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Magnetically Driven Ferroelectric Order in $Ni_3V_2O_8$

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Abstract
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Disciplines
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Comments
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We show that long-range ferroelectric and incommensurate magnetic order appear simultaneously in a single phase transition in $Ni_3V_2O_8$. The temperature and magnetic-field dependence of the spontaneous polarization show a strong coupling between magnetic and ferroelectric orders. We determine the magnetic symmetry using Landau theory for continuous phase transitions, which shows that the spin structure alone can break spatial inversion symmetry leading to ferroelectric order. This phenomenological theory explains our experimental observation that the spontaneous polarization is restricted to lie along the crystal b axis and predicts that the magnitude should be proportional to a magnetic order parameter.

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The coupling between long-range magnetic and ferroelectric order has been studied since the 1960s [1–3]. Although a number of systems which are ferroelectric at high temperatures become magnetically ordered at a lower temperature [2,4], the simultaneous appearance of both kinds of order at a single phase transition is much less common. For the most part, studies of these multiferroic materials have focussed on *commensurate* magnets. The magnetoelectric properties of these systems are typically discussed in terms of magnetic symmetry groups. The onset of magnetic ordering requires breaking the time-reversal symmetry, while ferroelectric order breaks spatial inversion symmetry. Therefore, only magnetic groups having the proper symmetries allow the possibility of simultaneous magnetic and ferroelectric order.

Recent studies of systems undergoing simultaneous ferroelectric order at a magnetic transition have identified new multiferroic compounds, including the perovskite Rare Earth manganites $TbMnO_3$ and $DyMnO_3$ [5], and $TbMn_2O_5$ [6]. However, the magnetic structures of these materials are complex [7–9], which makes an investigation of their magnetoelectric properties based on symmetry analysis problematic. In contrast, the magnetic structure of $Ni_3V_2O_8$ (NVO), which we have identified as a multiferroic material, is better determined. There are extensive neutron data on this compound [10], and a symmetry analysis of the data (discussed below) constrains the symmetries which are consistent with a continuous transition. Here we take advantage of our analysis of the magnetic symmetry of NVO to develop a phenomenological Landau theory which provides an explanation of our observations of ferroelectric order induced by magnetic ordering. This provides an alternate route to understanding the magnetoelectric coupling in multiferroic materials beyond the traditional magnetic symmetry group analysis.

We briefly review earlier results [10–12] for the structure (magnetic and crystal) of (NVO) since its symmetry is crucial to the development of our model. NVO is a magnetic insulator consisting of planes of spin-1 Ni^{2+} ions arranged in a kagomé staircase lattice. Figure 1(a) shows the positions of the two kinds of Ni^{+2} spins which we call ''spine'' and ''cross tie'' spins. Competition between several weak magnetic interactions and anisotropies yields the complex phase diagram of Fig. 2 and the variety of magnetic structures illustrated in Fig. 1(b)–1(d). Cooling at $\mathbf{H} = 0$, one first enters a high-temperature incommensurate (HTI) [13] phase at $T_H = 9.1$ K [Fig. 1(b)], then a low-temperature incommensurate (LTI) phase at $T_L = 6.3$ K [Fig. 1(c)]. Below 3.9 K the system displays two slightly different canted antiferromagnet (CAF) phases [Fig. 1(d)]. The transitions involving the HTI phase are continuous, whereas that from the LTI to one of the CAF phases is discontinuous. In the HTI phase the long-range order is mostly on the spine sites with their spins parallel to a, while in the LTI phase the spine and cross tie spins rotate within an a-b plane as shown in Fig. 1(b) and 1(c). We used representation analysis [14] to determine the symmetry of these phases rather than attempting to acquire the vast amount of data which would be necessary to experimentally fix the several complex order parameters [e.g., see Eq. (2), below] for these magnetic structures. Each magnetic order parameter is characterized by a phase factor of unit magnitude which specifies how the order parameter transforms under symmetry operations leaving the incommensurate wave vector invariant. Thus the HTI order parameter, σ_{H}, is odd under a twofold rotation about the a

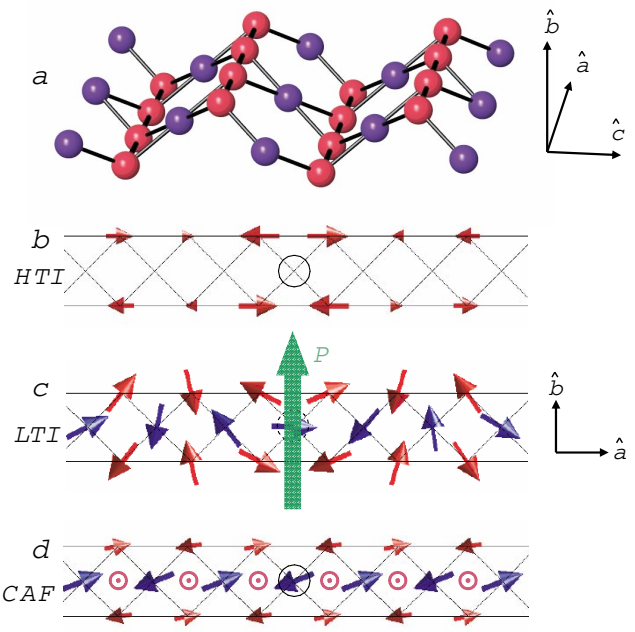

FIG. 1 (color). Crystal and magnetic structures of NVO. (a) Crystal structure showing spin-1 Ni^{2+} spine sites in red and cross tie sites in blue. (b), (c), (d) Simplified schematic representation of spin arrangement in the antiferromagnetic HTI, LTI, and CAF phases [10]. "⊙" indicates the direction of uniform magnetization distributed over spine and cross tie sites in the CAF phase. Only the HTI and CAF phases have inversion symmetry relative to the indicated central lattice point.

axis and is even under the glide plane whose mirror plane is an a-b plane. In the LTI phase an additional order parameter, σ_L appears which is even under both operations.

Single crystals of NVO were grown from BaO-V_2O_5 flux[10]. The single crystal samples were oriented using a Laue x-ray diffractometer. To probe the ferroelectric order, we sputtered two gold electrodes on opposite faces of the crystals and measured both the pyroelectric current at fixed **H**, and the magnetoelectric current at fixed T, using a Keithly electrometer. We then integrated the current to find the spontaneous polarization **P**, corresponding to the ordered moment arising in the ferroelectric state. We aligned the ferroelectric domains by applying a (~ 2 kV/cm) polarizing electric field E_0 as the sample was cooled through the transition temperature. After removing the electric field, we measured the polarization P_a, P_b, and P_c, along each of the three crystal axes. To within experimental error, only P_b was found to be nonzero.

Figures 3(a) and 3(b) show P_b, the electric polarization along the b axis, versus T at zero applied voltage for fixed magnetic fields applied along the a and c axes, respectively. Since the sign of the polarization in zero electric field changed when the sign of the polarizing field E_0 was changed, we infer that this polarization arises from ferroelectric order in NVO. From data for the magnetic field along different crystal axes, it became clear that the region in which P_b was nonzero coincided exactly with the region in which the LTI phase existed, as shown in Fig. 2. Furthermore the hysteresis in ferroelectric order as a function of magnetic field or temperature is connected with the fact that the LTI-CAF phase transition is discontinuous.

The isothermal data shown in Figs. 3(b) and 3(d) corroborate the above picture. Figure 3(d) shows P_b versus the magnetic field along c, H_c, at $T = 5$ K. At low H_c, P_b is insensitive to the external magnetic field. As H_c is increased, the sample undergoes CAF ordering, which completely suppresses the spontaneous polarization. On decreasing H_c, P_b returns to the initial value. The field hysteresis is attributed to the first order LTI to CAF transition. Figure 3(b) shows P_b at $T = 2$ K, versus $\mathbf{H} \parallel a$. At

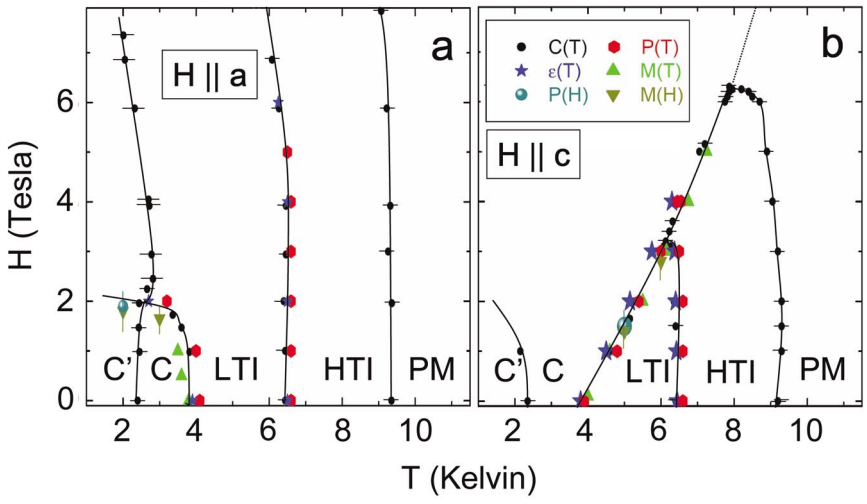

FIG. 2 (color). Phase diagram of NVO versus T and **H** for $\mathbf{H} \parallel a$ and $\mathbf{H} \parallel c$ in panels (a) and (b), respectively. The data points indicate anomalies in specific heat (C), magnetization (M), dielectric permittivity (ε), and electric polarization (P) traces versus **H** and T. Solid lines are guides to the eye. The phases are described in the text and illustrated in Figs. 1(b)–1(d)

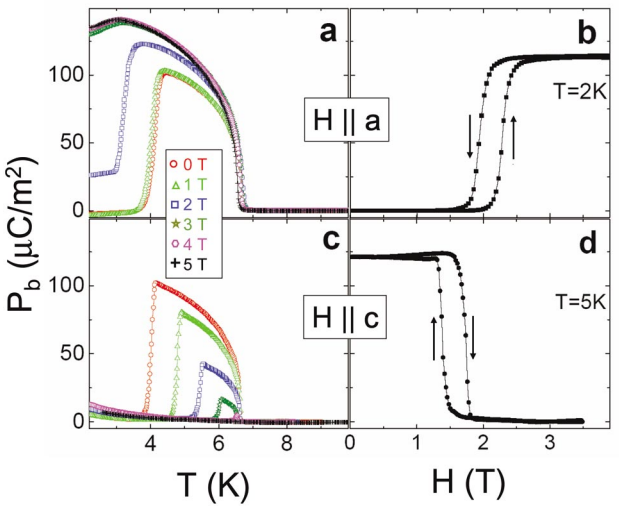

FIG. 3 (color). Promotion and suppression of electric polarization by applying magnetic fields in NVO. Temperature and magnetic-field dependence of electric polarization along the b axis for **H** along the a [frames (a) and (b)] and c [frames (c) and (d)] axes.

small H_a, there is no ferroelectric order in the CAF phase. However, increasing H_a produces a spontaneous polarization in the LTI phase which is independent of the sign of the magnetic field. The crucial observation is that we can magnetically gate NVO to either suppress or promote ferroelectric order, depending only on the direction of the applied field and the temperature.

We now give a phenomenological explanation of our results. The essence of this discussion is that the paramagnetic phase of the crystal has spatial inversion symmetry and that this inversion symmetry is broken solely by the complex spin structures in the LTI phase. In the HTI phase the incommensurate magnetic order cannot induce a nonzero value of **P** because the magnetic structure is inversion symmetric. This symmetry is not easy to establish directly by analyzing the neutron diffraction data. If one assumes the spin amplitudes are restricted according to a representation analysis [14], one still has to determine the complex-valued order parameters $\sigma_{\mathrm{H};i}(k) = \sigma_{\mathrm{H};i}(-k)^*$ which characterize the HTI phase, where k denotes the wave vector of the incommensurate ordering and $i = 1, \ldots, 6$, corresponds to the six spin components (the a, b, and c components of the spine and cross tie spins). In the LTI phase the additional order parameters $\sigma_{\mathrm{L};i}(k) = \sigma_{\mathrm{L};i}(-k)^*$ appear. Representation analysis considers only operations which leave the incommensurate wave vector invariant, but neglects additional symmetries (such as spatial inversion) possessed by the crystal. We use the additional constraints imposed by inversion symmetry of the crystal lattice to define the order parameters so that they satisfy

$$\mathcal{I}\,\sigma_{X;i}(k) = \sigma_{X;i}(k)^*, \tag{1}$$

where X denotes either H or L. The quadratic terms in the Landau free energy which describe the appearance of the HTI phase are

$$F = \sum_{i,j} F_{ij}\sigma_{\mathrm{H};i}(-k)\sigma_{\mathrm{H};j}(k), \tag{2}$$

where $F_{i,j} = F^*_{j,i}$. Then Eq. (1) implies that the coefficients F_{ij} are all real valued. This in turn means that the amplitudes $\sigma_{\mathrm{H},i}$ are all real valued (as eigenvectors of a real matrix), apart from a common overall phase:

$$\sigma_{\mathrm{H};i}(k) = c_i e^{i\phi_{\mathrm{H}}}\sigma_{\mathrm{H}}, \tag{3}$$

where the c_i, obtained from the critical eigenvector, are real. Thus, the HTI phase is described by a single complex-valued order parameter $e^{i\phi_{\mathrm{H}}}\sigma_{\mathrm{H}}$, whose overall phase, ϕ_{H}, is not fixed at this level of analysis. This overall phase ϕ_{H} can be eliminated by redefining the origin of coordinates. The resulting Fourier components $\sigma_{\mathrm{H};i}(k)$ are all real so the HTI magnetic structure is invariant under spatial inversion with respect to the redefined origin, and therefore this magnetic ordering cannot induce a spontaneous electric polarization. Since the CAF phase is also inversion symmetric [Fig. 1(d)], ferroelectricity is not induced by magnetic order in that phase either. These results confirm that this model based on our extension of representation analysis successfully predicts the experimental observation that there is no ferroelectric order in the HTI or CAF phases. We can also understand why when a sufficiently large magnetic field is applied so as to enter the CAF phase [Fig. 2(b)], the spontaneous polarization abruptly disappears.

We now introduce a phenomenological model to explain the symmetry of the magnetoelectric coupling which induces a spontaneous polarization in the LTI phase. While the specific details of this discussion apply to NVO, the general approach is applicable to other systems. To describe the incommensurate phases and ferroelectric behavior in a single model, we write the Landau free energy as

$$F = a(T - T_{\mathrm{H}})\sigma_{\mathrm{H}}^2 + b(T - T_{\mathrm{L}})\sigma_{\mathrm{L}}^2 + \mathcal{O}(\sigma^4) + (2\chi_E)^{-1}\mathbf{P}^2 + V, \tag{4}$$

where a and b are constants and χ_E is the electric susceptibility. In a conventional ferroelectric **P** becomes nonzero when χ_E becomes infinite, often associated with a structural phase transition. Here χ_E is finite and the appearance of a nonzero **P** is due to the term V coupling magnetic and ferroelectric orders. Note that this expansion is expressed in the disordered phase, so that all terms in this equation must be invariant under the complete set of symmetry operations of the disordered phase. In particular, this expression must be invariant under spatial inversion.

We now discuss the form of the magnetoelectric coupling V. To conserve wave vector this coupling must be at least trilinear [15], being proportional to one order parame-

ter at wave vector k, another at wave vector $(-k)$, and $\mathbf{P}$ which is associated with zero wave vector. As we have already argued, this coupling is zero with only a single magnetic order parameter σ_{H}. A similar argument made for the LTI variables shows that ferroelectricity cannot be induced if we only invoke the single order parameter σ_{L}. Accordingly, and in analogy with what has been done for the theory of second harmonic generation [16], we posit the following interaction which involves two different symmetry order parameters

$$V = -\sum_{ij\gamma}[a_{ij\gamma}\sigma_{\mathrm{H};i}(k)\sigma_{\mathrm{L};j}(-k) + a^{*}_{ij\gamma}\sigma_{\mathrm{H};i}(-k)\sigma_{\mathrm{L};j}(k)]P_{\gamma}. \quad (5)$$

Using $I\sigma_{X;i}(k) = \sigma_{X;i}(-k)$ and $IP_{\gamma} = -P_{\gamma}$, we see that the inversion invariance of V implies that the coefficients $a_{ij\gamma}$ must be purely imaginary. Using Eq. (3) and its analog for the L order parameters we then have

$$V_{\mathrm{LTI}} = \sum_{\gamma} a_{\gamma}\sigma_{\mathrm{H}}\sigma_{\mathrm{L}}\sin(\phi_{\mathrm{H}} - \phi_{\mathrm{L}})P_{\gamma}, \quad (6)$$

where a_{γ} is a real valued coefficient. At fourth order in the Landau expansion it can be shown that $\phi_{\mathrm{H}} - \phi_{\mathrm{L}} = \pi/2$, but to have $P_{\gamma} \neq 0$ it is only essential that $\phi_{\mathrm{H}} \neq \phi_{\mathrm{L}}$. We now insert Eq. (6) into Eq. (4) and minimize with respect to $\mathbf{P}$ to find a spontaneous polarization given by

$$P_{\gamma} \propto a_{\gamma}\chi_{\mathrm{el}}\sigma_{\mathrm{L}}\sigma_{\mathrm{H}}. \quad (7)$$

Note that this prediction can be checked by measuring all the quantities which appear in Eq. (7) as a function of magnetic field and temperature. This result for the dependence of the spontaneous polarization on the magnetic order parameter could not be obtained from magnetic symmetry group analysis alone.

To analyze the consequences of the trilinear coupling in Eq. (6), it is necessary to know how the order parameters transform under the symmetry operations of the crystal. As stated above, σ_{L} is even and σ_{H} is odd under a twofold rotation about the a axis, so for V to be an invariant, $\mathbf{P}$ must also be odd under this operation. (This implies that in Eq. (6), γ can only be b or c.) Furthermore, σ_{L} and σ_{H} are both even under the a-b glide plane, which restricts γ in Eq. (6) to be in this plane. Taking account of both symmetries, we see that a_{γ} in Eq. (6) can only be nonzero for $\gamma = b$. This simple argument therefore explains why the spontaneous polarization is confined to the b axis. Furthermore, since (a) the polarization P_b depends on the product of σ_{L} and σ_{H} and (b) σ_{H} is almost constant in the LTI phase, we expect P_b to be approximately proportional to σ_{L}, which qualitatively explains the observed temperature dependence of P_b. Note also that we do not expect any coupling between the uniform applied magnetic field H_a and the uniform polarization P_b, which explains why P_b was observed to be independent of the sign of H_a.

In summary, we have shown that the development of ferroelectric order is coincident with an incommensurate magnetic phase in NVO. Since ferroelectricity occurs only in the phase for which magnetic ordering breaks inversion symmetry, one can reversibly switch the polarization on and off using an external magnetic field. We develop a Landau-like model to explain how ferroelectricity is induced by incommensurate magnetic ordering. It is expected that this model will explain the behavior of other recently studied multiferroics with incommensurate or long wavelength structure [17,18] and will point the way to microscopic theories for these materials. In addition, we suggest that the spontaneous development of electric and magnetic long-range order may have been overlooked in simple antiferromagnets in which the lattice structure has inversion symmetry but the magnetic moments only have inversion symmetry relative to a *different* origin.

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