### **Magnetic modulations in bulk α-BiFeO3 described using monoclinic superspace groups**

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It is known that tiny differences in physical parameters can lead to significant effects, such as symmetry breaking. The small effects observed in the diffraction patterns of bismuth ferrite (α-BiFeO3—BFO) are the subject of the present review. These minor effects in the crystal and magnetic structures of BFO have altered our understanding of both the symmetry of the crystal structure of BFO and the real arrangement of the magnetic moments. Already in the 19th century, Pierre Curie postulated the magnetoelectric effect [1]. Bulk BFO, a multiferroic material at room temperature [2], is an interesting substance for fundamental studies and for various practical applications. Bismuth ferrite is known to have a rhombohedrally distorted perovskite structure (space group R3c), which allows for a ferroelectric atomic displacement [3, 4]. Earlier studies reported the G-type collinear antiferromagnetic order of BFO, e.g. [5, 6], while later studies have found the spiral modulated spin structure (SMSS) [7]. It was also shown that the crystal structure of BFO, instead of the widely used trigonal space group R3c, has lower symmetry, namely the monoclinic Cc [8] and triclinic P1 [9] groups were proposed. The finding of the magnetic cycloid superimposed on the G-type of the collinear antiferromagnetic ordering permitted the explanation of the experimentally identified quadratic magnetoelectric effect in BFO [10, 11]. This effect itself has been described in [12].

Recently, the structural and magnetic properties of the room-temperature multiferroic bulk BFO have been described [13] using magnetic superspace group formalism [14, 15]. The antiferromagnetic cycloid with its propagation vector along the hexagonal [1,1,0] direction cannot be described by using trigonal magnetic superspace groups derived from R3c. This disagreement shows the necessity to replace the trigonal symmetry by the monoclinic one [13]. Several phenomena observed experimentally in bulk BFO, e.g., antiferromagnetic cycloid [7], weak ferromagnetic spin-density wave [16], and hkl-dependent Bragg peaks’ broadening [8], can all be described by using the monoclinic magnetic superspace groups Cc(0β0)0 for clockwise rotation of the magnetic moments and Cc’(0β0)0 for counterclockwise rotation of the magnetic moments [13]. The proposed monoclinic superspace groups can also describe anharmonic magnetic modulations, charge modulations, atomic position modulations, and weak non-modulated ferromagnetic ordering or ferroelectric polarization in bulk BFO [13].

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