Dedicated to my late parent's memory that always encouraged me to follow my dreams and be consistent with them.

CERTIFICATE

It is certified that the work contained in the thesis entitled **"*NONCOLLINEAR MAGNETIC MATERIALS FOR ENERGY-EFFICIENT DATA STORAGE DEVICES*"** by **"*SHYAM BABU*"**, Roll Number **16111010**, has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy, and SOTA for the award of Ph.D. Degree.

Date: 15/06/2021
Place: Varanasi

Dr. Shrawan Kumar Mishra
(Supervisor)

Declaration

I, "***SHYAM BABU***", certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of "***Dr. SHRAWAN KUMAR MISHRA***" from "***JULY 2016***" to "***MAY 2021***" at the "***SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY***", Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research scholars/scientists wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any others' work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

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List of Abbreviations

SFO	$SmFeO_3$
SFMO	$SmFeMnO_3$
XRD	X- ray Diffraction
PXRD	Powder X-ray Diffraction JCPDS
JCPDS	Joint committee on powder diffraction standards
TEM	Transmission Electron Microscopy
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
MPMS	Magnetic Property Measurement System
PPMS	Physical Property Measurement System
SQUID	Superconducting Quantum Interfaces Devices
AF	Antiferromagnetic
EDX	Energy Dispersive X-ray spectroscopy
FWHM	Full Width Half Maximum
SANS	Small Angle Neutron Scattering
DMI	Dzyaloshinskii-Moriya interaction
ac	Alternating Current
dc	Direct Current
ZFC/FC	Zero Field Cooling/Field Cooling
AF	Antiferromagnetic
FM	Ferromagnetic
FE	Ferroelectric

List of Symbols

S	Total spin angular momentum
α	Helimagnetic angle
θ	Bragg's angle
β	Full-width half maxima
L	Total orbital angular momentum
J	Total angular momentum
μ	Magnetic permeability
μ_B	Bohr magneton
μ_{eff}	Effective magnetic moment
H	Magnetic field intensity
H_C	Coercivity
M	Magnetization
M_r	Remnant magnetization
T	Temperature
$\mathbf{H}$	Hamiltonian for triangular-lattice
χ	Magnetic susceptibility
χ_{dc}	dc magnetic susceptibility
χ_{ac}	ac magnetic susceptibility
$\chi^{''}$	The imaginary part of magnetic susceptibility
$\chi^{'}$	The real part of magnetic susceptibility
μ_0	The magnetic permeability of free space
T_{SR}	Spin reorientation temperature

T_C	Curie temperature
T_N	Neel temperature
θ_P	Curie-Weiss temperature
P	Polarization
λ	Wavelength
θ_i	Incidence or local incidence angle
$^\circ\mathbf{C}$	Degree celsius
(hkl)	Miller index
d	Lattice spacing
a, b, c	Lattice parameters

Preface

Nature has given us abundant materials with multiple structures, where spin phases have been playing a vital role in spintronic devices. Recently, it has been noted that not only from typical collinear spin materials such as collinear ferromagnets and collinear antiferromagnetically coupled materials, noncollinear spintronic materials are the new hot spots of research owing to their exotic physical phenomena. In this thesis, firstly, the introduction of three different types of noncollinear spin structures, that is, the helical spin structure that offers helical spin phases and the coplanar noncollinear spin structure that could yield momentum-space Berry phases, and then move to relevant physical phenomena, including the topological Hall effect, anomalous Hall effect, multiferroic, spin-polarised current, and spin Hall effect. Afterwards, this thesis summarises and elaborate on the magnetic-field control of the noncollinear spin structure and related physical effects, which could enable ultra-low power spintronic devices.

This thesis presents experimental investigations on $NiBr_2$, Cd-Cu_2OSeO_3, and Mn-doped $SmFeO_3$ single crystals by dc magnetisation, ac susceptibility, small-angle neutron scattering (SANS) measurements along with X-ray absorption spectroscopy (XAS). The main focus is on $NiBr_2$; CSO and SFMO are toward spin reorientation from commensurate to incommensurate magnetic structure and weak ferromagnetic to compensated antiferromagnetic, respectively, at low temperatures, which have immense scientific and technological implications for next-generation energy-efficient magnetic data storage devices.

The thesis consists of the following chapters:

- **Chapter 1:** presents a literature survey of the existing work related to the formation of a helical ground state, formation of complex magnetic structures: multi-q states and magnetic skyrmions and their experimental and theoretical realization.

- **Chapter 2:** describes the experimental techniques, structure, morphology, and composition employed in this work. Introduction of dc magnetisation and ac magnetic susceptibility measurements using a Superconducting Quantum Interference Device (SQUID), Small-Angle Neutron Scattering (SANS), and X-ray absorption spectroscopy (XAS) are presented.

- **Chapter 3:** presents magnetometry to study the low-temperature magnetic phase diagram of $NiBr_2$ single crystals in the vicinity of T_{IC} = 23 K and around the incommensurate phase. By covering a field range from 0.1 T to 3 T, the ac susceptibility reveals the characteristic relaxation associated with the transitions between the collinear and noncollinear phases, which shows the signature of the field-induced helimagnetic transition. The nature of field-induced transition and microscopic features were analysed in Chapter 5, with a broad range of magnetic fields and small-angle neutron scattering experiments.

- **Chapter 4:** represents the extended range of ac & dc magnetometry with the applied magnetic field (1 -14 T) in a-b basal plane and out of the plane, complemented by SANS. The results demonstrate a clear view of the magnetic-field-induced non-collinear to collinear spin transition in the triangular spin-lattice of helimagnet $NiBr_2$ single crystals. Our experimental outcomes are closely related to Okubo *et al.* (PRL 108, 017206 (2012)), where the formation of multi-q states and the skyrmions phase for a triangular spin-lattice has been suggested. This study searched for these states in $NiBr_2$ single crystals, but could not find any signature of the skrmionic phase in the $NiBr_2$ single crystal. Instead, a typical degeneracy occupation of the equivalent wave vector for the incommensurate state was detected.

- **Chapter 5:** In this chapter, the structural, electronic, and magnetic properties of Cd-doped Cu_2OSeO_3 nanocrystallites are described. In addition, cost-effective and fast synthesis of Cu_2OSeO_3 nanocrystallites with sizes ranges over 50-200 nm. The physical significance of Cd doping on the Cu_2OSeO_3 skyrmions will carry significant technological importance, as doping-induced chemical pressure can be used to tune and control the skyrmionic phases and their various physical properties.

- **Chapter 6:** presents the influence of Mn-doping on structural and magnetic properties of canted antiferromagnet $SmFeO_3$ single crystals obtained by optical float zone technique. SQUID magnetometry was performed in the temperature range from 5 to 400 K. The results reveal a new spin reorientation from the weak ferromagnetic state to the compensated antiferromagnetic state at nearly 180 K, which is missing in the parent compound for magnetic fields applied along with the different crystallographic directions due to Mn doping. Variations in the coercive field indicate the emergence of the exchange bias phenomenon at low temperatures. The microscopic origin of spin reorientations remains unclear.

• **Chapter 7:** Finally, in this chapter, concluding remarks are presented on the basis of the experimental findings and theoretical interpretation obtained in all the single crystal and nanocrystallite samples that are addressed in the thesis.