Chapter 4

Field-dependent competing magnetic ordering in multiferroic Ni$_3$V$_2$O$_8$

Abstract

Ni$_3$V$_2$O$_8$ (NVO) is a special type of spin frustrated Kagomé staircase magnetic lattice where full frustration of a conventional Kagomé lattice is partially relieved. Below 10 K NVO undergoes a series of competing magnetic ordering. Most importantly, NVO simultaneously develops ferroelectricity and incommensurate magnetic order caused by spin frustration which demonstrates that the two order parameters are strongly coupled. In this chapter we present an extensive thermodynamic, dielectric and magnetic study on polycrystalline samples of this novel multiferroic compound. The temperature and magnetic field dependent dielectric studies quantitatively estimate the strength of magnetoelectric coupling and investigate the possibility of another ferroelectric phase at 2 K in this improper multiferroic material. Specific heat measurement down to 1.8 K under magnetic field upto 14 T clearly identify the development of a new magnetic field induced phase transition below 2 K that also shows signatures of simultaneous electric ordering.
4.1 Introduction

Magnetic materials in which the constituent magnetic moments reside on networks of triangles and tetrahedra have been of great interest due to their propensity for exotic ground states as a consequence of geometrical frustration. Because of clearly defined geometry, frustrated low spin magnets form the group of ideal model systems to study the competing phases. A large number of different ground states have been discovered, such as 'spin glass', 'spin ice', and numerous spin liquid like states [1, 2]. Recently, geometrically frustrated magnetic systems have gained greater interest as new exciting materials, because of the coupling of the magnetic order with the ferroelectric properties [3, 4]. Examples include $M_3V_2O_8$ ($M = Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}$ and $Mg^{2+}$), $SrCr_9Ga_4O_{19}, Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ etc. [5, 6, 7]. These materials are unique in a way that they allow the study of a spin system which remains magnetically disordered when cooled well below the ordering temperature.

4.1-1 Crystal structure of NVO

Structurally Ni$_3$V$_2$O$_8$ belongs to a special class of orthorhombic compounds with general chemical formula $M_3V_2O_8$ and space group $Cmca$ [8, 9, 10, 11, 12, 13]. This group of compounds show rich variety of unusual magnetic and structural phases that are stabilized under different conditions. NVO is an insulating system with Ni$^{2+}$ ions ($d^8$, S=1) arranged in a Kagomé staircase or in a buckled Kagomé plane.

Figure 4.1: A two dimensional schematic picture of the corner shared triangular Kagomé lattice. Here spine sites (Ni$_{sp}$) are shown in blue and cross tie sites (Ni$_{ct}$) in cyan.
An ideal Kagome lattice (shown in Fig. 4.1) is comprised of a two-dimensional (2D) network of corner-sharing triangles of spins with antiferromagnetic coupling between nearest neighbours. Several realizations of magnetic moments on stacked Kagome lattices with varying degrees of crystalline order have been extensively studied.

NVO is particularly interesting magnetic material, because it contains weakly coupled Kagome staircase planes. It is thus a variant of the highly frustrated pure Kagome lattice. However the frustration of the underlying Kagome lattice relieves because of deviation from ideal Kagome geometry [14, 15]. Another striking feature of NVO is coupled magnetic and electric degrees of freedom and occurrence of various magnetic and electric phases as a function of temperature, and magnetic field [16]. Substantial coupling between different order parameters (spin, lattice and charge) in frustrated NVO results in multiple coupled magnetic and dielectric transitions [17, 18].

A unit cell of NVO contains four formula units and two Kagome layers of Ni$^{2+}$. Figure 4.2(a) illustrates the crystal structure of NVO having stacked Kagome staircase structure. In NVO, there are two crystallographically inequivalent magnetic sites, known as spine (Ni$_S$) and cross ties (Ni$_C$) in the Kagome plane. The Ni$_S$ centers form chains that run along the $a$ direction and are connected by Ni$_C$ sites in the $c$ direction, forming Ni$_C$-Ni$_S$-Ni$_C$ isosceles triangles (shown in Fig. 4.2(b)). Their Kagome layers are buckled and composed of edge-sharing Ni$^{2+}$O$_6$ octahedra lying in the $ac$ plane. These layers are separated by nonmagnetic V$^{5+}$O$_4$ tetrahedra in $b$ direction. The buckled Kagome layers are perpendicular to the orthorhombic $b$ axis and form stacked Kagome staircase structure. The nonmagnetic V$^{5+}$O$_4$ ($d^9$) tetrahedra provide isolation between the magnetic Ni-O layers.

Figure 4.1 shows the projection of this layer of Kagome staircase onto the $ac$ plane. The ratio of the Ni$_C$-Ni$_C$ (2.97 Å) and Ni$_S$-Ni$_C$ (2.94 Å) bond distances is $\sim 1.01$. Therefore the super exchange interaction between Ni$_S$ and Ni$_C$ sites ($J_{SC}$), and between two adjacent spine sites ($J_{SS}$) is of slightly different strength [20]. Also Ni$^{2+}$-Ni$^{2+}$ distance within the layers is $d_1 = 2.94$ Å, while the interlayer distance is $d_2 = 5.69$ Å. It provides interlayer to intralayer ratio, $d_2 / d_1 = 1.9$ which is large and a strong two dimensional magnetic character is observed in this compound [14]. So these properties provide an interesting and unique opportunity to investigate the thermodynamic, magnetic and dielectric behaviour of this two-dimensional
spin system at low temperatures because of inherent geometrical frustration present in the crystal structure.

Figure 4.2: (a) Crystal structure of Ni$_3$V$_2$O$_8$ showing spin-1 Ni$^{2+}$ spine sites in blue and cross tie sites in cyan. Competing interaction between spine and cross tie Ni$^{2+}$ and anisotropies yield a complex magnetic structure in NVO. (b) The two different Ni$^{2+}$ sites (spine and cross tie) are arranged in Kagomé-staircase structure.

4.1-2 Magnetic phase diagram

The magnetic field temperature (H-T) phase diagram of NVO has been studied from combined thermodynamic [15, 18, 21, 23], magnetic [15, 18, 22, 23, 24], neutron scattering [14, 15, 18, 20], optical [19], and dielectric measurements [18, 19]. Anisotropic magnetic structure of NVO generates competing nearest and next nearest neighbour interaction along the spines and several other weak magnetic interactions between cross ties. All these interactions yield a rich anisotropic H-T phase diagram and NVO shows an amplitude-modulated high temperature incommensurate phase and a helical low temperature incommensurate phase as temperature goes below 10 K. In NVO there is no electric and magnetic long range order above 10 K when it is in paramagnetic state. H-T phase diagram for NVO determined for the magnetic field applied along the $a$ and $c$ axis are shown in Fig 4.3 depicts that NVO
adopts at least four different magnetic phases below 10 K [18]. Three of the phase transitions at $T = 9.3, 6.4$ and $2.8 \, \text{K}$ are second order and the fourth one at $T = 4.0 \, \text{K}$ is first order phase transition [15, 18].

Figure 4.3: (a) Phase diagram for $\text{Ni}_3\text{V}_2\text{O}_8$ determined for the magnetic field $H$ applied along the $a$ axis. (b) Phase diagram for magnetic field $H$ along $c$ axis [18].

Brief description of these magnetic phases are as below:

1. **High temperature incommensurate (HTI) phase**: When $T$ is lowered through the value $T_{PH} \approx 9.1 \, \text{K}$, a longitudinal incommensurate phase appears in which the Ni spins on the spine chains are oriented along the $x$ axis with an amplitude modulation whose wave-vector lies along $a$ axis (shown in Fig 4.4 I).

2. **Low temperature incommensurate (LTI) phase**: As the temperature is further lowered through the value $T_{HL} \approx 6.3 \, \text{K}$, transverse order appears at the same incommensurate wave-vector on the cross-tie sites. Within the experimental uncertainty, HTI and LTI ordering transitions are continuous. The development of spontaneous ferroelectric polarization in LTI phase along $b$ axis is the most striking feature of this phase diagram (shown in Fig 4.4 II).

3. **Two commensurate ($C$, $C'$) phases**: As the temperature is lowered through the value $T_{LC} \approx 4 \, \text{K}$, two slightly different discontinuous transitions occur in which commensurate antiferromagnetic phase appears. In this phase, antiferromagnetism results
from the arrangement of spins within the unit cell in such a way that the magnetic unit cell remains identical to the paramagnetic unit cell (shown in Fig 4.4 III).

Figure 4.4: Simplified schematic representation of spin arrangement in the antiferromagnetic HTI, LTI, and CAF phases. Indicates the direction of uniform magnetization distributed over spine and cross tie sites in the CAF phase [15].

From H-T phase diagram it is clear that magnetic field along the c axis favours the C phase whereas field along a destroys the C phase and promotes the LTI phase. The transitions corresponding to HTI, LTI and C' are second ordered whereas C is first order phase transition. In all the H-T phase diagram studies, P-HTI and HTI-LTI phase boundaries are relatively insensitive to small applied magnetic fields. These phase boundaries are nearly constant in temperature as a function of magnetic field. Even for 10 T of applied magnetic fields a shift of less than 0.2 K is observed.

4.1-3 Motivation

The magnetic structure of low temperature commensurate phase (C'), which exists for $T < 2.3$ K, appears to be more complex and is not yet completely resolved. The field dependent neutron diffraction experiments clearly observe some ambiguity corresponding to this phase [14]. High field ($\mu_0 H = 10$ T) optical measurements on NVO indicate the presence of another additional phase below 2 K [25]. The presence of this new phase also got support from
4.2 Experimental Section

4.2-1 Sample preparation

Polycrystalline sample of NVO was prepared by using solid state reaction technique at ambient pressure. The high purity nickel oxide (NiO) and vanadium oxide (V$_2$O$_5$) were used as starting materials. The reagents were mixed thoroughly in stoichiometric proportion according to the equation shown below and made in pellet form of 10 mm diameter. The pellets were kept in high purity alumina (Al$_2$O$_3$) crucibles and heated in a horizontal tube furnace. The chemical reaction involved in this process is as follows:

$$3\text{NiO} + \text{V}_2\text{O}_5 \rightarrow \text{Ni}_3\text{V}_2\text{O}_8$$

The furnace was heated to 800 °C at the rate of 4 °C/min and held at 800 °C for 16 hours. To ensure the homogeneity and density of the pellets, the sintered pellets were crushed to powder form and ground for at least 2 hours. These powders were again made into pellets form and reheated at 800 °C for 16 hours. The furnace was cooled to 300 °C at the rate of 5 °C/hour, and then cooled to room temperature by switching off the furnace.

4.2-2 Measurement techniques

The sample was characterised using X-ray powder diffraction (XRD) by BRUKER D-8 advanced diffractometer with Cu K$\alpha$ ($\lambda = 1.5418$ Å) radiation. The diffraction pattern was measured in $\Theta$/2$\Theta$ scanning mode in the angle range 10-70° with a step of 0.02°. Composition analysis was performed using an energy dispersive X-ray spectroscopy (EDAX). The
4.3 Result and discussion

4.3-1 X-ray diffraction (XRD) and EDAX studies

Figure 4.5 shows the observed XRD pattern where all the major peaks of Ni$_3$V$_2$O$_8$ are identified and indexed. The sample exhibits a single phase orthorhombic structure with space group $Cmca$. The lattice parameters for Ni$_3$V$_2$O$_8$ are calculated to be $a = 5.917$ Å, $b = 11.365$ Å and $c = 8.289$ Å. These values are in close agreement with previously reported data [14, 15, 16].

EDAX spectrum shown in Fig. 4.6 confirms that there is no other metal element except Ni and V. Within the experimental error, the molar ratio of Ni:V:O is approximated to be 3:2:8, which is in general agreement with the chemical formula of Ni$_3$V$_2$O$_8$. 

Figure 4.5: Room temperature X-ray diffraction pattern of Ni$_3$V$_2$O$_8$ that establish orthorhombic crystal structure with space group $Cmca$. 

EDAX spectrum shown in Fig. 4.6 confirms that there is no other metal element except Ni and V. Within the experimental error, the molar ratio of Ni:V:O is approximated to be 3:2:8, which is in general agreement with the chemical formula of Ni$_3$V$_2$O$_8$. 

real ($\varepsilon$) and imaginary part ($\tan\delta$) of dielectric constant was measured with QUADTECH 1920 precision LCR meter. The dielectric measurements were performed in an 8 T cryogen free magnet system with an attached variable temperature insert. The DC magnetization was measured in temperature range of 2 to 300 K in presence of 1000 Oe magnetic field using commercial SQUID. The heat capacity of 15 mg polycrystalline sample was measured in the temperatures below 15 K, and magnetic fields upto 14 T by means of the relaxation method, using the heat capacity option of the commercial PPMS.
4.3-2 Magnetic Measurement:

The magnetic susceptibility ($\chi$) as a function of temperature at 1000 Oe for NVO is shown in the Fig. 4.7.

A broad maxima at around 3.7 K is suggestive of antiferromagnetic ordering. The in-
verse susceptibility \((1/\chi)\) versus temperature data is shown in the inset of Fig. 4.7. The high temperature \(1/\chi\) data were fitted with the Curie-Weiss law in the temperature range of 10 to 50 K. The high temperature data show excellent linearity, and departure from linearity could be observed around \(\sim 10\) K. The extrapolated Curie-Weiss fit to the \(1/\chi\) data yielded an intercept on negative \(x\) axis at \(\Theta_{CW} \sim -11\) K. The negative value of \(\Theta_{CW}\) indicates dominant role of antiferromagnetic interaction between Ni\(^{2+}\) spins amongst all other competing interactions. From magnetization measurement on single crystal NVO, a first order magnetic transition is observed across the low temperature incommensurate to canted antiferromagnetic phase boundary (\(\sim 4\) K), where strong anisotropic features set in [18]. It is understood that the antiferromagnetic alignment occurs along the \(a\) axis with canting towards the \(c\) axis. This canting leads to a sharp increase in magnetization along the \(c\) axis. At \(\sim 2.8\) K the magnetic state crosses over to the second canted antiferromagnetic phase with different anisotropies. This is indicated as a downturn in overall magnetization in our polycrystalline data. The canting along the \(c\) axis also gives rise to substantial hysteresis at 2 K as observed in Fig. 4.8. At 5 K, above the CAF phase, no hysteresis is observed in the incommensurate phase.

![Figure 4.8](image)

Figure 4.8: Magnetization is plotted as a function of magnetic field at \(T = 2\) K. The inset shows the M-H plot at 5 K that does not show hysteresis.
Dielectric measurements on NVO show evidence for dielectric anomalies associated with the magnetic phase transitions. Figure 4.9 shows the dielectric constant as a function of temperature measured on sintered NVO pellets of diameter 10 mm. This data were collected at $f = 5$ kHz, but measurements at different frequencies showed qualitatively similar effects with no measurable change in transition temperature. A peak in the dielectric constant at $T_{HL} = 6.9$ K indicates the onset of ferroelectric order corresponding to the onset of low temperature incommensurate phase. In the inset of Fig. 4.9, dielectric constant in zero field and in the presence of 3 T magnetic field at $f = 5$ kHz are shown.

![Dielectric Constant vs Temperature](image)

Figure 4.9: Temperature dependence of the dielectric constant measured at 5 kHz (■) is shown. The large peak in the dielectric constant at $T_{HL} = 6.4$ K shows the onset of ferroelectric order in NVO. Below 2.1 K there is also a large anomaly in $\varepsilon$ suggesting the possibility of another ferroelectric phase. Inset shows magnetoelectric coupling in NVO done at $\mu_0 H = 0$ (▲) and 3 T (●) magnetic field at $f = 5$ kHz.

The temperature and field dependence of the dielectric constant strongly suggests that there is significant spin-charge coupling present in NVO. In the presence of magnetic field, the peak in the dielectric constant becomes sharper as compared to zero field. This clearly shows NVO has a spontaneous ferroelectric polarization induced by the incommensurate magnetic ordering, which is intimately coupled to the magnetic behaviour. So dielectric
measurement gives another proof (other than neutron diffraction experiment) of magneto-electric coupling in this geometrically frustrated phase. The calculated magnetocapacitance \( ((\varepsilon(H,T)-\varepsilon(H=0,T))/\varepsilon(H=0,T)) \times 100 \) is about 0.3 which is small as compared to other frustrated magnetic systems such as orthorhombic HoMnO₃ and YMnO₃ [25]. We note that the degree of frustration which is quantified as \( f = \Theta_{CW}/T_H \) (\( \Theta_{CW} \) being the Curie-Weiss intercept and \( T_H \), the magnetic ordering temperature) for Ni₃V₂O₈ is \( \sim 3.1 \) which is large as compared to orthorhombic YMnO₃ (\( \sim 1.27 \)) and HoMnO₃ (\( \sim 0.5 \)). In the case of YMnO₃ the dielectric constant is decreased by 2% and in the case of HoMnO₃ this decrease is 8% in the presence of 7 T magnetic field [25]. While a microscopic understanding on this would need detailed study of the magnetic structure of each of these materials, we can qualitatively observe that the degree of frustration is inversely proportional to the magnetodielectric effect. Most importantly, we find that there is clear evidence of the onset of another electric ordering below \( \sim 2 \) K. It was suggested that only the LTI phase is ferroelectric so the origin of the possible second ferroelectric transition in the low temperature antiferromagnetic phase (C) needs to be assessed [18, 16].

![Graph showing frequency and temperature dependence of dielectric constant (ε). At all the measured frequencies both the anomalies at \( T_{HL} = 6.4 \) and \( T \sim 2 \) K are evident and reproducible. As we increase the frequency the magnitude of anomaly in \( ε \) decreases.](image)

Figure 4.10: Frequency and temperature dependence of dielectric constant (\( ε \)). At all the measured frequencies both the anomalies at \( T_{HL} = 6.4 \) and \( T \sim 2 \) K are evident and reproducible. As we increase the frequency the magnitude of anomaly in \( ε \) decreases.

We have done the zero field dielectric measurements at different frequencies and the increase in dielectric constant at lower temperature (below 2.3 K) is consistent and reproducible. The dielectric constant measured at 1, 3, and 5 kHz are shown in the Fig. 4.10.
The magnitude of this dielectric constant increases as the measuring frequency is reduced from 5 to 1 kHz. This is possibly related with the presence of some slow dynamics of Ni spins near the transition temperature. The dielectric anomaly present at \( \sim 2 \) K persists down to 1.6 K which is the lowest temperature in our measurement and gives an indication of long range electrical correlation at low temperatures. So all these frequency dependence of dielectric constant can be correlated with the formation of multiple multiferroic domains at low temperatures.

### 4.3-4 Specific heat measurement

The low temperature heat capacity data for NVO as function of temperature and magnetic field is shown in different panels of Fig. 4.11. The zero field specific heat, \( C/T \) versus \( T \) is shown in the first panel. Four peaks at 9.3, 6.4, 4.0 and 2.8 K are observed corresponding to magnetic phase transitions. From Neutron diffraction experiments it is well established that these four anomalies in the specific heat data correspond to four different complex spin arrangements of spine and cross tie magnetic Ni\(^{2+}\) atoms. Both the phases at 9.3 and 6.4 K are in incommensurate state. At \( T_{PH} = 9.3 \) K, the NVO goes from paramagnetic state to HTI phase and at \( T_{HL} = 6.4 \) K, NVO magnetic structure changes from HTI to LTI. The distinct peak at \( T = 4.0 \) K (\( T_{LC} \)) corresponds to the magnetic phase transition from an incommensurate to canted antiferromagnetic phase (CAF). The LTI phase which lies in between the temperature range 6.4 and 4 K is the most remarkable phase of NVO where ferroelectric phase along with field dependent dielectric polarization appears. This is well supported by our magnetodielectric measurements. Neutron diffraction experiments as well as theoretical calculations proved that the rotation of spine and cross tie spins within the \( ab \) plane leads to this unusual phase. Our zero field specific heat data strongly suggests that below \( T_{LC} \) there are two commensurate phases \( C \) and \( C' \). The temperature corresponding to these commensurate phases are \( T_{LC} = 4 \) K and \( T_{CC'} = 2.8 \) K. The microscopic arrangement of Ni\(_S\) and Ni\(_C\) below \( T_{CC'} = 2.8 \) K is not yet completely resolved. Neutron diffraction and optical measurements give rise to some indication towards presence of another new magnetic phase.
Figure 4.11: Low temperature specific heat of NVO at $H = 0, 1, 9,$ and $14$ T magnetic fields. In zero field measurement four sharp peaks are observed at 2.6, 4.0, 6.4, and $9.3$ K. At $H = 1$ T and $H = 9$ T, the emergence of a field induced phase is observed (marked by an arrow).

Comparing the separation of $T_{PH} - T_{HL}, T_{HL} - T_{LC}$ and $T_{LC} - T_{CC'}$, the separation of $T_{LC} - T_{CC'}$ is the smallest, which imply that NVO crystal structure consists of two kinds of magnetic Ni$^{2+}$ ions. So our specific heat measurement gives indirect proof for the presence of cross tie Ni$^{2+}$ and spine Ni$^{2+}$, and the number of spine sites is twice that of cross sites. The Ni$^{2+}$ ions are coupled antiferromagnetically with each other and hence produce zero mean field on Ni$^{2+}$ which leads to weakly coupled two subsystems of Ni$^{2+}_C$ and Ni$^{2+}_S$ in the absence of magnetic field. In the temperature region, $T_{CC'} < T < T_{LC}$ the subsystem of Ni$^{2+}_C$ primarily constitutes the commensurate low temperature phase and the Ni$^{2+}_S$ ions begin to transit to this phase at $T_{CC'}$. It is expected that these transitions will merge together when one switches on the magnetic field. This hypothesis appears to be true in our field.
dependent specific heat data shown in different panels for $\mu_0H = 1, 9$ and $14$ T. All the peaks at $T_{CC'}, T_{LC}, T_{HL}$, and $T_{PH}$ broaden when 1 T magnetic field is switched on but no significant change is observed in any of the transition temperatures. The two peaks, $T_{CC'}$ and $T_{LC}$, in the lower temperature region merge together when higher magnetic fields of 9 T and 14 T are applied. It is to be noted that broadening of the other two peaks, $T_{HL}$ and $T_{PH}$, in the higher temperature side increases and the peak position shifts toward the lower temperature side. At 14 T only one peak remains and all other peaks vanish.

We calculated the entropy of the system by integrating the $C/T$ versus $T$ plots up to 13 K. For 0 T, the entropy calculated for the NVO system is 6.10 J/mol-K. This value is approximately equal to 67 % of the value expected for spin-1 systems. As we apply the magnetic field, the entropy of the system decreases quite consistently. The values of the calculated entropy after the application of 1 T, 9 T, and 14 T magnetic fields in the temperature range 0 to 13 K are 6.03, 5.47, and 5.10 J/mol-K. Further we observe the emergence of a low temperature field induced phase for $\mu_0H = 1$ T and 9 T below 2 K that disappears both at 0 T and 14 T. Because of the temperature limitation of the measurement system, we could not access further low temperature and this low temperature peak is not fully developed but its onset is effectively established. This is also indicated in the dielectric data shown in Fig. 4.9 and Fig. 4.10. This result gives thermodynamic credence to what was reported from theoretical calculations and optical measurements [10].

4.4 Conclusion

High quality polycrystalline samples of the Kagomé staircase lattice $\text{Ni}_3\text{V}_2\text{O}_8$ was prepared by solid state reaction method. The magnetic measurements reveal short range ferromagnetic correlations below $T_{CC'}$ corresponding to canted antiferromagnetic phases. Field dependent heat capacity clearly establishes the merging of two peaks corresponding to two canted antiferromagnetic phases ($C$ and $C'$) below 4 K. Most importantly, the onset of a new low temperature ($< 2$ K) field induced phase that is accompanied by simultaneous development of a robust electric ordering is observed. In essence evidence of a re-entrant multiferroic phase in this magnetically rich frustrated spin system is provided.
References


