by large spontaneous polarizations as well; however, this did not seem to cause much consternation in the research community, since magnetism in this system is quite exotic and thus captured a lot of interest.

During the 1980s, the magnetic structure of $BiFeO_3$ was studied in detail. Early studies indicated that $BiFeO_3$ was a G-type antiferromagnet (G-type antiferromagnetic order is shown schematically in Fig. 2d) with a Néel temperature of ~673 K [24] and possessed a cycloidal spin structure with a period of ~620 Å [25]. This spin structure was found to be incommensurate with the structural lattice and was superimposed on the antiferromagnetic order. It was also noted that if the moments were oriented perpendicular to the $\langle 1 1 1 \rangle$-polarization direction the symmetry also permits a small canting of the moments in the structure, resulting in a weak canted ferromagnetic moment of the Dzyaloshinskii–Moriya type (Fig. 2d) [26,27].

In 2003 a paper focusing on the growth and properties of thin films of $BiFeO_3$ spawned a dramatic increase in the study of $BiFeO_3$ thin films that continues to the present day. The paper reported enhancements of polarization and related properties in heteroepitaxially constrained thin films of $BiFeO_3$ [28]. Structural analysis of the films suggested differences between films (with a monoclinic structure) and bulk single crystals (with a rhombohedral structure) as well as enhancement of the polarization up to ~90 $\mu C\ cm^{-2}$ at room temperature and enhanced thickness-dependent magnetism compared to bulk samples. It is now clear that the high values of polarization observed actually represented the intrinsic polarization of $BiFeO_3$. Limitations in the quality of bulk crystals had kept researchers from observing such high polarization values until much later in bulk samples [29]. A series of detailed first principles calculations methods helped shed light on the findings of Ref. [28]. Calculations of the spontaneous polarization in $BiFeO_3$ suggested a value between 90 and 100 $\mu C\ cm^{-2}$ (consistent with those measured in 2003) [30] that have since been confirmed by many other experimental reports. Other theoretical treatments attempted to

understand the nature of magnetism and coupling between order parameters in $BiFeO_3$. Such calculations confirmed the possibility of weak ferromagnetism arising from a canting of the antiferromagnetic moments in $BiFeO_3$. The canting angle was calculated to be ~1° and would result in a small, but measurable, magnetization of ~0.05 μ_B per unit cell [31]. It was also found that the magnetization should be confined to an energetically degenerate, easy {111}, perpendicular to the spontaneous polarization direction in $BiFeO_3$. These same calculations further discussed the connection of the weak ferromagnetism and the structure (and therefore ferroelectric nature) of $BiFeO_3$. This allowed the extraction of three conditions necessary to achieve electric-field-induced magnetization reversal: (i) the rotational and polar distortions must be coupled; (ii) the degeneracy between different configurations of polarization and magnetization alignment must be broken; (iii) there must be only one easy magnetization axis in the {111} which could be easily achieved by straining the material [31].

Nonetheless, the true nature of magnetism in thin film $BiFeO_3$ continues to be a contentious subject. The work of Wang et al. presented an anomalously large value of magnetic moment (of the order of 70 emu cm^{-3}) [28], which is significantly higher than the expected canted moment of ~8 emu cm^{-3}. There have been several studies aimed at clarifying the origins of this anomalous magnetism. Eerenstein et al. [32] proposed that the excess magnetism was associated with magnetic second phases (such as γ-Fe_2O_3); this was supported by the studies of Béa et al. [33], who showed that $BiFeO_3$ films, when grown under highly reducing conditions (for example under oxygen pressures lower than 1×10^{-3} Torr) showed enhanced magnetism as a consequence of the formation of magnetic second phases. It is, however, important to note that low oxygen pressure during growth is not the cause for the enhanced moment in the 2003 report by Wang et al., where films were grown in oxygen pressures between 100 and 200 mTorr and cooled in 760 Torr, rendering formation of such secondary magnetic phases thermodynamically
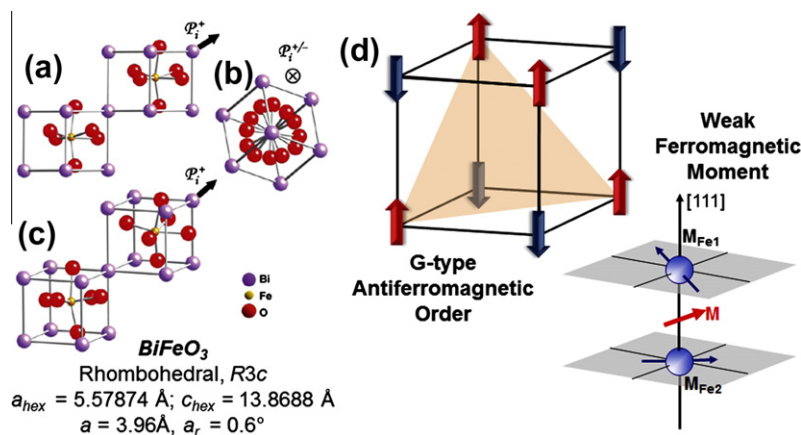

Fig. 2. Structure of $BiFeO_3$ shown looking (a) down the pseudocubic-[1 1 0], (b) down the pseudocubic-[1 1 1] polarization direction, and (c) at a general three-dimensional view of the structure. (d) The magnetic structure of $BiFeO_3$ is shown, including G-type antiferromagnetic ordering and the formation of the weak ferromagnetic moment (adapted from Ref. [23]).