

In conclusion, we have shown that cubic BaBiO<sub>3</sub> contains a breathing-mode distortion resulting from the shifted O ions. This can be interpreted in terms of an ordered array of Bi<sup>3+</sup> and Bi<sup>5+</sup> cations. The structural features survive in phase I of oxygen-deficient BaBiO<sub>3-x</sub>, where the oxygen deficit is likely to be entirely accounted for by the coexisting tetragonal component. The ordered Bi arrangement in cubic BaBiO<sub>3</sub> is consistent with the semiconductor-like properties of the material, which have been shown to extend into phase I. In more-reduced phase II compounds both cubic and tetragonal structures appear to be oxygen deficient. The lack of the breathing-mode distortion in the cubic structure tempts us to favor the 4+ valence state for the Bi cations, which does not contradict the metal-like properties of the phase II material. The real structures of the tetragonal phases are still obscure owing to their low concentrations in the mixtures.

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## Structure of a Ferroelectric and Ferroelastic Monodomain Crystal of the Perovskite BiFeO<sub>3</sub>

BY F. KUBEL AND H. SCHMID

*Département de Chimie Minérale, Analytique et Appliquée, Université de Genève, CH-1211 Genève 4, Switzerland*

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### Abstract

X-ray diffraction data on a ferroelectric and ferroelastic monodomain single crystal of BiFeO<sub>3</sub> at 294 K are reported. Bismuth iron oxide,  $M_r = 312.83$ ,  $R3c$ ,  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$ ,  $a_{\text{hex}} = 5.57874 (16)$ ,  $c_{\text{hex}} = 13.8688 (3) \text{ \AA}$ ,  $V_{\text{hex}} = 373.802 (17) \text{ \AA}^3$ ,  $a_{\text{rh}} = 5.6343 \text{ \AA}$ ,  $\alpha_{\text{rh}} = 59.348^\circ$ ,  $V_{\text{rh}} = 124.601 \text{ \AA}^3$ ,  $Z = 6$ ,  $D_x = 8.337 \text{ Mg m}^{-3}$ ,  $\mu = 75.97 \text{ mm}^{-1}$ ,  $F(000) = 798$ ,  $R = 2.4$ ,  $wR = 1.9\%$  for 422 independent reflections. The structure can be described as a rhombohedrally distorted simple cubic perovskite cell. The oxygen octahedron is distorted with minimum and maximum O—O distances of

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2.710 (7) and 3.015 (9) Å, respectively, and rotated by about  $\pm \alpha = 13.8 (3)^\circ$  around the threefold axis. The iron atom is shifted away from the centre of the deformed oxygen octahedron by about 0.134 (7) Å along the threefold axis. The bismuth atom is shifted with respect to two neighbouring octahedron centres by about 0.540 (7) Å along the threefold axis. Bi—Fe distances are 3.0617 (11) and 3.8726 (11) Å. The oxygen atom is displaced by 0.2877 (6) Å away from the Bi<sub>4</sub> plane. The iron–oxygen chain has angles of 165.04 (21) (O—Fe—O) and 154.1 (4)° (Fe—O—Fe), and dihedral angles of 127.8 (9) (O—Fe—O—Fe) and 121.6 (9)° (Fe—O—Fe—O). The ferroelectric poling mechanism was analyzed: atom displacements

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were calculated for 60, 120 and 180° switching of  $P_s$  and found to be 0.44, 0.62 and 0.82 Å for iron. Average oxygen displacements for  $+\alpha$  ( $-\alpha$ ) rotated octahedra were 0.87 (0.89), 1.13 (1.24) and 1.34 (1.53) Å. Average bismuth shifts were less than 0.06 Å. As the displacements increase in the order 60, 120 and 180° switching of  $P_s$ , the 180° reversal must have a very high activation energy and will be avoided.

### Introduction

Since the first synthesis of the perovskite  $\text{BiFeO}_3$  (Royen & Swars, 1957), numerous studies have been devoted to this compound – nearly exclusively on ceramics – which were to a great extent motivated by its potential magnetoelectric properties. However, for many years the physical and structural properties of  $\text{BiFeO}_3$  remained the subject of controversy between different laboratories: ferroelectric or anti-ferroelectric? Weakly ferromagnetic or antiferromagnetic? About eight structural transitions (Krainik, Khuchua, Zhdanova & Evseev, 1982) and two magnetic transitions (Polomska, Kaczmarek & Pajak, 1974) have been reported. The controversies have been reviewed and critically analyzed with respect to physical and structural properties (Skinner, 1970; Fischer, Polomska, Sosnowska & Szymański, 1980; Sosnowska, Peterlin-Neumaier & Steichele, 1982).

The ferroelectric character of  $\text{BiFeO}_3$  was claimed on the basis of a hysteresis cycle measured at 80 K (Teague, Gerson & James, 1970), consistent with the rhombohedral polar space group  $R3c$  established in the course of structure determinations by single-crystal X-ray methods (Michel, Moreau, Achenbach, Gerson & James, 1969) and by neutron diffraction on a ceramic (Moreau, Michel, Gerson & James, 1971). Later the ferroelectric character of  $\text{BiFeO}_3$  at room temperature was once more questioned (Ismailzade, Ismailov, Alekberov & Salaev, 1981), but chemical etching experiments on ferroelastic single domains (Tabares-Muñoz, Rivera, Bezinge, Monnier & Schmid, 1985) definitively proved the polar character of  $\text{BiFeO}_3$  and allowed the hypothesis of antiferroelectricity to be discarded. Using polarized light microscopy it has been established (Tabares-Muñoz *et al.*, 1985) that the ferroelectric/ferroelastic phase is stable from at least 4 to  $\sim 1110$  K, where it transforms to another ferroelastic phase. Below the Néel temperature of about  $T_N = 670$  K it is a compensated antiferromagnet (Fischer *et al.*, 1980) with a cycloidal spin structure, incommensurate with the lattice (Sosnowska *et al.*, 1982).

With a view to gaining a better understanding of the unusual ferroelectric switching properties (no 180° switching is observed; Tabares-Muñoz *et al.*, 1985), the magnetoelectric effect and the cycloidal

spin structure, more accurate X-ray and neutron diffraction structural data are necessary. The present study describes the structure determination of a single crystal representing both a ferroelastic and ferroelectric single domain state. In the previous single-crystal work (Michel *et al.*, 1969) no attempt was made to verify the ferroelectric and ferroelastic single domain state.

### Experimental

Ferroelectric/ferroelastic single domain crystals of  $\text{BiFeO}_3$  in the form of small brownish transparent plates with pseudocubic (100) faces were grown below the ferroelectric phase transition temperature  $T_f \approx 1110$  K using a  $\text{Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3/\text{B}_2\text{O}_3$  (1:4:1 mole ratio) flux. They can be isolated mechanically from the crushed sample or by dissolving the flux in dilute nitric acid. The crystals were selected under a polarizing microscope. Owing to their extinction at 45° to the pseudocubic [100] directions, they can easily be distinguished from crystals of the parasitic phase,  $\text{Bi}_2\text{Fe}_4\text{O}_9$  ( $\approx 3\%$ ), which has parallel extinction. Precession photographs of crystals of  $\text{BiFeO}_3$  confirmed the superstructure found in this compound (Moreau *et al.*, 1971). An optically homogeneous ferroelastic single domain crystal was mounted on a CAD-4 diffractometer for the X-ray measurements. Cell parameters were determined by least-squares refinement of 25 measured diffraction angles in the region  $32.9 > \theta > 41.4^\circ$ ,  $a_{\text{hex}} = 5.57874$  (16),  $c_{\text{hex}} = 13.8688$  (3) Å. Intensities of 2444 reflections ( $2430 > 3\sigma$ ) including Friedel pairs were collected. Three standard reflections (see Table 1) were measured every hour; the variation was 5%. Intensities were corrected for this variation. Absorption effects were corrected by a Gaussian absorption correction with description of the crystal faces; the maximum and minimum transmission factors were 316.3 and 10.2, respectively. The refinement was performed with 16 variables (one scale factor, one extinction factor, four positional and ten thermal factors) using the *XTAL* program system (Hall & Stewart, 1987) by minimizing  $\sum w_i(|F_o|_i - |F_c|_i/k_i)^2$  with  $w_i = 1/\sigma^2(F_o)_i$ . In the refinement 422 reflections including 18 superstructure reflections with  $l = 2n + 1$  were used, 11 reflections presumably suffering from extinction were excluded. The starting parameters were taken from Moreau *et al.* (1971). The results of the refinement are summarized in Tables 1 and 2.\* Interatomic distances and angles are summarized in Table 3. Atomic scattering factors were taken from

\* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53304 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental conditions and agreement factors for BiFeO<sub>3</sub> with e.s.d.'s in parentheses*

Lattice parameters	$a_{\text{hex}}$ (Å)	5.57874 (16)
	$c_{\text{hex}}$ (Å)	13.8688 (3)
	$V_{\text{hex}}$ (Å <sup>3</sup> )	373.802 (17)
	$a_{\text{rh}}$ (Å)	5.6343
	$\alpha_{\text{rh}}$ (°)	59.348
	$V_{\text{rh}}$ (Å <sup>3</sup> )	124.601
Crystal size (mm)		0.166 × 0.140 × 0.032
$\lambda$ (Mo K $\alpha$ ) (Å)		0.7107
$\mu$ (mm <sup>-1</sup> )		75.97
( $\sin\theta/\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )		0.994
Range of $hkl$	$h$	-9 to 9
	$k$	-8 to 8
	$l$	-26 to 26
Standard reflections		02 $\bar{2}$ , 2 $\bar{2}$ $\bar{4}$ , 2 $\bar{2}$ 0
Max. intensity variation of standard reflections		5.0%
Number of formula units		6
Number of reflections measured		2444
Number of reflections > 3 $\sigma$ (unique)		2430 (433)
$R_{\text{int}}$		0.042
Max. shift/e.s.d.		< 10 <sup>-2</sup>
Scan type		2 $\theta$ - $\omega$
Scan speed (° min <sup>-1</sup> )		3.5-5.5*
Number of parameters		16
$R$ ( $wR$ )		0.024 (0.019)
Goodness of fit $S$		1.471
Extinction parameter $g$ (× 10 <sup>-4</sup> )		0.0197 (12)
$\Delta\rho_{\text{max}}$ (e Å <sup>-3</sup> )		1.847

\* Depending on prescan intensity.

*International Tables for X-ray Crystallography* (1974, Vol. IV).

### Discussion

The lattice parameters obtained for BiFeO<sub>3</sub> [ $a_{\text{hex}} = 5.57874$  (16),  $c_{\text{hex}} = 13.8688$  (3) Å] agree with those obtained by an X-ray precision determination (Bucci, Robertson & James, 1972) [ $a_{\text{hex}} = 5.5799$  (3),  $c_{\text{hex}} = 13.8670$  (5) Å] and by neutron diffraction (Fischer *et al.*, 1980) [ $a_{\text{hex}} = 5.585$  (7),  $c_{\text{hex}} = 13.884$  (18) Å], but are significantly different from those obtained by other neutron diffraction experiments (Moreau *et al.*, 1971; Jacobson & Fender, 1975) [ $a_{\text{hex}} = 5.5876$  (3),  $c_{\text{hex}} = 13.8670$  (5) Å;  $a_{\text{hex}} = 5.561$ ,  $c_{\text{hex}} = 13.824$  Å, respectively]. This disagreement is presumably associated with the neutron wavelength calibration. No superstructure reflections indicating a doubling of the simple perovskite cell were found for crystals 'claimed to be monodomain' prepared at 1128 K from a Bi<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub> flux containing a small amount of NaCl as additive (Rakov, Murashov, Bush & Venetsev, 1986, 1988). These crystals were however grown above the phase transition temperature. As a consequence they presumably split into 180° ferroelectric domains or antiphase domains even though these were not observed. Lattice constants are given as  $a = 3.965$  (1) Å and  $\alpha = 89.45$  (5)°.

Compared with an ideal perovskite structure BiFeO<sub>3</sub> shows the following differences: (1) The basic

Table 2. *Positional and anisotropic temperature parameters (Å<sup>2</sup> × 100) of BiFeO<sub>3</sub> with e.s.d.'s in parentheses*

The form of the temperature factors is  $\exp \{-2\pi^2[U(1,1)h^2a^{*2} + U(2,2)k^2b^{*2} + U(3,3)l^2c^{*2} + 2U(1,2)hka^*b^* + 2U(1,3)hla^*c^* + 2U(2,3)k/b^*c^*]\}$ .

	Wyckoff position		
Bi	6(a)	$x = y =$	0.0
		$z =$	0.0
Fe	6(a)	$x = y =$	0.0
		$z =$	0.22077 (8)
O	18(b)	$x =$	0.4428 (11)
		$y =$	0.0187 (10)
		$z =$	0.9520 (4)
Bi		$U_{11} = U_{22} = 2U_{12} =$	0.996 (15)
		$U_{33} =$	0.614 (14)
		$U_{13} = U_{23} =$	0.0
Fe		$U_{11} = U_{22} = 2U_{12} =$	0.659 (23)
		$U_{33} =$	0.54 (3)
		$U_{13} = U_{23} =$	0.0
O		$U_{11} =$	1.12 (14)
		$U_{22} =$	0.78 (14)
		$U_{33} =$	0.78 (12)
		$U_{12} =$	0.52 (12)
		$U_{13} =$	-0.02 (11)
		$U_{23} =$	-0.17 (11)

Table 3. *Bond distances (Å) and angles (°) of BiFeO<sub>3</sub>*

	Label in Figs. 1-4		Label in Figs. 1-4		
O—O	$a$	2.710 (7)	Bi—O	$g$ 2.271 (5)	
	$b$	3.015 (9)		$h$ 2.510 (7)	
	$c$	2.825 (9)		$i$ 3.449 (5)	
	$d$	2.866 (7)		$j$ 3.231 (7)	
Fe—O	$e$	1.958 (6)	Bi—Fe	$k$ 3.0617 (11)	
	$f$	2.110 (5)		$l$ 3.8726 (11)	
Octahedron angle	$\alpha$	13.8 (3)	Fe—O—Fe	$\gamma$ 154.1 (4)	
	O—Fe—O	$\beta$	165.04 (21)	Fe—O—Fe—O	$\delta$ 121.6 (9)
				O—Fe—O—Fe	$\epsilon$ 127.8 (9)
				$m$ 3.3071 (3)	
			$n$ 3.5793 (5)		

rhombohedral unit cell contains two connected BiFeO<sub>3</sub> perovskite units, the two oxygen octahedra being turned by + and -13.8 (3)° around the threefold axis (angle  $\alpha$  in Fig. 1). (2) The oxygen octahedron is distorted with a minimum (maximum) O—O distance of 2.710 (7) [3.015 (9) Å] [bond labels  $a$  ( $b$ ) in Fig. 1]. The other O—O distances in the octahedron are 2.825 (9) and 2.866 (7) Å (labels  $c$  and  $d$ ). (3) The iron atom is shifted by about 0.134 (7) Å away from the centre of the oxygen octahedron along the threefold axis. As a consequence two types of Fe—O distances, 1.958 (6) (bond label  $e$  in Fig. 2) and 2.110 (5) Å (bond label  $f$ ) were found. (4) The bismuth atom is shifted by about 0.540 (7) Å along the threefold axis away from the ideal position between two octahedron centres. Bi—O distances are 2.271 (5) (label  $g$  in Fig. 3), 2.510 (7) (label  $h$ ) and 3.449 (5) Å (label  $i$ ) in direction of the threefold axis (perovskite units 1 and 2 in Fig. 3), and 2.271 (5)

(label *g*), 2.510 (7) (label *h*), 3.449 (5) (label *i*) and 3.231 (7) Å (label *j*) in direction of a 'pseudo-threefold' axis [ $3_{ps}$ , between two linked perovskite units (1 and 3) in Fig. 3].

The ferroelectricity can be explained by two different Bi—Fe distances along the threefold axis, 3.0617 (11) (label *k*) and 3.8726 (11) Å (bond label *l*). Other Bi—Fe distances are 3.3071 (3) (label *m*) and 3.5793 (5) Å (label *n* in Fig. 2).

The antiferromagnetic superexchange occurs along the iron–oxygen chains even if the Fe—O angles are not exactly 180°. In BiFeO<sub>3</sub> they are found to be

165.04 (21) (angle  $\beta$ ) and 154.1 (4)° (angle  $\gamma$ ). The dihedral angle O—Fe—O—Fe is 127.8 (9)° (angle  $\delta$ ) and Fe—O—Fe—O is 121.6 (9)° (angle  $\epsilon$ ).

Preliminary experiments with a view to ferroelectric/non-ferroelastic poling along the  $[111]_{\text{rhom}}$  direction were made on a polished thin section of a BiFeO<sub>3</sub> crystal, composed predominantly of a ferroelectric single domain with the optical axis ( $\parallel \mathbf{P}_s$ ) perpendicular to the section. By control in polarized light the application of an electric field along the polar axis of this optically and ferroelastically homogeneous, but ferroelectrically unpoled domain was found to lead to important unpoling by reorientation of the polar (*i.e.* optical) axis to the three remaining equivalent pseudocubic  $[111]$  directions, rather than to ferroelectric saturation by means of 180° switching of  $\mathbf{P}_s$  (Tabares-Muñoz *et al.*, 1985). This suggests that the 180° reversal of  $\mathbf{P}_s$  is energetically less favourable than ferroelastic and ferroelectric reorientation into equivalent directions. In fact a 180° switching would require the iron atom to move by 0.82 Å along the threefold axis (180° switching) but six (two times three) equivalent positions on a 'pseudo-threefold' axis are available for the iron by shifting only by 0.44 Å (60° switching) or by 0.62 Å (120° switching). For these displacements the iron atom has to move away from the threefold axis in a direction forming an angle of  $\zeta = 129.9^\circ$  (60° switching) or  $\zeta' = 147.3^\circ$  (120° switching) with

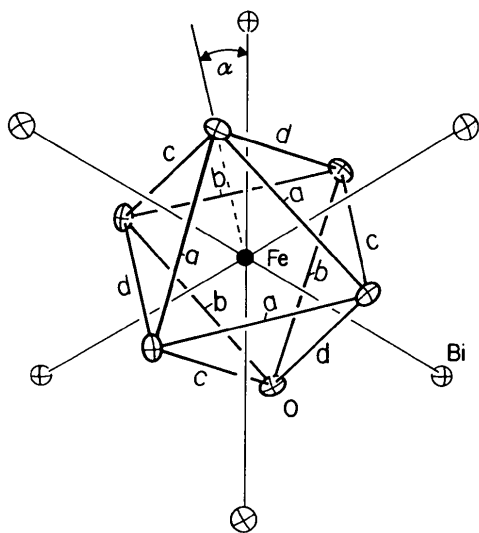


Fig. 1. One perovskite unit of BiFeO<sub>3</sub> viewed along the threefold axis. Thin open circles, Bi; thick open circles, O; filled circle, Fe.

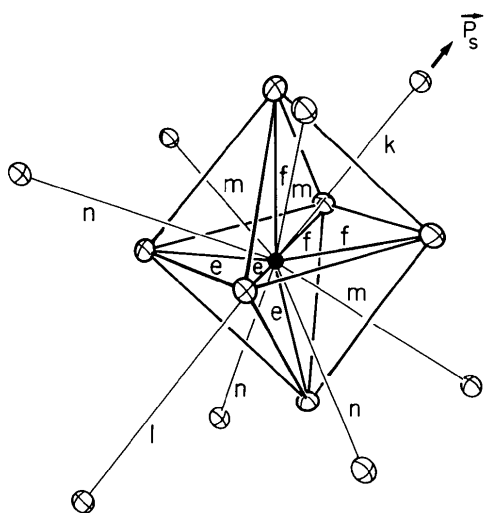


Fig. 2. One perovskite unit of BiFeO<sub>3</sub> viewed approximately perpendicular to the threefold axis. Thin open circles, Bi; thick open circles, O; filled circle, Fe.

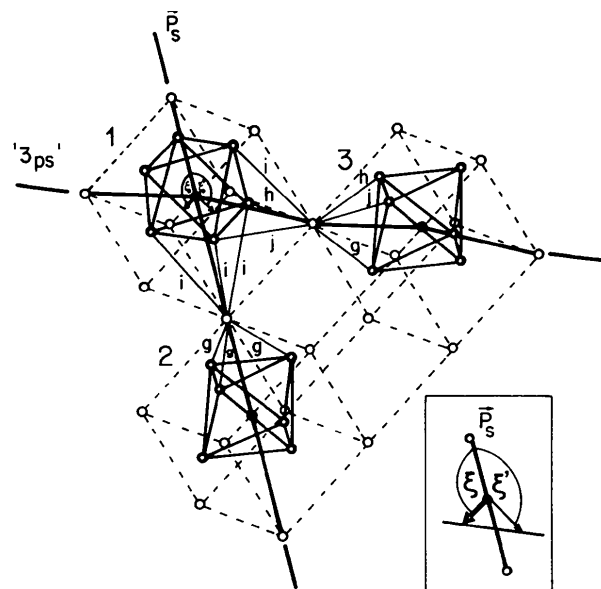


Fig. 3. Three perovskite units [two connected (1 and 2) and one linked (3)] viewed perpendicular to the threefold axis and one 'pseudo-threefold' axis. Thin open circles, Bi; thick open circles, O; filled circles, Fe. Thick (thin) arrows show iron displacement to equivalent positions for 60° (120°) switching of  $\mathbf{P}_s$  (see also inset).

Table 4. Summary of atomic displacements (Å) for different switching modes of P<sub>r</sub>

Switching	Fe	O		Bi	
		+α	-α	+α	-α
60°	0.44	0.87	0.89	0.04	0.04
120°	0.62	1.13	1.24	0.04	0.06
180°	0.82	1.34	1.53	0.0	0.0

that axis (see arrows and angles in Fig. 3). For either of the two new iron positions in two linked perovskite units, two equivalent oxygen positions belong to the +α or -α (13.7°) rotated oxygen octahedron. Equivalent iron and oxygen positions can be calculated for both units with the XTAL program system (Hall & Stewart, 1987) by keeping the Bi positions approximately fixed (Bi shifts < 0.06 Å, see Table 4). If the oxygen in perovskite unit 1 is displaced to the +α rotated octahedron, the oxygen in the linked unit 3 should move to the -α rotated octahedron to

respect the '3c' symmetry and vice-versa. Fig. 4 shows the displacements of iron and oxygen atoms to equivalent positions for one of the three possibilities of 60° poling (a) and one of the two positions of 180° poling (b). The average oxygen displacements into +α (-α) rotated equivalent octahedron positions are summarized in Table 4. They are found to be 1.34 (1.53) Å (180° switching), 0.87 (0.89) Å (60° switching) and 1.13 (1.24) Å (120° switching). As the movements of the iron and oxygen atoms are smaller for 60 and 120° switching, these new atom positions seem to be favoured compared to atom positions for 180° poling. Further it can be seen that the oxygen displacements are similar for new +α or -α rotated octahedron positions. This would allow a BiFeO<sub>3</sub> structure to be built up with statistically rotated oxygen octahedrons which would show no superstructure reflections.

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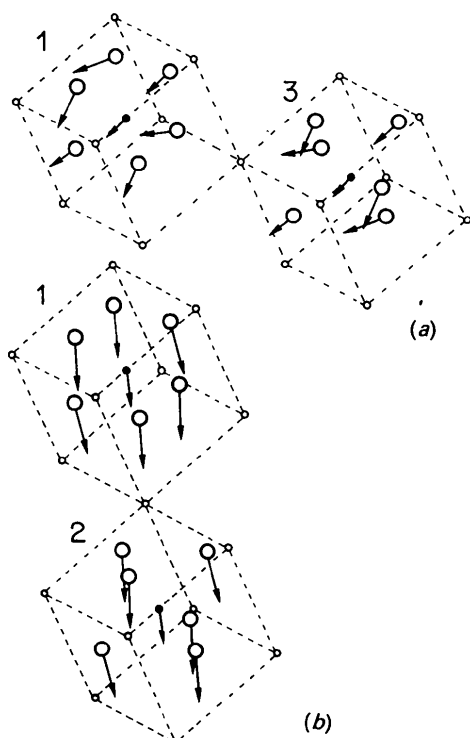


Fig. 4. Two linked (a) and two connected (b) perovskite units viewed perpendicular to the threefold (a) and 'pseudo-threefold' (b) axis. Small open circles, Bi; large open circles, O; filled circles, Fe. Arrows indicate the possible iron and oxygen shifts to equivalent positions for 60° (a) and 180° (b) poling.

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