Chapter 10 Summary and Suggestions for Future Work

10.1 Summary

The present investigation was undertaken to critically examine the Gorter model of the collinear magnetic structure of the technologically important $BaFe_{12}O_{19}$, an M-type hexaferrite with a huge market share as a permanent magnetic material, and investigate the consequences of the departure from the collinear model on the low temperature behaviour of this compound. This investigation involved X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD), X-ray and neutron powder diffraction, single-crystal neutron scattering, dc and ac magnetic susceptibility, dielectric and specific heat studies using in-house facilities as well as advanced synchrotron and neutron facilities at Petra-III, DESY, Hamburg, FRM-II, Garching and ISIS at Rutherford Appleton Laboratory, Harwell. Well characterised phase pure polycrystalline powder, sintered ceramic and single crystal samples, prepared as part of this thesis work, were used in all these investigations. The most significant findings of the present work are summarised below:

(1) XAS and XMCD studies carried out at the Fe $L_{2,3}$-edges of $BaFe_{12}O_{19}$ single crystals in the temperature range 1.2 K to 30 K in the normal incidence (NI) and grazing incidence (GI) geometries with and without dc field bias have confirmed significant component of the magnetic moments in the basal plane also in sharp departure from the collinear Gorter model, assumed all along in the literature.

(2) The non-collinear magnetic structure of $BaFe_{12}O_{19}$ was further confirmed by the observation of satellite peaks in single-crystal neutron diffraction patterns along the *00l* reciprocal lattice row around $l = 2n \pm 1$ positions, which are otherwise forbidden by the

nuclear and magnetic space groups $P6_3/mmc$ and $P6_3/mm'c'$, respectively, for the collinear magnetic structure.

(3). The satellite peaks were shown to be linked with an incommensurate longitudinal conical magnetic order for all temperatures below 300 K, except in the narrow temperature range 15 K to 35 K in which the conical magnetic order was shown to correspond to a commensurate modulation with a very long periodicity of 28c. This is the first evidence for longitudinal conical magnetic structure in pure $BaFe_{12}O_{19}$ compound without any chemical substitution.

(4). Based on the dc susceptibility measurements as a function of temperature (T), time (t), magnetic field (H) and ac susceptibility measurements as a function of T, frequency (ω), t and H on polycrystalline and single-crystal samples, five spin-glass transitions were discovered below 300 K. The signatures of all these transitions were also shown to be present in the temperature dependence of the integrated intensities of the Bragg and satellite peaks in single-crystal neutron diffraction patterns with characteristics diminution of intensities around the spin-glass transition temperatures. These studies confirmed the coexistence of spin-glass and long-range ordered (LRO) ferrimagnetic phases of $BaFe_{12}O_{19}$ for all the five transitions. Although multiple magnetic transitions have been observed in several systems with competing interactions, there is no report of as many as five spin-glass transitions in any homogeneous system with or without frozen-in disorder. This shows the complexity and richness of the magnetic phase diagram of $BaFe_{12}O_{19}$.

(5) Of the five spin-glass transitions, four were shown to be associated with the successive freezing of some part of either the transverse or the longitudinal component of the magnetic spins while the fifth spin-glass transition was shown to be linked with the precession dynamics of the magnetic moments involved in the longitudinal conical

magnetic order. The conical modulation associated with the two longitudinal spin-glass phases was shown to be commensurate while the spin-glass phases associated with the transverse freezing of the spins as well as the precession dynamics of the magnetic moments were shown to be linked with incommensurate longitudinal conical modulation. Theoretical insight is required to understand as to why the nature longitudinal conical modulation changes from incommensurate to commensurate and vice-versa.

(6) The genesis of the spin-glass phases in $BaFe_{12}O_{19}$ was shown to be emergence of kagome spin configurations at low temperatures. Along with the geometrical frustration, evidence was also presented for the presence of significant magnetoelastic strains below 175 K, which may provide the much-needed randomness in the few body exchange interactions for the occurrence of a spin-glass transition in an ordered compound, as per the existing theoretical models. In analogy with the transverse and longitudinal spin-glass freezing in disordered Heisenberg systems, the role of single ion anisotropy and temperature dependent change in exchange anisotropy was discussed as the possible reason for the occurrence of the two rounds of longitudinal and transverse spin-glass freezing.

(7) The existence of the electric dipole liquid phase of $BaFe_{12}O_{19}$ was confirmed by specific heat studies under various magnetic fields. It was shown for the first time that the non-Debye part of the specific heat varies linearly with temperature and is independent of magnetic field for temperatures below 3 K.

(8) By applying chemical pressure, a quantum electric dipole glass phase was discovered in the $(Ba_{1-x}Ca_x)Fe_{12}O_{19}$ system whose T_c varies as $(x - x_c)^{1/2}$, where x_c is the composition for the quantum critical point (QCP). It was shown that $BaFe_{12}O_{19}$ is not at its QCP but is very close to it. To reach the QCP of $BaFe_{12}O_{19}$, it was argued that a negative pressure is required either chemically or by applying tensile stress.

10.2 Suggestions for Future work.

The discovery of five spin-glass phases in coexistence with the LRO ferrimagnetic phase during the present work opens several possibilities for future theoretical and experimental investigations and we outline a few of them below:

(1) For the concentrated disordered Heisenberg systems near the percolation threshold composition, a succession of two spin-glass transitions involving longitudinal and transverse freezing in coexistence with the LRO phase has been theoretically predicted for small values of single-ion anisotropy or exchange anisotropy. Our results mimic the predictions for small negative single-ion anisotropy for the first set of longitudinal and transverse spin-glass transitions from the high temperature side. There is, however, no theory that predicts four spin-glass transitions involving longitudinal and transverse components of spins in a 3D Heisenberg system with or without substitutional disorder. Further, the existing theories of spin-glass transition in geometrically frustrated systems are not applicable to $BaFe_{12}O_{19}$, as the geometrical frustration emerges in a LRO phase as a function of temperature unlike the case of other ordered compounds where the geometrical frustration pre-exists in the paramagnetic phase due to the geometry of the lattice. We hope that our results would encourage theorists to revisit the existing theories of spin-glass transition in ordered systems to account for multiple spin-glass transitions as a result of emergent kagome spin configuration in the presence of magnetoelastic strains as a function of temperature in LRO systems like $BaFe_{12}O_{19}$.

(2) The discovery of the fifth spin-glass transition, linked with the precession dynamics and conical modulation of the spins in $BaFe_{12}O_{19}$, calls for similar studies on other multiferroic hexaferrites showing longitudinal conical magnetic structure.

(3) The observation of anomaly in C_P/T versus T^2 and C_P/T^3 versus T plots around the five spin-glass transitions suggests the presence of new excitations in $BaFe_{12}O_{19}$ which requires further investigation using Raman and inelastic neutron scattering studies.

(4) Effect of transverse magnetic field and magnetoelectric response of $BaFe_{12}O_{19}$ under such a field needs to be investigated in a future work.

(5) The spin-glass phases of $BaFe_{12}O_{19}$ show phenomenological similarities with conventional spin/cluster glass transitions in disordered systems, except for the unusually low value of $z\nu$. It swould be of great interest to undertaken a systematic test of static and dynamic scaling in $BaFe_{12}O_{19}$, in a manner similar to that reported in conventional spin glasses, but with different exponents.