Field-dependent competing magnetic ordering in multiferroic \( \text{Ni}_3\text{V}_2\text{O}_8 \)

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Abstract – The geometrically frustrated magnet \( \text{Ni}_3\text{V}_2\text{O}_8 \) undergoes a series of competing magnetic ordering at low temperatures. Most importantly, one of the incommensurate phases has been reported to develop a ferroelectric correlation caused by spin frustration. Here we report an extensive thermodynamic, dielectric and magnetic study on clean polycrystalline samples of this novel multiferroic compound. Our low-temperature specific heat data at high fields up to 14 Tesla clearly identify the development of a new magnetic-field–induced phase transition below 2 K that shows signatures of simultaneous electric ordering. We also report temperature- and field-dependent dielectric constant that enables us to quantitatively estimate the strength of magnetoelectric coupling in this improper ferroelectric material.

Introduction. – Multiferroic materials exhibit juxtaposition of electric and magnetic ordered phases and thus give rise to the long cherished possibility of switching electric polarization by application of magnetic field and magnetization by electric field. This has formed the basis of many of the futuristic device propositions based on electric control of spin-polarized current- and voltage-controlled magnetic-storage media [1–4]. While the subject is old, the current excitement stems from two recent developments: the discovery of improper ferroelectricity in geometrically frustrated magnetic systems [5–7] and a better understanding on the microscopic origin of multiferroicity in BiFeO\( _3 \) and YMnO\( _3 \) [8,9]. In this paper we report an extensive thermodynamic, magnetic and dielectric study of one of the keenly studied multiferroic of recent times; the geometrically frustrated system of \( \text{Ni}_3\text{V}_2\text{O}_8 \) (NVO). The magnetic field-temperature (\( H-T \)) phase diagram of NVO has been studied from combined thermodynamic \([10,11]\), magnetic \([10–14]\), neutron scattering \([10,11,15]\), optical \([15]\), and dielectric \([16,17]\) measurements. The consensus is that at low temperature NVO undergoes at least four distinct magnetic-phase transitions below 12 K, above which a robust paramagnetic phase dominates. These phases are the i) high-temperature incommensurate phase (HTI), ii) low-temperature incommensurate phase (LTI), and iii) two canted antiferromagnetic phases (C and C’). There have been some reports indicating a possibility of a fifth magnetic-field–induced phase at temperature below 2.5 K from optical measurements \([18,19]\). However, these were open to interpretation as no thermodynamic features were confirmed. In this letter we present the synthesis and characterization of phase pure polycrystalline \( \text{Ni}_3\text{V}_2\text{O}_8 \) samples prepared by solid-state reaction processing. The specific-heat data below ~2 K in the presence of magnetic field unambiguously shows the onset of a new magnetic-field–induced phase that exhibits clear signatures of a robust electric correlation.

Structurally NVO belongs to the compounds with general chemical formula \( \text{M}_3\text{V}_2\text{O}_8 \) (\( \text{M}=\text{Ni}^{2+}, \text{Co}^{2+}, \text{Zn}^{2+}, \text{and Cu}^{2+} \)) \([12–14,20–22]\). Some of these materials are characterised by triangular lattices and short-range antiferromagnetic interactions as is the case with NVO \([23,24]\). Here the magnetic lattice is based on a staircase Kagomé net where magnetic Ni\(^{2+} \) (\( S=1,d^8 \)) is arranged anisotropically (fig. 1a). The planes that contain the edge-sharing NiO\(_6 \) octahedra are not flat (as in a regular Kagomé lattice) but buckled forming a staircase-like structure. These magnetic layers are separated by non-magnetic VO\(_4 \) tetrahedra. As a consequence

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the geometric frustration is reduced allowing long-range magnetic order. As elucidated in fig 1(a), there are two crystallographically inequivalent magnetic sites $N_{c}$ (cross tie) and $N_{s}$ (spine) in the Kagomé plane. The isosceles triangles are formed by $N_{c}$-$N_{c}$-$N_{c}$ and the ratio of the $N_{c}$-$N_{c}$ and $N_{c}$-$N_{s}$ bond length is estimated to be $\sim 1.01$. The positions of the two kinds of Ni$^{2+}$ which have been referred to as “spine” and “cross tie” are shown as blue and cyan spheres. The deviation from the ideal Kagomé geometry introduces several new interactions that relieve the frustration of underlying Kagomé antiferromagnets in unexpected ways [10]. These smaller interactions play a crucial role to trace an explanation of the microscopic origins of multiferrocity observed in NVO.

**Experiments.** – Polycrystalline samples of Ni$_3$V$_2$O$_8$ were prepared by a solid-state reaction at ambient pressure. 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, compacted and calcinated at 800°C for 16 hours in dense Al$_2$O$_3$ crucibles. The reacted product was ground, compacted, and reheated at 800°C for 16 hours. The product was characterized using X-ray powder diffraction (XRD) by using BRUKER D-8 advanced diffractometer with Cu K$\alpha$ ($\lambda = 1.5418 \, \text{Å}$) radiation and with a scan step width of 0.02°. Composition analysis was performed using an electron diffraction energy dispersive X-ray spectroscopy (EDAX).

The dielectric measurements were performed in a “Cryogenic” 8T cryogen-free magnet system with an attached variable temperature insert [25,26]. The dc magnetization was measured using Quantum Design SQUID. Heat capacity measurements were performed on a sintered powder sample using a relaxation technique for temperatures below 15 K and fields upto 14 T.

**Results and discussion.** – Figure 1(b) 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 $a = 5.9178 \, \text{Å}$, $b = 11.3652 \, \text{Å}$ and $c = 8.2896 \, \text{Å}$. EDAX measurement (fig. 1(c)) confirms that there is no other metal element except for 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. The dielectric constant as a function of temperature (at 5 kHz) is shown in fig. 2. A peak in dielectric constant at $T_{HL} = 6.9 \, \text{K}$ indicates the onset of ferroelectric order corresponding to the onset of low-temperature incommensurate phase. In the inset of fig. 2 dielectric constant in zero field and in the presence of 3 T magnetic field (at 5 kHz) are shown. In the presence of magnetic field, the peak in the dielectric constant becomes sharper as compared to the case in

Fig. 1: (Color online) 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) Room temperature X-ray diffraction patterns of Ni$_3$V$_2$O$_8$ that establish orthorhombic crystal structure with space group $Cmca$. All the peaks are identified and indexed. (c) Energy dispersive X-ray spectroscopy exhibits the elements Ni, V and O in the specimen. Star (*) marked peaks are from the carbon tape used to glue the sample.
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zero field. This is a clear signature of magnetoelectric 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 HoMnO$_3$ and YMnO$_3$ [27,28]. We note that the degree of frustration which is quantified as $\theta/T_H$ ($\theta$ being the Curie-Weiss intercept and $T_H$, the magnetic-ordering temperature) for Ni$_3$V$_2$O$_8$ is $\sim 3.1$ which is large as compared to orthorhombic YMnO$_3$ ($\sim 1.27$) and HoMnO$_3$ ($\sim 0.5$). In the case of YMnO$_3$ the dielectric constant is decreased by 2% and in the case of HoMnO$_3$ this decrease is 8% in the presence of a 7 T magnetic field [27]. 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 magneto-dielectric effect. Most importantly, we find that there is clear evidence of the onset of another electric ordering below $\sim 2$ K. Hitherto it was suggested [13] 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. We emphasize that we have done the zero-field dielectric measurement at different frequencies and this lower temperature increase in dielectric constant is consistent and reproducible. At lower frequencies both the anomalies at $T_{HL} = 6.4$ K and $T \sim 2$ K in the dielectric constant is higher than that measured at higher frequencies. This onset of re-entrant long-range electric correlation persists up to 1.6 K which is the lowest temperature in our measurement.

The magnetization data for Ni$_3$V$_2$O$_8$ in an applied field of 0.1 T are shown in fig. 3(a). The inverse susceptibility $1/\chi$ data are shown in the inset of fig. 3(a).

The high-temperature inverse susceptibility data show excellent linearity and as shown in inset of fig. 3(a). Departure from linearity could be observed around $\sim 10$ K with extrapolated Curie-Weiss intercept $\theta \sim -11$ K. The negative value of $\theta$ 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 [17]. 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 3b. At 5 K, above the CAF phase, no hysteresis is observed in the incommensurate phase.

The low-temperature heat capacity data for Ni$_3$V$_2$O$_8$ is shown in the different panels of fig. 4. The zero-field heat capacity as a function of temperature is shown in the first panel. It shows four anomalies at 2.8, 4.0, 6.4, and 9.3 K corresponding to four magnetic phase transitions. These four peaks in NVO specific heat correspond to the development of complex spin structures as established by neutron diffraction measurements [11,15]. The peaks at $T = 9.3$ K (T$_{PH}$) and 6.4 K (T$_{HL}$) correspond to second-order phase transitions. Both these phases are magnetically incommensurate states. There is another distinct peak at $T = 4.0$ K (T$_{LC}$) corresponding to a first-order magnetic phase transition consequent upon a progression from an incommensurate to canted antiferromagnetic phase. In the LTI phase (between 6.4 and 4 K), the spine and cross tie spin rotate within a-b planes leading to remarkable ferroelectric behaviour along with field-dependent electric polarization [13,17]. This is well supported by our magneto-dielectric measurement. 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 magnetic structure of this fourth transition at 2.8 K (T$_{CC'}$) is yet to be fully understood. We also note that as compared to the separation of T$_{PH}$-T$_{HL}$ and T$_{HL}$-T$_{LC}$, the separation of T$_{LC}$-T$_{CC'}$ is small and this is related to the fact that there exist two subsystems of Ni$^{2+}$ ions. One Ni$^{2+}$ corresponds to cross-tie site (Ni$_i$) and second corresponds to spine sites (Ni$_s$) and the number of spine sites is twice that of cross sites. In the temperature region, T$_{CC'} < T < T_{LC}$ the subsystem of Ni$^{2+}$ primarily constitutes the commensurate low-temperature phase and the Ni$^{2+}$ ions begin to transit to this phase at T$_{CC'}$. With the application of magnetic field these two transitions are expected to merge. This hypothesis appears to be true in our field-dependent specific-heat data shown in panels for $H = 0$, 9 and 14 T. Applying a 1 T magnetic field produces substantial broadening in all the peaks (T$_{CC'}$, T$_{LC}$, T$_{HL}$, T$_{PH}$), but does not significantly shift the transition temperatures. With the application of higher magnetic fields of 9 T and 14 T the two peaks at the lower temperature region T$_{CC'}$, and T$_{LC}$ merge together. The other two peaks T$_{HL}$, and T$_{PH}$ are distinct even at 9 T magnetic field but the broadness of these peaks increases. At 14 T only one peak remains. Next we calculate the entropy of the Ni$_3$V$_2$O$_8$ system by integrating C/T vs. T plots up to 13 K. For 0 T, the entropy calculated for the Ni$_3$V$_2$O$_8$ 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 $H = 1$ T and 9 T below 2 K that disappears both at 0 T and 14 T. Because of the temperature limitation of our 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 has also been indicated in our dielectric data shown in fig. 2. This result gives thermodynamic credence to what was reported from theoretical calculations and optical measurements [19].

In conclusion high-quality polycrystalline samples of the Kagomé staircase lattice Ni$_3$V$_2$O$_8$ have been prepared. 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 below 4 K. Most importantly we observe the onset of a new low-temperature (< 2 K) field-induced phase that is accompanied by simultaneous development of a robust electric ordering. In essence we provide evidence of a re-entrant multiferroic phase in this magnetically rich frustrated spin system.

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