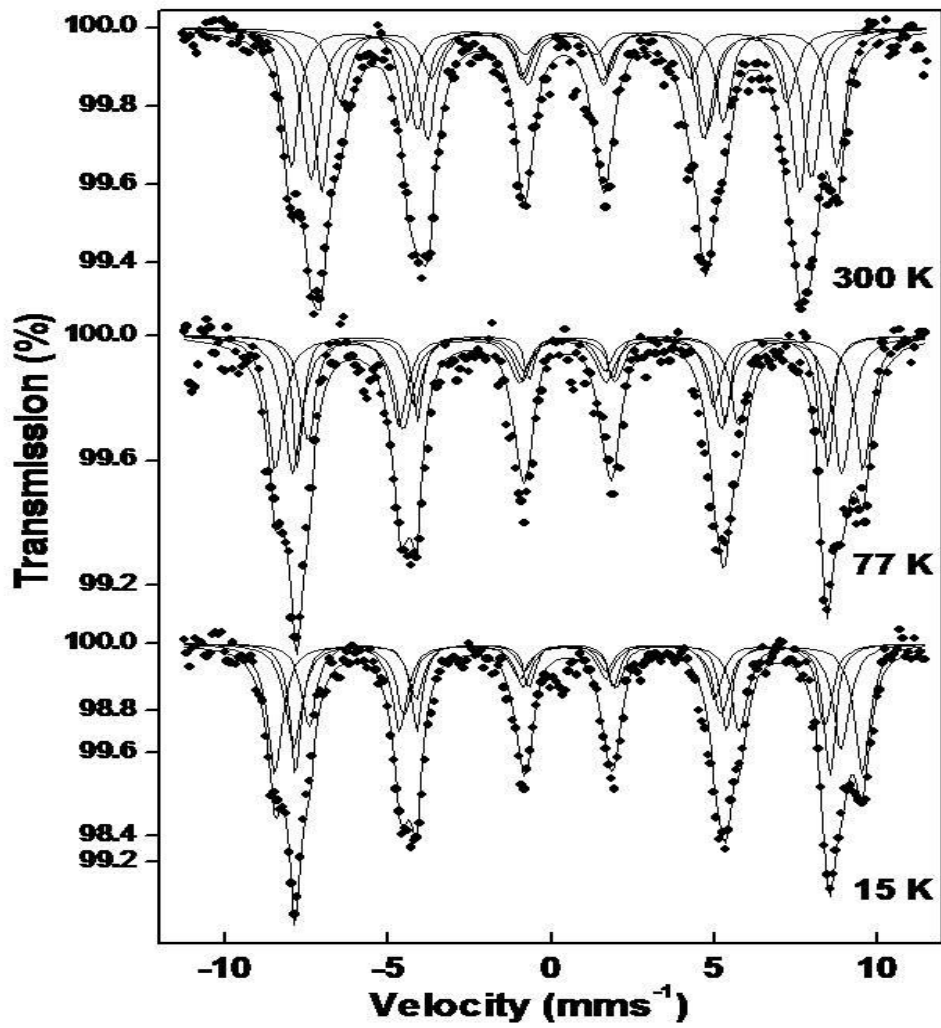


Figure 2.  $^{57}\text{Fe}$  Mössbauer spectra recorded from  $6\text{H-BaFeO}_2\text{F}$  at low temperatures

Table 1.  $^{57}\text{Fe}$  Mössbauer parameters recorded from 6H-BaFeO<sub>2</sub>F at low temperatures

Temperature (K)	$\delta \pm 0.02$ (mms <sup>-1</sup> )	$e^2qQ/2 \pm 0.02$ (mms <sup>-1</sup> )	$B \pm 0.5$ (T)	Relative Area $\pm 3$ (%)
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

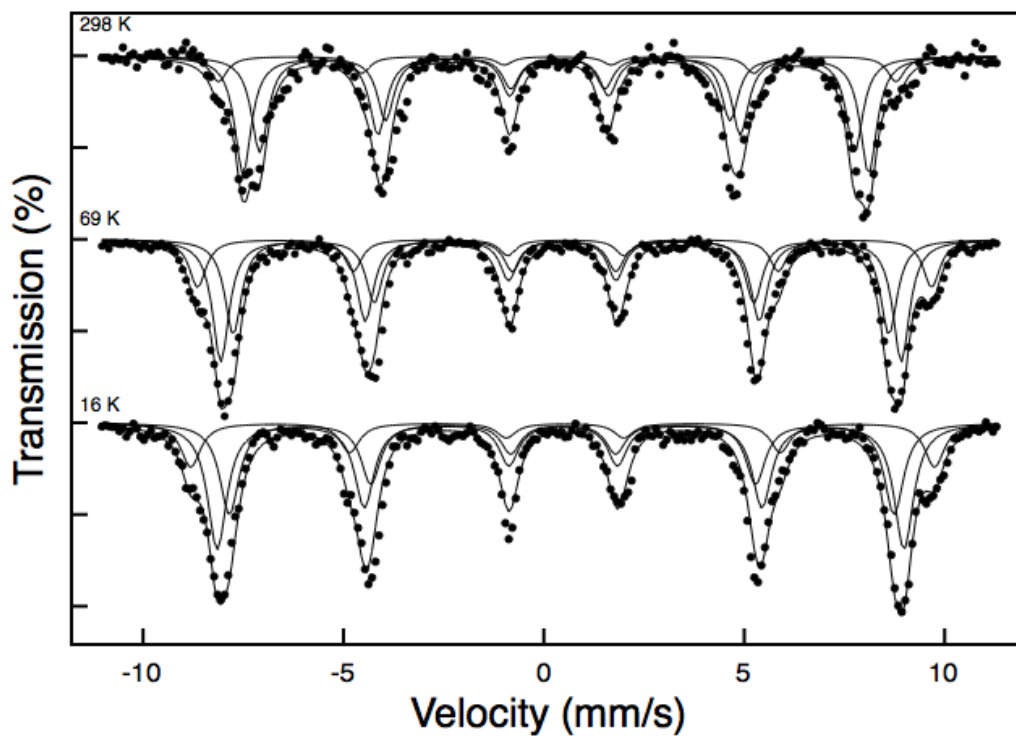
Figure 3.  $^{57}\text{Fe}$  Mössbauer spectra recorded from 15R-BaFeO<sub>2</sub>F at low temperatures

Table 2.  $^{57}\text{Fe}$  Mössbauer parameters recorded from 15R-BaFeO<sub>2</sub>F at low temperatures

Temperature (K)	$\delta \pm 0.02$ (mms <sup>-1</sup> )	$e^2qQ/2 \pm 0.02$ (mms <sup>-1</sup> )	$B \pm 0.05$ (T)	Relative Area $\pm 3$ (%)
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 BaFeO<sub>2</sub>F

The  $^{57}\text{Fe}$  Mössbauer spectra of hexagonal 6H-BaFeO<sub>2</sub>F 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  $47.5\text{T}$  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  $B_{\text{hf}}$  (T) versus temperature T is shown in Figure 6. In order to extract the value of  $T_N$  points evaluated from the expression

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

which describes the variation of the mean hyperfine field with temperature as  $T \rightarrow T_N$  were compared with the experimental points. This expression, valid as  $T \rightarrow T_N$ , 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  $T_N = 597 \pm 3\text{K}$ .

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3 Spectra recorded from trigonal 15R-BaFeO<sub>2</sub>F 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  $T_N = 636 \pm 3\text{K}$ .  
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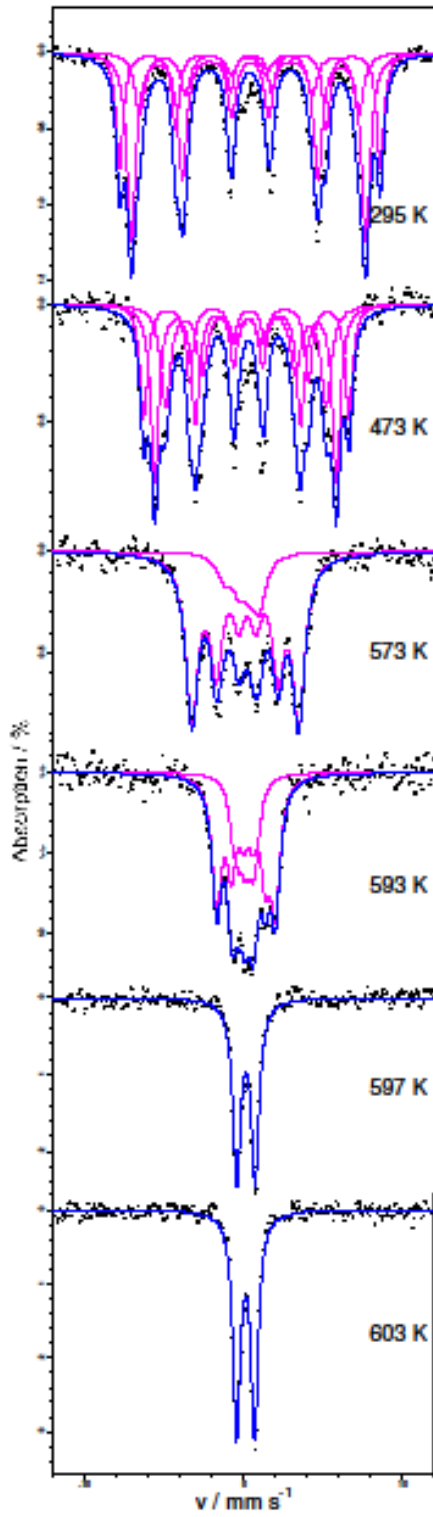


Figure 4.  $^{57}\text{Fe}$  Mössbauer spectra recorded from 6H-BaFeO<sub>2</sub>F at temperatures above ambient temperature.

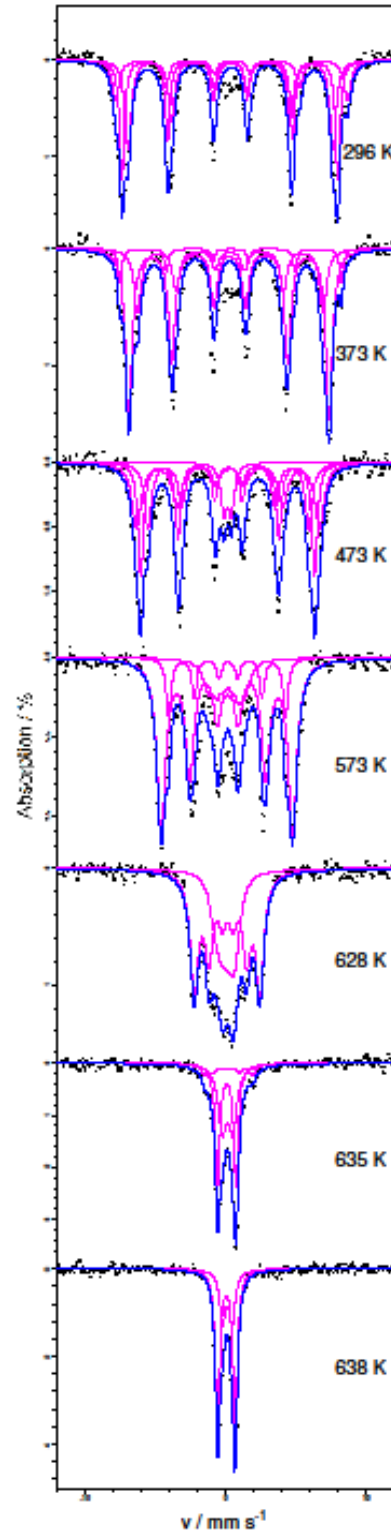


Figure 5.  $^{57}\text{Fe}$  Mössbauer spectra recorded from 15R-BaFeO<sub>2</sub>F at temperatures above ambient temperature.

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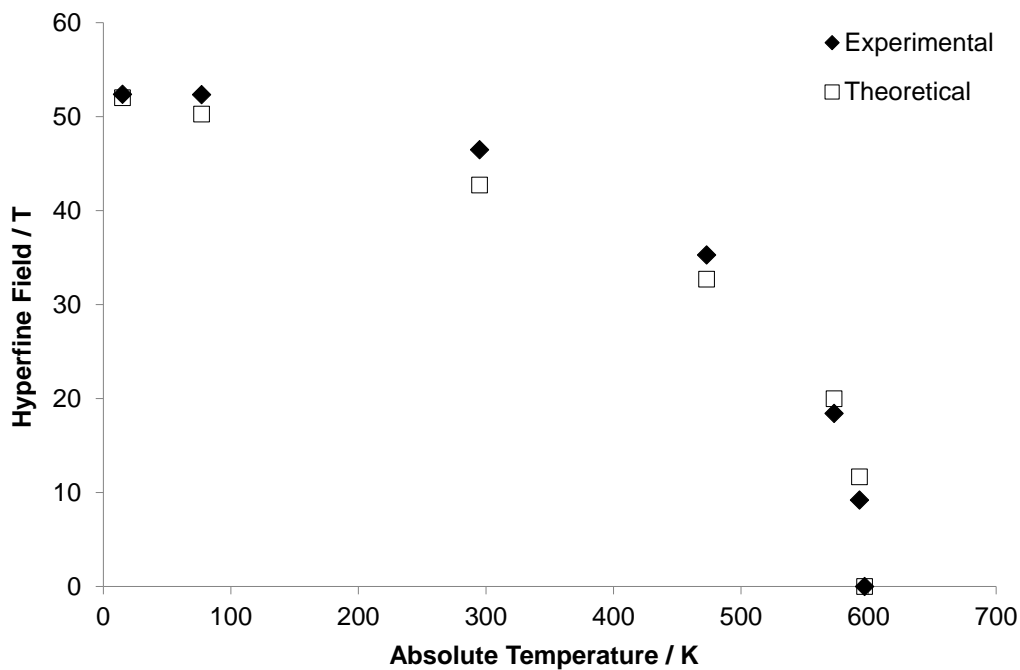


Figure 6. Plot of magnetic hyperfine field as a function of temperature for 6H-BaFeO<sub>2</sub>F

Table 3. <sup>57</sup>Fe Mössbauer parameters recorded above ambient temperature for 6H-BaFeO<sub>2</sub>F.

Temperature (K)	$\delta \pm 0.02$ (mm s <sup>-1</sup> )	$e^2Qq/2 / \Delta \pm 0.02$ (mm s <sup>-1</sup> )	$B \pm 0.05$ (T)	Relative area $\pm 2$ (%)
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

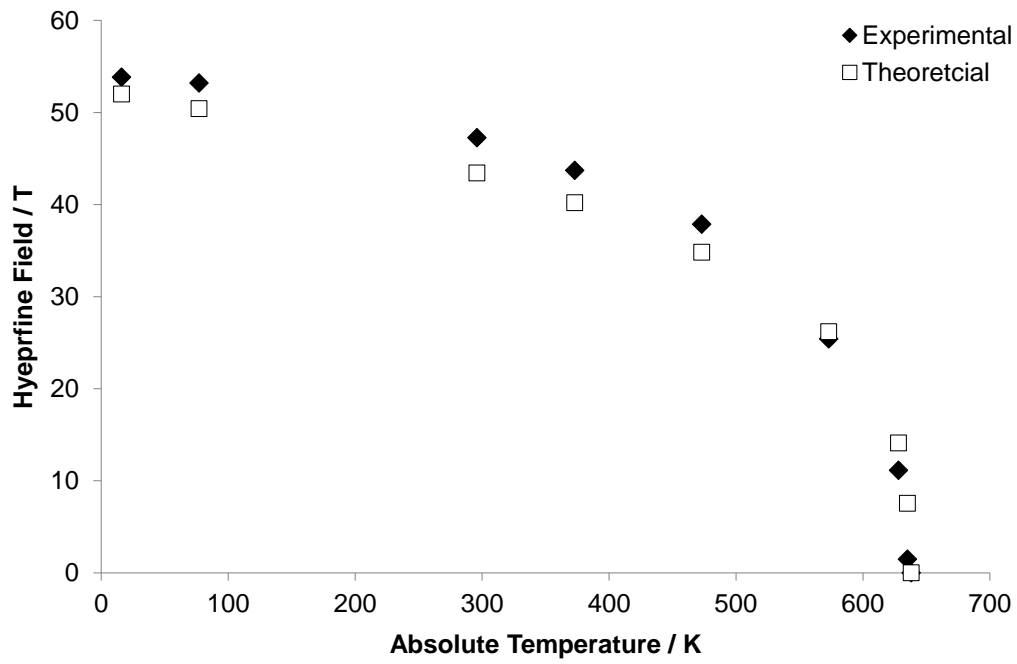


Figure 7. Plot of magnetic hyperfine field as a function of temperature for 15R-BaFeO<sub>2</sub>F

Table 4.  $^{57}\text{Fe}$  Mössbauer parameters recorded above ambient temperature for 15R-BaFeO<sub>2</sub>F.

Temperature (K)	$\delta \pm 0.02$ (mm s <sup>-1</sup> )	$e^2Qq/2 / \Delta \pm 0.02$ (mm s <sup>-1</sup> )	$B \pm 0.05$ (T)	Relative area $\pm 2$ (%)
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 BaFeO<sub>2</sub>F 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-BaFeO<sub>2</sub>F.

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

Table 6. Summary of magnetic moments on Fe<sup>3+</sup> in cubic-, 6H- and 15R-BaFeO<sub>2</sub>F from neutron diffraction data.

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

#### 4.1.1 Cubic BaFeO<sub>2</sub>F (*Pm-3m*)

It can be seen in Figure 1a that each Fe<sup>3+</sup> ion in cubic BaFeO<sub>2</sub>F is surrounded by an octahedron of anions. The octahedra are connected via corner sharing of anions. The <sup>57</sup>Fe Mössbauer spectra recorded in the magnetically ordered temperature range

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3 consist of a single magnetic sextet with broadened lines [9]. The single sextet arises  
4 from the single crystallographic site of the  $\text{Fe}^{3+}$  ions and the broadening is attributed  
5 to the effect of different quadrupole interactions where different configurations of  $\text{O}^{2-}$   
6 and  $\text{F}^-$  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  $\text{Fe}^{3+}$  ions [9].  
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#### 16 **4.1.2 Hexagonal 6H-BaFeO<sub>2</sub>F (*P6<sub>3</sub>/mmc*)**

17 From Figure 1b the  $\text{Fe}^{3+}$  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  $B_{\text{hf}}$  and  $\delta$ . 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  $\text{O}^{2-}$  anions of the octahedron than to the three  $\text{F}^-$  ions which define the common face.  
31 Proximity to the  $\text{O}^{2-}$  ions can lead to a more covalent interaction which will result in  
32 the observed smaller values of  $B_{\text{hf}}$  and  $\delta$  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  $B_{\text{hf}}$ .  
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### 4.1.3 Trigonal 15R-BaFeO<sub>2</sub>F (*R-3m*)

In Figure 1c it is seen that the Fe<sup>3+</sup> 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 O<sup>2-</sup> 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 BaFeO<sub>2</sub>F

The magnetic ordering temperatures of the cubic, hexagonal and trigonal forms of BaFeO<sub>2</sub>F have been found to be  $645 \pm 5$ K [9],  $597 \pm 3$ K and  $636 \pm 3$ K respectively.

The striking feature of these values is their similarity. In these different structures the iron is always present as Fe<sup>3+</sup> 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 180<sup>0</sup> superexchange pathways via corner sharing O<sup>2-</sup> anions (as shown in Figure 8a) which is known to give strong antiferromagnetic interaction.

In the hexagonal phase the Fe1 sites interact via six 180<sup>0</sup> superexchange paths (as in the cubic phase) but the Fe2 sites interact with three 180<sup>0</sup> superexchange paths and three 90<sup>0</sup> superexchange paths via the three F<sup>-</sup> ions that define the shared face of the adjacent octahedron.

In the trigonal phase the Fe3 site couples via six 180<sup>0</sup> superexchange paths (as in the cubic phase and in the Fe1 site of the hexagonal compound) but the Fe1 and Fe2

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3 sites interact via three  $180^\circ$  superexchange paths and three  $90^\circ$  superexchange  
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5 paths.  
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8 It is expected that the  $90^\circ$  superexchange coupling across the shared face of the  
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10 adjacent octahedron would be different from the  $180^\circ$  coupling of the cubic phase.  
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12 This should lead to weaker links in the chain of magnetic interactions along the z axis  
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14 and in appreciable lowering of the magnetic ordering in the hexagonal and trigonal  
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16 phases from that of the cubic phase.

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

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

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

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32 We consider these aspects in turn.

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

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41 (i) The  $90^\circ$  superexchange interaction between  $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$  can occur via  
42  
43 charge transfer between  $\text{Fe}(d\varepsilon) \leftrightarrow \text{O}(p_\pi)$  and non-orthogonal  
44  
45 (antiferromagnetic) exchange ( $p_\sigma - d\gamma'$ ) as sketched in Figure 8c. Such  
46  
47 interactions occur in  $\text{MnCl}_2$  [23].

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49 (ii) Direct exchange [22] may also occur – arising from the proximity of the Fe  
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51 ions on Fe2 sites in the 6H phase or the Fe1 and Fe2 sites in the 15R  
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53 phase. This interaction is sketched in Figure 8b.  
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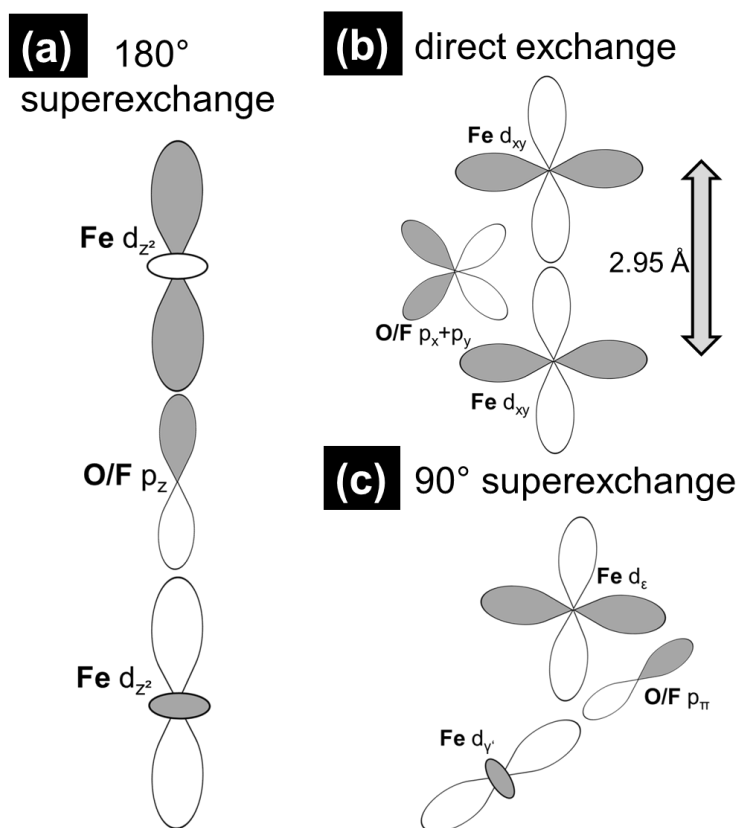


Figure 8. Exchange interactions for (a) corner sharing Fe octahedra and (b) and (c) face sharing octahedra

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  $180^\circ$  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.

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3 Similar combinations of strong  $180^\circ$  superexchange and the  $90^\circ$  superexchange and  
4 direct exchange interactions occur for the Fe1 and Fe2 site  $\text{Fe}^{3+}$  ions in the trigonal  
5 form which similarly lead to a limited reduction in the magnetic ordering temperature  
6 compared to the cubic form.  
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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  $\text{BaFeO}_2\text{F}$ ).  
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31 Robust antiferromagnetism in some fluorinated hexagonal perovskites has been  
32 reported [19] but in these compounds,  $6\text{H-Ba}_{0.8}\text{Sr}_{0.2}\text{FeF}_x\text{O}_{3-\delta}$  and  $15\text{R-BaFeF}_x\text{O}_{3-\delta}$ ,  
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  $\text{BaFeO}_2\text{F}$  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  $\text{BaFeO}_2\text{F}$ .  
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53 It is noted that the magnetic ordering temperatures of the 6H-  $\text{BaFeO}_2\text{F}$  ( $597 \pm 3$  K)  
54 and the 15R –  $\text{BaFeO}_2\text{F}$  ( $636 \pm 3$  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  
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(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  $^{57}\text{Fe}$  Mössbauer spectra recorded from the cubic-, hexagonal- and trigonal modifications of  $\text{BaFeO}_2\text{F}$  can be related to the structural characteristics surrounding the  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  sites in the three materials.

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